IN SITU INFRARED STUDY OF G-S / L-S ADSORPTION
AND PHOTOCATALYTIC PROCESSES

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AND PHOTOCATALYTIC PROCESSES

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Dissertation

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ABSTRACT

Coal fired power plants release large quantities of CO$_2$ and trace amounts of SO$_2$ into the atmosphere, affecting global warming and worldwide climate change. CO$_2$ is a concern as a greenhouse gas in relation to global temperature raise. SO$_2$ is a concern in environmental protection as a precursor for acid rain. The impact of CO$_2$, SO$_2$, and H$_2$S on the environment demonstrate the removal process is a subject of study of great importance. Removal of these gases has been focused on the development of amine based sorbents for sequestration by the adsorption and desorption process. Fourier Transform Infrared spectroscopy (FTIR) is a powerful tool for investigating the adsorption/desorption process and structure of adsorbing molecules. The application of FTIR, coupled with ab initio quantum chemistry, can provide a direct means for understanding the interactions that occur during chemisorption.

The removal of CO$_2$ and H$_2$S by an amine based sorbent has been studied. The hypothesis for this study is to investigate the use of polyethylene glycol (PEG) to promote tetraethylenepentamine (TEPA) CO$_2$ and H$_2$S removal capacity. It is thought that the use of PEG may improve the catalytic adsorption capacity through hydrogen bonding. This study used in situ FTIR and ab initio quantum chemistry to investigate the adsorption and desorption processes during CO$_2$ and H$_2$S capture at the molecular level. The FTIR results determine that PEG interacts with the primary amine functional groups.
of TEPA dispersing the adsorption sites leading to improved adsorption capacity for CO\textsubscript{2} and H\textsubscript{2}S. Ab initio quantum chemistry determined that PEG lowers the binding energy of CO\textsubscript{2} and H\textsubscript{2}S leading to a lower desorption temperature.

Removal of the nauseous gas SO\textsubscript{2} by an amine based sorbent is studied. The hypothesis investigated the use of 1,3-phenylenediamine low basic property for creating a reusable solid amine based sorbent for SO\textsubscript{2} removal. It is thought that the low basic property of the aromatic amine will allow the effective SO\textsubscript{2} adsorption and desorption at low temperature. This study used in situ FTIR spectroscopy to investigate the adsorption and desorption processes during SO\textsubscript{2} capture. The result of this study determined that 1,3-phenylenediamine basic property allowed SO\textsubscript{2} adsorption and desorption at 373 K, however, sorbent deactivation occurs. The in situ UV-Visible spectroscopic technique provided insight that deactivation is the result of agglomeration of 1,3-phenylenediamine. Addition of PEG prevented the agglomeration and improved the adsorption capacity of 1,3-phenylenediamine through hydrogen bonding with the primary amine functional group.

Amine based sorbents have been proven as an effective and economic process for the removal of CO\textsubscript{2} and the hazardous gases H\textsubscript{2}S and SO\textsubscript{2}. Advancing knowledge in the area of amine based sorbents will improve our ability for hazardous waste management. Hazardous waste management may also be achieved by the oxidation and reduction (redox) of toxic materials. TiO\textsubscript{2} based catalysts have the ability to oxidize a number of hazardous materials to nontoxic products where TiO\textsubscript{2} has become the benchmark semiconductor in photo-detoxification of contaminated water. This work also investigates the photocatalytic dehydrogenation process over TiO\textsubscript{2} based catalysts. The
hypothesis investigated the relationship of the photogenerated electrons and adsorbed species during the photocatalytic dehydrogenation of 2-propanol. It is thought that the interaction of the photogenerated electrons and adsorb species may be elucidated from the reaction mechanism during the photocatalytic dehydrogenation of 2-propanol. 2-propanol is used as a model compound because it provides a simple and standard way to measure the photo-catalytic activity during the gas/liquid phase reactions. This study suggest that in the presence of adsorbed H₂O, the dehydrogenation process proceeded by a hydroxyl radical species while in the absence of adsorbed H₂O the active species is an adsorbed $O_2^-$ ion. Au/TiO₂ unique ability to generate adsorbed oxygen ions resulted in higher catalytic activity in the absence of adsorbed H₂O under UV-irradiation. The reaction pathway for the photocatalytic dehydrogenation of 2-propanol is strongly dependent on the coverage of surface H₂O.
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CHAPTER I
INTRODUCTION

1.1 Objectives

The world’s energy production has increased dramatically between 1950 and 2009 and the increasing trend for energy consumption continues as a result of the expansion and economic growth of both industrial and emerging countries. The negative effects of energy use result from the amount of non-renewable energy resources that are consumed and the total emissions of pollution and greenhouse gases emitted from the production of that energy. Thus, there is a need to decrease the amount of these emissions that are harmful to the environment and contribute to the global greenhouse effect. These emissions related to energy production are studied in the science of atmospheric environmental catalysis which deals with the removal of pollutants from the product streams of combustion and chemical reaction processes. The study of atmospheric environmental catalysis is a very broad subject area; however, these three areas (i) CO$_2$ and H$_2$S capture, (ii) SO$_2$ capture, and (iii) photocatalytic oxidation by oxygen species have become a very relevant subject of study as a result of their direct involvement in the energy generation process.

In the combustion technologies that convert energy resources such as fossil fuels into electricity, technologies for removing H$_2$S in the pre-combustion process, along with
CO₂ and SO₂ in the post-combustion process are essential. Therefore, it is necessary to improve on existing technologies such as amine based sorbents for CO₂ and H₂S capture. A portion of this dissertation deals with improving an amine based sorbent for CO₂ and H₂S capture. The effect of SO₂ emissions is directly related to the release of SO₂ into the atmosphere. In order to reduce acid rain formation, an amine based sorbent is developed in order to lower SO₂ emissions from coal based power plants. Finally, studying the photocatalytic oxidation of 2-propanol may help understand the atmospheric environment and the rate of photocatalytic oxidation in both the gas and liquid phases. A catalyst, such as TiO₂, is active under UV illumination allowing one to study the surface oxidation reaction at a laboratory scale.

A catalyst may be gaseous, liquid, or a solid substance. Catalysts may consist of inorganic, organic, or a complex combination which help to accelerate a chemical reaction by providing an alternate reaction pathway. Heterogeneous catalysis research involves the study of catalysts that are commonly present as solids where the reactants and products are liquids or gases. The Solid-Liquid and Solid-Gas catalytic process may occur by the following steps: (i) mass transfer through the bulk phase, diffusion from the bulk phase to the catalyst surface, (ii) chemisorption (form chemical bonds) with the catalyst surface, (iii) reactions on the surface leading to adsorbed intermediate and product species, (iv) desorption of products from the catalyst surface and (v) the diffusion of products back into the bulk phase. Understanding the reaction process in heterogeneous catalysis involves the study of each of these reaction steps (i.e. diffusion, adsorption, reaction, and desorption).
The key principle for designing a heterogeneous catalyst is to understand the influence of different surface structures on adsorbed species under reaction conditions. On the solid surface, some of the surface sites may be able to interact specifically with a gaseous or liquid molecule to form a chemical bond which is called an adsorption site. Among the adsorption sites for a particular reactant there may be a number of sites which possess the ability to activate an adsorbed molecule to form an intermediate. This may be a new compound which is more loosely bound by chemical bonds which are ready to form the reaction products upon interaction with other surface or gaseous species where upon desorption forms the desired product. These sites are called the catalytic active sites. Understanding these catalytic active sites is possible through the observation of adsorbed species (i.e. adsorbates) and distribution of products formed during the reaction. Utilizing Fourier Transform Infrared Spectroscopy (FTIR) allows the observation of infrared (IR) active adsorbed species during the reaction. Mass Spectrometry (MS) allows for determination of product formation, distribution, activity, selectivity, and reaction rates. The FTIR and MS instruments together with a transient dynamic approach can provide information on the structure, reactivity, and reaction mechanism which may lead to more efficient catalyst design and development of more practical industrial systems.

1.2 Transient Techniques

In the transient method, a signal is introduced over a catalyst in a reactor and the response is observed (the response of reactants, products, and adsorbed species or some
variable associated with the reactor). Typically, a steady flow of reactants to a reactor is used with a concentration signal imposed on the inlet stream and the concentration response is monitored at the outlet. A transient signal is introduced to the reactor system via (i) a step response (inlet flow is switched from the reactants to another set of reactants) while maintaining the total flow rate or (ii) a pulse injection into the reactant flow over the catalyst to be studied. The core concept of the transient method, applied to heterogeneous catalysis [1], is measurement of the changes during the catalytic reaction and FTIR is used to measure the behaviour of adsorbed species during the reaction [2]. Though advances in spectroscopic techniques have contributed to identification of reaction intermediates responsible for certain elementary steps [3], reaction mechanisms and identification of new adsorbed species presents a challenge in heterogeneous catalysis research.

Transient methods are of interest for understanding the kinetics of a sequence of steps in heterogeneous catalysis through obtaining dynamic behaviour which may not be available from steady state experiments. Using transient techniques to determine the reactivity and dynamic behaviour of adsorbates is ideally suited for the study of the adsorption and desorption process during of CO₂, H₂S, and SO₂ capture over a mixed inorganic/organic heterogeneous catalyst. Fundamental research in photocatalysis may also significantly benefit from methods that can probe the catalytic surface under transient conditions. Correlating the properties of the catalyst, catalytic active sites and sorbent molecules, the nature of the adsorbates and their reactivity can provide
information on the reaction mechanism on these important topics which are currently of interest in the catalysis field.

1.3 Energy Demand, Emissions, and Environment

Energy utilization worldwide in the past has primarily been one of selecting fuel that offers low cost and ease of use. With the explosive growth in energy consumption in the 20\textsuperscript{th} century followed by advancement in technology and industry demands for manmade materials has led to an increase in fuel utilization such as gasoline, diesel, and jet fuels. Advances in technology (electronics, computers, mobile phones, etc) have led to an increase in the demand for electricity from power plants. The generation of electricity has been largely carbon-based resources such as coal and natural gas. One of the challenges today results not only from the environmental problems due to emissions of pollutants (SO\textsubscript{x}, NO\textsubscript{x}, H\textsubscript{2}S, CO, HC, particulate matter, etc) but also greenhouse gases such as CO\textsubscript{2} from the combustion of solid, liquid, and gaseous fuels in various stationary and mobile systems around the world.

Legislators have enacted laws to slow, stop and even reverse emissions of these gases in order to protect the environment. These Environmental control strategies pertinent to control of emissions from stationary power sources can generally be divided into two categories relating to pre-treatment (i.e. H\textsubscript{2}S removal), combustion modifications (burner optimizations), and post-treatment of combustion flue gas. These measures have lead to various technologies for the sequestration of CO\textsubscript{2} and elimination of H\textsubscript{2}S and SO\textsubscript{2} gases.
1.4 Flue gases from stationary sources

Typical emission ranges in large scale coal fired power plants are listed in Table 1.1. The average temperature leaving the boiler is 650-760 °C. The composition is approximately 3-4% O₂, 12-15% CO₂, 5-7% H₂O, 300-5000 ppmv SO₂, and 150-300 ppmv NOₓ at a total flue gas volume of approximately 3500-4500 cfm based upon power output capacity of the power plant.

Pollutants are emitted continuously from stationary sources worldwide. Catalysis can play a role by improving energy demands on chemical processes by improving process efficiencies, lower temperature, lower pressure operation, reducing energy intensive separation steps, reducing unit operations and improving chemical selectivity. For example, a continuous scrubbing system is used to separate CO₂ from the flue gas stream. The system consists of two main sections, an absorber section where CO₂ is removed and a regenerator section where CO₂ is released in a concentrated form and the original solvent is recovered. The key feature of a solid sorbent is the recovery of the sorbent for reusability purposes while improving removal efficiency of CO₂.
Table 1.1 Gaseous emissions for stationary sources without flue gas cleaning for heat and power generation.

<table>
<thead>
<tr>
<th>Source</th>
<th>Fuel Type</th>
<th>NOx (ppmv)</th>
<th>SOx (ppmv)</th>
<th>CO (ppmv)</th>
<th>Particles ((1 \times 10^{-6} \text{ kg m}^{-2} \text{ s}^{-2}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiler</td>
<td>coal</td>
<td>150-700</td>
<td>300-2500</td>
<td>-</td>
<td>10</td>
<td>[4]</td>
</tr>
<tr>
<td>Boiler</td>
<td>Oil/Pet Coke</td>
<td>200-500</td>
<td>1000-</td>
<td>-</td>
<td>10</td>
<td>[5]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td></td>
<td>5000</td>
<td></td>
</tr>
<tr>
<td>Boiler</td>
<td>Biofuel</td>
<td>100-300</td>
<td>0-50</td>
<td>-</td>
<td>-</td>
<td>[6-7]</td>
</tr>
<tr>
<td>Gas</td>
<td>Gasoline</td>
<td>15-50</td>
<td>-</td>
<td>1-200</td>
<td>-</td>
<td>[8-9]</td>
</tr>
<tr>
<td>Turbine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.5 CO₂ removal methods

CO₂ removal occurs naturally upon the earth in a number of ways such as the oceans, forests, and soil ecosystems. Due to the influence of man-made CO₂ emissions, and the earth’s natural CO₂ absorption capacity, it is necessary to control CO₂ emissions which are derived from human sources to preserve the earth for future generations. In the effort to eliminate CO₂ emissions several technologies have been employed for that purpose. Absorption of CO₂ by liquid amines or by cold methanol method is the most
The most popular way for removing CO₂ in industry today [10]. The cost of sequestration is large in terms of energy usage. For example, the heat required to regenerate the solvent reduces the efficiency of the power plant. CO₂ scrubbing using a liquid amine system is energy intensive and reduces the coal plants efficiency by 14% [11]. Efficiency is defined by the ratio of work performed to the total energy expended, or in other words, the output divided by the amount of work put in. For example, a machine with an efficiency of 0.8 returns 80% of the work input as work output. The remaining 20% of work is unrecoverable (lost). This relation to energy input and energy output can be expressed according to eqn. (1):

\[
\text{efficiency } (\eta) = \frac{\text{energy output}}{\text{energy input}} \times (100\%) = \frac{E_{\text{act}}}{E_{\text{theory}}} \times (100\%)
\] (1)

The energy that is output divided by the energy input determines the overall efficiency of a system. Eqn. (1) can be used to determine the overall efficiency of a steam powered power plant equipped with a CO₂ removal system. The energy required for the removal of CO₂ at atmospheric concentration would provide the lower possible limit on CO₂ removal. Concentration in the flue gas would be higher than that of atmospheric concentration and thus raise the efficiency for its removal. This may be investigated by looking at the efficiency of a model steam powered power plant, modeled from the rankine cycle, with and without a CO₂ removal system.
1.5.1 Steam Power Plant

The rankine vapor cycle is the basis for the combustion cycle that uses coal, fuel oil, or natural gas to compress and heat water to saturated steam and then expand the saturated steam through a turbine in order to convert the heat to mechanical energy. The process for converting heat to mechanical energy consists of (i) compression of the fluid (water) using a pump, (ii) heating of the compressed fluid to the inlet temperature of the turbine which includes heating the water to the boiling point and phase change from liquid to vapor, (iii) expansion of the vapor in the turbine and (iv) condensation of the vapor in a condenser. The fluid is then returned to the pump and the cycle is repeated.

It is instructive to investigate the drop in efficiency of a power station when a 30% CO₂ removal is required from the effluent stream. An isentropic rankine cycle turbine system is used to model such an electric power station. Suppose the electric coal powered power station operates between 4 MPa steam at the inlet of the turbine and 100kPa in the condenser. From the steam tables, $h_3$ is 2800.8 kJ/kg (enthalpy of saturated steam at 4 MPa), $h_1$ is 417.5 kJ/kg (enthalpy of water at 100 kPa), and $s_3$ equals $s_4$ is 6.070 kJ/kg·K (isentropic expansion). The pump work is pressure times volume (PV) determined to be 4.0 kJ/kg (note the volume V is determined from the specific volume of water at 100 kPa) shown in eqn. 2.

$$w_{\text{pump}} = PV = 3.9 \text{MPa} \times 0.104 \text{m}^3 / \text{kg} = 4.0 \text{kJ} / \text{kg} \quad (2)$$

$$h_2 = h_1 + w_{\text{pump}} = 417.5 + 4.0 = 421.5 \text{kJ} / \text{kg} \quad (3)$$
In order to solve for the work output from the turbine, we need to evaluate the enthalpy at the exit of the turbine \( (h_4) \). This is accomplished from a calculation of the quality of the steam leaving the turbine. The percent of the mixture that is vapor using the entropy values for liquid water and saturated steam at 100 kPa \( (s_f \text{ is } 1.2028 \text{ kJ/kg and } s_g \text{ is } 7.3589 \text{ kJ/kg}) \). The quality may be evaluated according to equation 4.

\[
x = \frac{s_4 - s_f}{s_g - s_f} = \frac{(2800.8 - 2194.5) - 4.0}{2800.8 - 421.5} = 78.7\%
\]

(4)

The steam quality leaving the turbine is 78.7%. Using the quality and enthalpy values from the steam tables for liquid water and saturated steam at 100 kPa, \( h_f \) is 417.5 kJ/kg and \( h_g \) is 2675.0 kJ/kg we can evaluate the enthalpy exiting the turbine. The enthalpy \( (h_4) \) may be determined from equation 5 and 6.

\[
x = \frac{h_4 - h_f}{h_g - h_f}
\]

(5)

\[
h_4 = x(h_g - h_f) + h_f = 2194.5 \text{ kJ/kg}
\]

(6)

The efficiency may then be determined calculating the difference between the work output minus the work input divided by the heat input into the system shown in equation 7.
\[
\eta = \frac{w_{\text{out}} - w_{\text{in}}}{q_{\text{in}}} = \left(\frac{2800.8 - 2194.5}{2800.8 - 421.5}\right) - 4.0 = 25.3\% 
\tag{7}
\]

For comparisons purposes we may check the theoretical upper limit for this system using the Carnot cycle. The steam tables reports the temperature for water completely condensed at 100 kPa is 372 K and for saturated steam at 4 MPa is 523.5 K. The Carnot efficiency is 28.8 % according to equation 8.

\[
\eta_{\text{carnot}} = \frac{(T_H - T_L)}{T_H} = \frac{(523.5 - 372.7)}{523.5} = 28.8\% 
\tag{8}
\]

The energy balance over the turbine, shown in Eqn 9, allows us to determine the mass flow rate of steam through the turbine.

\[
\Delta \left( H + \frac{1}{2} u^2 + zg \right) m = \dot{Q} + \dot{W} 
\tag{9}
\]

Assuming the potential energy, kinetic energy, and heat transfer of the turbine is negligible, the energy balance reduces to Eqn. 10.

\[
\dot{w}_s = \dot{m} \Delta H 
\tag{10}
\]

Assuming the power plant produces 56,400 kJ/s power, the mass flow rate is 93.0 kg/s saturated steam, show in Eqn. 11.
\[
\dot{m} = \frac{\dot{w}}{\Delta H} = \frac{56,400 \text{ kJ/s}}{2800.8 \text{ kJ/kg} - 2194.5 \text{ kJ/kg}} = 39.0 \text{ kg/s}
\]

(11)

From the mass flow rate of steam it is possible to determine the mass rate of formation of CO\(_2\) to produce 4.0 MPa saturated steam. The heat of combustion of coal is the energy released as heat when one mole of a compound undergoes complete combustion with oxygen. The heat of combustion for CO\(_2\) is equal to the heat of formation of CO\(_2\) (carbon + O\(_2\) \rightarrow CO\(_2\)). The heat of formation \(\Delta_f H^o\) for CO\(_2\) formation is -393.5 kJ/mol-CO\(_2\) or -8.94 kJ/kg-CO\(_2\). The mass rate of CO\(_2\) formation per steam produced is determined by dividing the enthalpy difference of condensed water and saturated steam by the heat of formation of CO\(_2\) according to equation 12.

\[
\frac{\Delta H}{\Delta_f H^o} = \frac{(417.5 - 2800.8)}{-8943.2} = 0.2665 \text{ kg-CO}_2/\text{kg-Steam}
\]

(12)

The mass flow rate of CO\(_2\) may then be determined according to equation 13.

\[
\dot{m}_{CO2} = 0.2665(93.0) = 24.78 \text{ kg/s} = 84,224.2 \text{ kg/h}
\]

(13)

Assuming the boiler is fed 100% air (21% O\(_2\) and 79% N\(_2\)) and complete combustion with O\(_2\), the power plant effluent is 21% CO\(_2\) (84,224 kg/h). It is desired to reduce the carbon emissions by 30% by the year 2020. From the Gibbs free energy of mixing, that is
82.09 kJ/kg steam. Assuming that the power plant generates the same amount of power, the efficiency decreases to 24.9% as shown in Eqn. 14.

\[
\eta = \frac{\Delta G_a - \Delta G_r}{\Delta G_a} \frac{w_{out} - w_{in}}{q_{in} + q_{CO2}} = \frac{602.3 - 6.67}{602.3} \frac{(2800.8 - 2194.5) - 4.0}{(2800.8 - 421.5) + 2021.5} = 24.9\% \quad (14)
\]

The DOE “Fossil Energy Power Plant Desk Reference” reports the energy required for compressing CO₂ (100% and 60 °C) to liquid CO₂ requires 51,600 kWh at a flow rate of 38,826 lbmol/h which gives 10.54 kJ/mol CO₂. The captured CO₂ may then be sequestered and stored in a geologic formation in the earth’s crust at a further reduction in power plant efficiency to 24.9%.

1.6 SO₂ removal methods

Sulfur dioxide (SO₂) emitted in flue gases from combustion processes such as coal fired power plants is a serious air pollutant whose emissions have been linked to the formation of acid rain, urban smog, and other environmental hazards. A typical wet SO₂ removal process involves lime or limestone scrubbers [12]. The disadvantage of limestone scrubbers are the large quantity of H₂O and landfill space required for the storage of the resulting solid waste product. A number of other SO₂ removal processes have been developed (i.e. wet, semi-dry, and dry methods) and applied in various industries to reduce SO₂ emissions. Previous attempts to recover SO₂ can be categorized by three methods:
SO₂ Recovery Methods

1. **Wet method** involving input of a sorbent in suspension, output of desulphurisation produces also as a suspension.

2. **Semi-dry method** involving input of a sorbent suspension and output of a dry sulfur saturated solid.

3. **Dry method** involving input of sorbent and output of sulfur saturated solid waste product.

As a result of the wet and semi-dry methods the dry method has attracted considerable interest in the last decade [13-16]. The SO₂ removal research using a dry sorbent has been generally prepared from a calcium based waste derived siliceous material even in the most recent literature [12-13]. For economic feasibility, the lifetime and reusability of the sorbent must be taken into consideration. Low utilization of calcium based sorbents caused by the formation of sulphates and the blockage of pores can prevent SO₂ diffusion into the surfaces of an un-reacted sorbent. A practical low temperature and reusable sorbent is needed.

1.7 H₂S removal methods

Hydrogen sulphide (H₂S) is a highly toxic, corrosive and odorous gas which is found as a component of natural gas (NG) and is also generated at oil refineries during the processing of sulfur-containing crude oil. Sulfur compounds however which are
naturally present in NG can behave as a poison for fuel cell applications. The removal of sulfur compounds from the NG fuel is a key component for fuel cell technology.

Fuel desulfurization has typically been carried out using the following technologies: (i) adsorption, (ii) selective catalytic oxidation (SCO) [17-19], and (iii) hydrodesulfurization (HDS). The most commonly used H$_2$S removal process can be classified into two categories: (i) liquid phase oxidation process and (ii) dry oxidation process. Generally elimination of H$_2$S from a gas stream occurs by the following steps, (i) separation from gas stream by amine extraction, (ii) fed to a Claus reactor unit which includes thermal and three stage catalytic treatments to ultimately produce elemental sulfur (S$_2$) and H$_2$O. This process results in up to 99.8% sulfur recovery [20].

Recent literature [21-25] has been focusing upon the selective removal of H$_2$S and other sulfur containing compounds from natural gas even with a high content of CO$_2$. The selective absorption of H$_2$S has been achieved with amines as weak acidic functional groups that may operate at lower pressure and temperature. Weak acidic functional groups and metal ions play an important role in adsorption and oxidation of sulfur compounds such as H$_2$S, sulphuric acid [26-27], mercaptan, and disulfides [28-30].

In the past various materials have been utilized for H$_2$S capture such as activated carbon [31], modified activated carbon [32], $\square$-Al$_2$O$_3$, modified clay [33], and modified zeolites [34]. There are however some disadvantages with these solid sorbents. Activated carbons suffer from low mechanical stability. $\square$-Al$_2$O$_3$ forms chemical reaction between the support and the active phase reducing the performance and hindering the recovery of sulfur compounds. Modified clays and zeolite materials
present mass transfer limitations when larger sulfur containing molecules are involved. The performance of H$_2$S adsorbents depends upon the porosity and surface chemistry of the sorbent catalyst. Substitution of active components such as amine containing compounds into the framework of the support materials in order to immobilize the active sulfur species has advantages providing low temperature catalyst with uniform properties for H$_2$S capture technology.

1.8 Hypothesis CO$_2$ and H$_2$S Capture

Industrially relevant gas-separation processes, the removal of acidic gases such as CO$_2$ and H$_2$S, from gas streams have become a major concern. Separation processes have been commonly accomplished by adsorbing the gas into a chemically reactive liquid or solid solution. Dissolving the gas into a chemical reactive liquid or solid consists of a mass transfer process accompanied by a Lewis acid-base reaction. To fully understand the gas separation process we need to have a comprehensive understanding of the reacting system as well as the molecular chemistry involved. It is reported in the literature that improvement in CO$_2$ removal efficiency in aqueous sorbent systems may be improved by the addition of alcohol additives [35]. The hypothesis for the study is the addition of polyethylene glycol (PEG, MW 200) to tetraethylenepentamine (TEPA) will promote removal efficiency of CO$_2$ by lowering it’s desorption temperature. Through hydrogen bonding, polyethylene glycol may also behave as a dispersing agent for the active amine functional sites enabling higher adsorption capacity. Polyethylene glycol is better than ethanol and other low molecular weight alcohols because of its higher boiling
point temperature. Polyethylene glycol may have a crucial role in the mechanism of adhesion. Using the in situ infrared technique to study the bonding and interaction chemistry in CO₂ capture over the TEPA + PEG system will help to understand PEG role in CO₂ and H₂S adsorption.

1.9 Hypothesis SO₂ Capture

Industrial sulfur dioxide emissions are a serious air pollutant whose emissions are linked to the formation of acid rain, smog, and other environmental hazards. In the literature SO₂ adsorption is slower than that of CO₂ adsorption and the adsorbed SO₂ species is capable of site blocking by poisoning the active amine sites for CO₂ adsorption [36]. There is a need for a selective sorbent which weakly adsorbs CO₂ (pKₐ 6.35) [37] but strongly adsorbs SO₂ (pKₐ 1.71) [37] without poisoning for selective removal of this acidic gas. Aromatic amines are weaker bases than simple aliphatic amines. The reduced basicity is due to resonance delocalization of nonbonding electrons in the free amine. The hypothesis for this study, by using a di-substituted aromatic amine such as 1,3-phenylenediamine, the low basic property of the amine will allow the adsorption and release of the high acidic SO₂ molecule at the proper temperature. The study of the amine by ATR-IR spectroscopy is ideally suited, the spectra provides information related to the changes in the chemical structure during the SO₂ adsorption process.
1.10 Hypothesis Photocatalytic dehydrogenation

In situ Fourier transform attenuated total reflection infrared (ATR-IR) spectroscopy are used to yield simultaneous time resolved information on dissolved reaction products, adsorbed species and catalytic oxidation at the liquid-solid interface. Fundamental research in photocatalysis may significantly benefit from methods that can probe the catalytic liquid-solid interface. The objective of photocatalytic dehydrogenation is to investigate its reaction mechanism over Au/TiO₂, Pd/TiO₂, and Pd/Al₂O₃ during UV-irradiation to study both liquid-solid reaction using ATR-IR and gas-solid reaction using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Photo-generated electrons causing a broad band adsorption (background shift) in the 900 to 3000 cm⁻¹ mid-IR region may be monitored using the DRIFTS technique [38-40] and the ATR-IR may also be used to observe the background shift phenomena. The hypothesis of this study is the background shift could be related to the activity and selectivity of isopropanol differently in the liquid phase as compared to the gas phase. A comparison of the liquid-solid and gas-solid photocatalytic reaction has not been established. This study will help to elucidate the relationship between the background shift and the adsorbed species through understanding of the reaction mechanism of catalytic dehydrogenation under the gas and liquid phase.

1.11 Background

The following sections provide information on the hydrogen bonding phenomena during the CO₂ and SO₂ adsorption and the photocatalytic dehydrogenation processes.
1.11.1 Hydrogen Bonding in Lewis Acid-Base complexes

Hydrogen bonding [41-45] is an interaction between $X-H\cdots Y$ where X and Y are F, O, N, or Cl (electronegative atoms). Infrared spectroscopy is particularly suited for detecting interactions between intermolecular hydrogen bonding groups (i.e. ethanol or polyethylene glycol). For example, the O-H stretching band for ethanol is narrow in a dilute solution of CCl$_4$. Upon increasing the concentration, intermolecular hydrogen bonding occurs in the form of $-O-H\cdots O$, as a result the O-H stretching band shifts to lower wavenumbers and broadens in the infrared [46].

Hydrogen bonding interactions have been suggested as a key factor in the solubility of CO$_2$-philic molecules [47]. It has been reported that the oxygen atom of CO$_2$, having a partially negative charge, is involved in weak electrostatic interactions with X-H bonds to form a hydrogen bond [35]. Depending upon the functional groups to which the CO$_2$ is bound, an amine (-NH$_2$) or hydroxide (-OH) [35, 48], different types of cooperative hydrogen bonding may be observed in the infrared. Hydrogen bonding may further provide stabilization energy to increase CO$_2$ solubility and has been reported to occur in super critical CO$_2$ [47, 49].

It has been reported in recent literature, (i) the loss of aqueous amine is reduced and (ii) removal efficiency improved by the addition of alcohol additives [35] in liquid based amines. The improvements are attributed to interactions between amine, additives, and CO$_2$ by hydrogen bonding.

The addition of alcohol additives lead to a broadening and shift in the ammonia IR bands and are attributed to hydrogen bonding between ammonia and the hydroxyl
groups of the additives. The hydroxyl group interactions may lower the binding energy of gaseous CO$_2$. The CO$_2$ molecule can form a complex through the conjugation of a Lewis acid-base interaction and a new hydrogen bond [48]. Figure 1.1 show a possible structure [35] of complexation with the hydroxyl group of a alcohol additive, ammonia and CO$_2$. IR N-H stretching shift to lower frequencies suggest alcohol-amonia-CO$_2$ interaction.

![Figure 1.1 Complex interaction in aqueous ammonia and alcohol additive in the presence of CO$_2$.](image)

Polyurethanes have been extensively studied using infrared spectroscopy [50-56] for characterizing the hydrogen bonding occurring in polymer solid solutions. The hydrogen bonding is evidenced by an N-H stretching frequency shift to lower values as compared to those observed in its absence [57]. These frequency shifts may be the result of $NH \cdots N$ hydrogen bonds. The hydrogen bonding is weaker for amino groups which may act as proton donors [58] or as proton acceptors in conjunction with weak acids [59]. Intramolecular hydrogen bonds are weaker when the geometry is unflavored. During CO$_2$ solvation in supercritical solutions, broadening of the N-H stretching region may be related to intermolecular $N-H \cdots O=C$ interaction. It is possible to elucidate these effects by looking at the relative variation of the X-H bond lengths upon complex
formation. In vibrational spectroscopy, the magnitude of the shift is a measure of the strength of hydrogen bonding, therefore, if the X-H bond contraction is the result of $X-H \cdots O$ from CO$_2$ or carboxyl oxygen; there should be a correlation.

1.11.2 Basicity of Amines

An amine may behave as a Lewis base because its nonbonding lone pair of electrons can form a bond with an electrophile. An amine can also behave as a Brönsted-Lowry base by accepting a proton from a proton acid. The Lewis base and Brönsted-Lowry behaviour are illustrated in reaction schemes (1) and (2) respectively.

$$
\text{(1)}
$$

$$
\text{(2)}
$$

Aqueous solutions of amines are basic because an amine can abstract hydrogen from water giving an ammonium ion and a hydroxide ion. In the aqueous phase this is an equilibrium reaction therefore the equilibrium constant that is associated with base-dissociation for the amine is symbolized by $K_b$ and is defined by equation (3).
\[ K_b = \frac{[RNH_3^+][-OH]}{[RH_2]} \]  

(3)

The \( K_b \) values for amines are small approximately \( 10^{-3} \) and lower. For ease of comparison of various basic amines the \( pK_b \) value indicates the relative strengths of amines and is defined in equation (4).

\[ pK_b = \log_{10} K_b \]  

(4)

Stronger amine bases have lower \( pK_b \) values and weaker bases have higher \( pK_b \) values.

Table 1.2 lists the \( pK_b \) values for alkyl and aryl amine bases.
<table>
<thead>
<tr>
<th>Amine</th>
<th>$K_b$</th>
<th>$pK_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary alkyl amines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylamine</td>
<td>$4.3 \times 10^{-4}$</td>
<td>3.36</td>
</tr>
<tr>
<td>Ethylamine</td>
<td>$4.4 \times 10^{-4}$</td>
<td>3.36</td>
</tr>
<tr>
<td>n-propylamine</td>
<td>$4.7 \times 10^{-4}$</td>
<td>3.32</td>
</tr>
<tr>
<td><strong>Secondary alkyl amines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethylamine</td>
<td>$5.3 \times 10^{-4}$</td>
<td>3.28</td>
</tr>
<tr>
<td>Diethylamine</td>
<td>$9.8 \times 10^{-4}$</td>
<td>3.01</td>
</tr>
<tr>
<td><strong>Tertiary amines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trimethylamine</td>
<td>$5.5 \times 10^{-5}$</td>
<td>4.26</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>$5.7 \times 10^{-4}$</td>
<td>3.24</td>
</tr>
<tr>
<td><strong>Aryl amines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aniline</td>
<td>$4.0 \times 10^{-10}$</td>
<td>9.40</td>
</tr>
<tr>
<td>1,3-phenylenediamine</td>
<td>-</td>
<td>9.21</td>
</tr>
<tr>
<td>N-methylaniline</td>
<td>$6.1 \times 10^{-10}$</td>
<td>9.21</td>
</tr>
<tr>
<td>p-chloraniline</td>
<td>$1.0 \times 10^{-10}$</td>
<td>10.00</td>
</tr>
<tr>
<td>p-nitroaniline</td>
<td>$1.0 \times 10^{-13}$</td>
<td>13.00</td>
</tr>
</tbody>
</table>
1.11.3 Tetraethylenepentamine (TEPA) infrared band assignments

Figure 1.2 shows the single beam infrared spectra during the formation of the tetraethylenepentamine thin-film at 298 K upon an ZnSe window of an ATR-IR accessory unit. All of the absorptions of linear TEPA can be ascribed to well known group frequencies [61] shown in Table 1.1. In Figure 1.2, the NH$_2$ functional group of amines in TEPA give a band due to the deformation band at 1650-1590 cm$^{-1}$, the anti-symmetric mode at 3500 cm$^{-1}$ and the symmetric mode at 3400 cm$^{-1}$. Secondary amines in TEPA exhibit N-H stretching mode at 3400 cm$^{-1}$. Hydrogen bonding may cause a small shift to lower frequencies in the liquid phase. The bands due to these modes in TEPA occur at 3290 cm$^{-1}$ where the symmetric stretch of the NH$_2$ and N-H group coincide. A higher frequency at 3360 cm$^{-1}$ results from the anti-symmetric stretch mode of NH$_2$ functional group. A band at 3200 cm$^{-1}$ is also an overtone of the NH$_2$ bending vibrations in 1650-1590 cm$^{-1}$ region. NH$_2$ twisting and wagging vibrations result in vibrations at 950-850 cm$^{-1}$. The adsorption at 1301 cm$^{-1}$ corresponds with the CH$_2$ twisting vibration in the 1300-1340 cm$^{-1}$ region. The broad absorption at 780 cm$^{-1}$ is due to N-H wagging of secondary amine groups. The C-N stretch for –CH$_2$-NH$_2$ adsorb weakly at 1043-1037 cm$^{-1}$ and more strongly at 1140-1080 cm$^{-1}$. The anti-symmetric stretching of the C-C-N and C-N-C groups occurs in the 1146-1132 cm$^{-1}$ region. The anti-symmetric stretch for CH$_2$ methylene group is 2936-2916 cm$^{-1}$ and symmetric stretch at 3863-2843 cm$^{-1}$. Finally, the deformation bending occurs in the 1475-1450 cm$^{-1}$ region.
Table 1.3  Band assignments and the vibrational modes for TEPA.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Band assignment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_2$</td>
<td>$\nu$ $650-1590$</td>
<td>[62-63]</td>
</tr>
<tr>
<td></td>
<td>$\nu_{\text{as}}$ 3550-3330</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\nu_{\text{s}}$ 3450-3250</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\nu_{\text{twist-wag}}$ 950-850</td>
<td></td>
</tr>
<tr>
<td>$-\text{CH}_2-\text{NH}_2$</td>
<td>$\nu_{\text{weak}}$ 1043-1037</td>
<td>[63]</td>
</tr>
<tr>
<td></td>
<td>$\nu_{\text{strong}}$ 1140-1080</td>
<td></td>
</tr>
<tr>
<td>$\text{C-C-N}$</td>
<td>$\nu_{\text{as}}$ 1146-1132</td>
<td>[63]</td>
</tr>
<tr>
<td>$\text{C-N-C}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_2$ (methylene)</td>
<td>$\nu$ 1475-1450</td>
<td>[64-65]</td>
</tr>
<tr>
<td></td>
<td>$\nu_{\text{as}}$ 2936-2916</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\nu_{\text{sy}}$ 2930, 2863-2843</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_2$ (twisting)</td>
<td>$\nu$ 1300-1340</td>
<td>[66]</td>
</tr>
</tbody>
</table>


Figure 1.2  Single beam spectra of tetraethylenepentamine + EtOH solution on ZnSe ATR window and subsequent evaporation of EtOH solvent, thin-film format at 298 K.
1.11.4 1,3-phenylenediamine infrared band assignments

Figure 1.2 shows the single beam infrared spectra during the formation of 1,3-phenylenediamine thin-film at 298 K upon an ZnSe window in an ATR-IR accessory unit. The infrared spectra show the adsorption bands for the amino compound, the N-H antisymmetric and symmetric stretching bands at 3338 and 3425 cm$^{-1}$ respectively [62]. Strong broad bands are observed at 1493 and 1609 cm$^{-1}$. These bands correspond to the $–\text{NH}_2$ deformation mode. The $–\text{NH}_2$ scissor deformation band is 1609 cm$^{-1}$ and its overtone is located at 3208 cm$^{-1}$. The ring-N (C-N) stretch is located at 1325 cm$^{-1}$ [63] and its overtone is located at 2656 cm$^{-1}$. The infrared absorption at 2807 cm$^{-1}$ is a combination band resulting from the C-N stretch at 1325 cm$^{-1}$ and the deformation band for $–\text{NH}_2$ at 1609 cm$^{-1}$. The infrared adsorption at 2927 cm$^{-1}$ is an overtone band for 1493 cm$^{-1}$.
Figure 1.3 Single beam spectra of 1,3-phenylenediamine + EtOH solution on ZnSe ATR window and subsequent evaporation of EtOH solvent, thin-film formation at 298 K.
1.11.5 SO$_2$ and adsorbed SO$_2$ infrared band assignments

Table 1.3 lists the infrared band assignments, vibrational modes and spectral regions for SO$_2$ and adsorbed SO$_2$ molecular species. The SO$_2$ molecule gives a symmetric absorption at 1151 cm$^{-1}$, anti-symmetric absorption at 1362 cm$^{-1}$ and bending vibration at 518 cm$^{-1}$ in the mid-IR region. Absorbed SO$_2$ causes two strong bands due to symmetric stretch in the 1200-1100 cm$^{-1}$ region, and anti-symmetric stretch in the 1400-1300 cm$^{-1}$ region as shown in Table 1.3. SO$_2$ adsorbs strongly as sulfones in the 1340-1290 cm$^{-1}$ and 1165-1120 cm$^{-1}$ region for the anti-symmetric and symmetric stretch of the SO$_2$ functional group. Sulfones have an absorption band at 610-499 cm$^{-1}$ assigned as scissor deformation and absorption at 525-463 cm$^{-1}$ assigned as wagging. Sulfonamides produce an absorption band corresponding to symmetric stretch at 1180-1140 cm$^{-1}$ and anti-symmetric stretch in 1380-1310 cm$^{-1}$ region. Sulfonamides adsorb strongly at 1180-1140 cm$^{-1}$ and 1380-1310 cm$^{-1}$ region due to anti-symmetric and symmetric stretch of the SO$_2$ functional group. Anhydrous sulfonic acids absorb at 1352-1342 cm$^{-1}$ and 1165-1150 cm$^{-1}$ region for the anti-symmetric and symmetric stretch. Sulfonates absorb in the 1375-1335 cm$^{-1}$ and 1195-1165 cm$^{-1}$ region for anti-symmetric and symmetric stretch respectively. The anti-symmetric stretch for dialkyl sulphate occurs at 1415-1390 cm$^{-1}$ and symmetric stretch in the 1200-1187 cm$^{-1}$ region.
Table 1.4  SO$_2$ band assignments, vibrational modes, and spectral regions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Functional Group</th>
<th>Symmetric stretch (cm$^{-1}$)</th>
<th>Asymmetric stretch (cm$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur dioxide</td>
<td>SO$_2$</td>
<td>1151</td>
<td>1362</td>
<td>[67]</td>
</tr>
<tr>
<td></td>
<td>-SO$_2$ scissor</td>
<td>610-499</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-SO$_2$ wagging</td>
<td>525-463</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfones</td>
<td>C-SO$_2$-C</td>
<td>1165-1120</td>
<td>1340-1290</td>
<td>[68-70]</td>
</tr>
<tr>
<td>Sulfonamides</td>
<td>C-SO$_2$-N</td>
<td>1180-1140</td>
<td>1380-1310</td>
<td>[70-72]</td>
</tr>
<tr>
<td>Anhydrous sulfonic acids</td>
<td>C-SO$_2$-OH</td>
<td>1165-1150</td>
<td>1352-1342</td>
<td>[70, 73]</td>
</tr>
<tr>
<td>Sulfonates</td>
<td>C-SO$_2$-O-C</td>
<td>1195-1165</td>
<td>1375-1335</td>
<td>[70, 74]</td>
</tr>
<tr>
<td>Dialkyl sulfates</td>
<td>C-O-SO$_2$-O-C</td>
<td>1200-1187</td>
<td>1415-1390</td>
<td>[70, 73]</td>
</tr>
</tbody>
</table>


1.11.6 H$_2$S and adsorbed H$_2$S infrared band assignments

The hydrogen sulphide (H$_2$S) molecule is nonlinear and similar to the H$_2$O molecule in its normal vibrational modes [75-77] including its electron structure. H$_2$S is a very strong reducing agent thus its high reactivity with metal oxide surfaces. Table 1.4 lists the infrared band assignments for H$_2$S and adsorbed H$_2$S upon NaX zeolite and Al$_2$O$_3$ metal oxides. The region at 2570-2585 cm$^{-1}$ has a doublet absorption band indicating an HSH adsorbed species. H$_2$S is physically adsorbed on zeolites at 2565 cm$^{-1}$. A strong hydrogen bonding is also possible with surface –OH species and can be observed in the 3400-3500 cm$^{-1}$ region. H$_2$S adsorption on zeolites and alumina show low coverage H$_2$S dissociates to form SH- species adsorbed at 2500 cm$^{-1}$ [78]. The HS group on H$_2$S may also hydrogen bond reversibly on Na zeolites as Brönsted acid site [79-80]. The adsorption of H$_2$S on NaX zeolite and aluminium oxide is listed in Table 1.4. The most important bands resulting from H$_2$S adsorption, on for example alumina oxide occur around 2560-2570 cm$^{-1}$ for S-H stretching vibration and 1335-1340 cm$^{-1}$ for scissor deformation vibrations.
Table 1.5  H$_2$S band assignments and vibrational modes on NaX and Al$_2$O$_3$ metal oxides.

<table>
<thead>
<tr>
<th>NaX Zeolite (cm$^{-1}$)</th>
<th>Al$_2$O$_3$ (cm$^{-1}$)</th>
<th>Species</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2560 2570</td>
<td></td>
<td>HS$^-$</td>
<td>[78, 81-84]</td>
</tr>
<tr>
<td>2565 2570</td>
<td></td>
<td>H$_2$S</td>
<td>[81, 83, 85]</td>
</tr>
<tr>
<td>1240</td>
<td>1080</td>
<td>HSO$_3$-</td>
<td>[84, 86]</td>
</tr>
<tr>
<td>1315 1330</td>
<td></td>
<td>SO$_2$</td>
<td>[82, 85]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>physisorbed</td>
<td></td>
</tr>
</tbody>
</table>


1.11.7 Photocatalysis

Charge carriers induced by UV radiation are the requirement of a semiconductor in the application for photocatalytic reactions [87-89]. The phenomenon of photogenerated electrons and holes is illustrated by reaction step (3):

\[
\text{TiO}_2 + h\nu \rightarrow h^+ + e^- \quad (3)
\]

Upon generation, the photogenerated electron and hole pairs may undergo recombination, trapping, or transfer to the donors and acceptors adsorbed on the semiconductor catalyst surface. A useful technique for studying these processes is by infrared spectroscopy. Infrared spectroscopy shows that photogenerated electrons can give a featureless infrared adsorption (background shift) in the 900 to 3000 cm\(^{-1}\) mid-IR region [90-94]. The background shift can be used to follow changes of the metal catalyst and may be correlated with the observation of adsorbed species and the formation of reaction products. The following advantages may be summarized by observation of the photogenerated background shift during the photocatalytic reaction.

1.11.8 Advantages on observing the IR background shift

1. Changes may be correlated with information on the adsorbate layer or reaction products with free electrons measured simultaneously by in situ infrared.
2. Time resolution allows following the response of the catalytic process.
3. The appearance of the reaction product such as a ketone or aldehyde may be followed by the state of the Pd and Au metal.

1.11.9 Catalytic Dehydrogenation

Catalytic dehydrogenation of alcohol is an important process for the production of aldehyde and ketone [95]. Aldehyde and ketone compounds such as formaldehyde, acetaldehyde, acetone, 2-butanone, etc are very important industrial chemicals used by themselves as starting materials for a host of other substances. As a result, the carbonyl group occupies a central place in organic chemistry. The electronegative oxygen polarizes the carbon-oxygen bond enabling the carbon to be subject to nucleophilic substitution for reactions with the carbonyl group. Many reactions of the carbonyl group are acid catalysed where the acid attacks the carbonyl site to create a carbocation that subsequently reacts with the nucleophile. Isopropyl alcohol (2-propanol) dehydrogenation may be used as a model compound because it provides a simple and standard way to measure the photocatalyst activity in liquid phase reactions. Infrared spectroscopy is extremely useful in analysing carbonyl containing compounds including aldehydes and ketones. The carbonyl infrared frequencies for various ketones and aldehydes are listed in Table 1.6 thru 1.8. Whether the carbonyl group is located next to a double bond, an aromatic ring, or oxygen substitution the carbonyl stretching frequency remains within 1650-to-1740 cm\(^{-1}\) in the mid-IR region. Therefore, the photocatalytic study of alcohol dehydrogenation upon a model catalyst such as isopropanol may be applied to a host of industrial relevant intermediate starting materials.
Table 1.6  Characteristic infrared carbonyl stretching peaks, molecular species in chloroform solutions [60, 96-97].

<table>
<thead>
<tr>
<th>Structure</th>
<th>Carbonyl Containing Compound</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexones</td>
<td>1725-1705</td>
<td></td>
</tr>
<tr>
<td>Aliphatic Ketones</td>
<td>1725-1705</td>
<td></td>
</tr>
<tr>
<td>Acid</td>
<td>1815-1785</td>
<td></td>
</tr>
<tr>
<td>Chlorides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>□ □-unsaturated Ketones</td>
<td>1685-1666</td>
<td></td>
</tr>
<tr>
<td>Aryl Ketones</td>
<td>1700-1680</td>
<td></td>
</tr>
<tr>
<td>□-diketones</td>
<td>1640-1540</td>
<td></td>
</tr>
</tbody>
</table>
Table 1.6  Characteristic infrared carbonyl stretching peaks, molecular species in chloroform solutions [60, 96-97]. (continued)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Carbonyl Containing Compound</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>Aliphatic</td>
<td>1740-1720</td>
</tr>
<tr>
<td>RCH</td>
<td>Aldehydes</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>☐, ☐unsaturated</td>
<td>1705-1685</td>
</tr>
<tr>
<td>R-C=O-C=O-H</td>
<td>Aldehydes</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>Aryl</td>
<td>1715-1695</td>
</tr>
<tr>
<td>Ar C H</td>
<td>Aldehydes</td>
<td></td>
</tr>
<tr>
<td>RCOOH</td>
<td>Aliphatic acids</td>
<td>1725-1700</td>
</tr>
<tr>
<td>☐</td>
<td>☐unsaturated acids</td>
<td>1700-1680</td>
</tr>
<tr>
<td>ArCOOH</td>
<td>Aryl acids</td>
<td>1700-1680</td>
</tr>
</tbody>
</table>
Table 1.6  Characteristic infrared carbonyl stretching peaks, molecular species in chloroform solutions [60, 96-97]. (continued)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Carbonyl Containing Compound</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O [\square] [\square] [\square] RCOR’</td>
<td>Aliphatic</td>
<td>1740</td>
</tr>
<tr>
<td>R—C=C—COR’</td>
<td>Esters</td>
<td>1730-1715</td>
</tr>
<tr>
<td>O [\square] Ar COR’</td>
<td>Aryl esters</td>
<td>1730-1715</td>
</tr>
<tr>
<td>O [\square] HCOR</td>
<td>Formate esters</td>
<td>1730-1715</td>
</tr>
<tr>
<td>O [\square] C₆H₅OCCH₃</td>
<td>Vinyl and Phenyl acetate</td>
<td>1776</td>
</tr>
<tr>
<td>Structure</td>
<td>Carbonyl Containing Compound</td>
<td>Wavenumber (cm⁻¹)</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>R-C-O</td>
<td>Acyclic</td>
<td>1840-1800</td>
</tr>
<tr>
<td>R-C-O</td>
<td>Aldehydes</td>
<td></td>
</tr>
<tr>
<td>R-C-O</td>
<td>(two peaks)</td>
<td>1780-1740</td>
</tr>
<tr>
<td>R-C-O</td>
<td>Primary</td>
<td>1694-1650</td>
</tr>
<tr>
<td>R-C-NH₂</td>
<td>Amides</td>
<td></td>
</tr>
<tr>
<td>R-C-NH₂</td>
<td>Secondary</td>
<td>1700-1670</td>
</tr>
<tr>
<td>R-C-NR’</td>
<td>Amides</td>
<td></td>
</tr>
<tr>
<td>R-C-NR’₂</td>
<td>Tertiary</td>
<td>1670-1630</td>
</tr>
<tr>
<td>R-C-NR’₂</td>
<td>Amides</td>
<td></td>
</tr>
</tbody>
</table>
The motivation for this study

The majority of in situ infrared catalytic studies reported in the literature focus upon catalytic solid-gas reactions whereas the catalytic liquid-solid reactions have been less studied in spite of the importance of liquid phase reactions. Attenuated total reflection (ATR) infrared spectroscopy has been shown to be useful in studying the liquid-solid interface of model catalysts [98-100]. Vibrational spectroscopy is well suited for liquid phase reactions; the vibrational spectrum contains structural information on the adsorbate later such as interaction between surface and adsorbate, orientation, and intermolecular interactions within the adsorbate layer. Additionally, the availability of sophisticated ab initio quantum chemical calculations makes it possible to simulate spectra with predictive accuracy of the adsorption bands for key molecularly adsorbed species during the catalytic reaction.

The objective of the study is to use ATR-IR and DRIFTS spectroscopy to study the liquid-solid and gas-solid interface to investigate the mechanism of photocatalytic alcohol dehydrogenation over Au/TiO₂, Pd/TiO₂, and Pd/Al₂O₃ catalysts during UV irradiation. These in situ infrared techniques allow monitoring of photogenerated electrons along with changes in the concentration of adsorbed species under UV irradiation. The dehydrogenation reaction will be carried out in the presence and absence of UV irradiation. Au/TiO₂ catalyst is used for its activity and selectivity for partial oxidation which may facilitate oxidative dehydrogenation; Pd/TiO₂ and Pd/Al₂O₃ catalysts are used for their activities in alcohol dehydrogenation reaction. The goal is to (i) present the relationship between the IR intensity related to photogenerated electrons,
adsorbed species, and rate of their formation, (ii) discuss the reaction mechanism of gas-solid and liquid-solid photocatalytic reactions over Pd and Au catalysts, and (iii) provide a coherent picture bridging gas-solid and liquid-solid photocatalytic reaction mechanisms. There may be a correlation with the observation of adsorbed species and the formation of reaction products with the production of photogenerated electrons.

1.12 Bibliography


CHAPTER II
EXPERIMENTAL

2.1 Catalyst Preparation Photocatalytic Dehydrogenation Reaction

The 1 wt% Pd/TiO₂ catalyst was prepared by incipient wetness impregnation of Pd(NO₃) (Aldrich) solution on Degussa P25 TiO₂. The 1 wt% Pd/Al₂O₃ catalyst is prepared by incipient wetness co-impregnation of Pd(NO₃)₂·2·H₂O (Aldrich) solution onto γ-Al₂O₃ (STREM). After impregnation, each catalyst was filtered and rinsed with deionized water. The Pd/TiO₂ and Pd/Al₂O₃ catalysts were then dried and calcined at 773 K in air at a heating rate of 10 K/min. The Pd/TiO₂ and Pd/Al₂O₃ catalysts were characterized by X-ray Diffraction (XRD) Philips Analytical X-Ray PW1710 diffractometer using Cu Kα radiation operating at 40 kV and 35 mA.

The 1 wt % Au/TiO₂ was prepared by the homogeneous deposition precipitation of Au onto TiO₂. One 1 wt% Au/TiO₂ catalyst was prepared by Homogeneous Deposition-Precipitation (HDP) method [1] of HAuCl₄·4H₂O (Aldrich) onto Degussa-P25 TiO₂. The specific procedure involves (i) dissolving excess urea in an appropriate amount of aqueous solution 0.004M of HAuCl₄·4H₂O with 5 g TiO₂ at 343 K. The temperature of the solution was raised to 348 K for 5-6 h until the pH =7, (ii) washing the resulting solid five times with warm distilled water, (iii) centrifuging to remove the Na⁺ and Cl⁻ ions, (iv) drying the sample at 353 K for 12 h, (v) reducing the catalyst under H₂
(100 Vol%) 5 cm$^3$/min for 30 minutes, and then (vi) calcining the sample in air at 673 K for 30 minutes.

A thin-film was prepared from 10 mg catalyst in 5 ml 2-propanol upon an ZnSe window in an ATR-IR accessory unit. The catalysts were reduced in situ in flowing H$_2$ at 523 K for 30 minutes. Following the in situ reduction of the catalysts, the CO adsorption and TPR was carried out at room temperature and 623 K respectively.

2.2 Catalyst Preparation for CO$_2$, H$_2$S, and SO$_2$ Capture

The catalyst preparation of the solid and liquid sorbent for the CO$_2$, H$_2$S, and SO$_2$ adsorption processes are described below.

2.2.1 Amine Sorbent Catalyst Preparation

The Amine sorbent catalysts were prepared by two methods (i) ex-situ and (ii) in situ preparation. The ex-situ preparation, 5 wt% and 20 wt% 1,3 phenylenediamine/SiO$_2$ and 1,3-phenylenediamine/Al$_2$O$_3$ were prepared by depositing 1,3-phenylenediamine (Aldrich) onto SiO$_2$ (CABOT) and Al$_2$O$_3$ (STREM) using the incipient wetness impregnation method. Ethanol solution with the appropriate concentration of 1,3-phenylenediamine was prepared. 5 g of SiO$_2$ and Al$_2$O$_3$ powders were weighed and placed directly into 10 ml ethanol amine solution. The resulting slurry was stirred at room temperature for 30 min. The solution is then heated at 353 K until complete evaporation of the solvent. The resulting catalyst is further dried for 12 h in air at 353 K.

In situ preparation was accomplished by preparation of the ethanol amine solution and direct injection into the DRIFTS reactor onto the silica and alumina support under
reaction conditions. Incremental loadings by volume, 30, 100, 200, 300, 400, and 500 µl loadings were prepared and subsequent SO₂ capture cycles were performed. The in situ technique models a high-throughput platform which promises enhancing synthesis of catalysts and their screening versus conventional (manual) catalyst preparation ex-situ. The in situ technique allows for fast evaporation of the ethanol solvent solution and rapid screening of various amine loadings on SiO₂ and Al₂O₃ supports.

2.2.2 Liquid Amine

A series of 5 preparations are obtained by varying the thin film thickness of the amine layer on the ATR-IR ZnSe window. The 5.37, 261.4, 522.9 and 784.4 µmole thin films of tetraethylenepentamine (Aldrich, MW 189.31) and 1,3-phenylenediamine (Aldrich, MW 108.14) where prepared by direct injection of an amine/ethanol solution onto the ZnSe window at 373 K. The thin film was created from 0.1 ml of 0.05732 M amine/ethanol solution which was added dropwise onto the ZnSe window. The amine thin film was allowed to dry by evaporation of the ethanol solution at 323 K. The thin film was then heated to 373 K at 10 K/min under 100% N₂ flowing at 100 cm³/min and then cooled to 323 K for the absorption study.

Five thin film preparations were obtained by varying the loading of Polyethylene glycol (Aldrich, MW 200) on the 5.37 µmol tetraethylenepentamine thin film. The PEG ethanol solution was prepared by adding 1.085 g PEG to 0.5 ml ethanol for a 0.001085 M concentration alcohol solution. 10, 20, 30, 40, and 50 wt% loadings onto the tetraethylenepentamine thin film were prepared by direct injection of 0.1 ml alcohol
solution at 323 K. The resulting thin film was then heated to 373 K at 10 K/min under 100% N₂ flowing at 100 cm³/min and then cooled to 323 K for the absorption study.

2.3 Experimental System for CO₂, H₂S, SO₂ Capture

The experimental system, shown in Figure 2.1, consists of three sections (i) a gas metering section including a 4-port and 6-port valves, (ii) a reactor section including in situ diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) reactor in a Digilab FTS4000 FTIR, and (iii) an effluent gas analysis section including a mass spectrometer and gas chromatograph. Section (i), the gas metering system, is designed to deliver controlled gas flows to the reactor system. Brooks 5850 mass flow controllers are used to regulate the flow rates of all gases used during the experiments. Section (ii), consisted of a DRIFTS reactor Harrick Scientific, or an Thermo Nicolet ATR accessory, placed inside a FTS4000 FTIR from Varian Inc. Section (iii), the analysis section consists of a Pfeiffer OmnistarTM quadrapole MS. The catalyst (50 mg SiO₂ + amine) was placed inside the DRIFTS or the liquid amine layer was injected onto the ATR ZnSe window without pretreatment of the catalysts. The background IR spectra were collected over blank SiO₂ powder in the DRIFTS reactor and over the blank ZnSe window in the ATR apparatus at room temperature. Additional background spectra were collected over the liquid amine in 100% N₂ while heating the ATR plate from 323 to 373 K. The temperature programmed desorption was carried out after having adsorbed molecular CO₂, H₂S or SO₂ onto the solid or liquid amine solutions, by heating the reactor at a heating rate of 10 K/min from 298 K to 373 K and the IR spectra were collected every 10 K. The infrared absorbance spectra were obtained by taking the ratio of the spectra
collected during the reaction to the background spectra at each respective temperature. The reactor effluent was analysed by MS. The FTIR along with a gas chromatographer equipped with a MS detector Shimadzu GCMS-QP5050 was utilized to cross check the MS concentration profiles developed from the data analysis of the MS spectra.

2.4 Experimental System for Photocatalytic Dehydrogenation Reaction

The experimental apparatus consists of a gas flow system with a four port valve similar to that shown in Figure 2.1, the reactor system was modified with a multi-
reflection Attenuated Total Reflection infrared (ATR-IR) accessory from Pike Technologies with a custom reactor head shown in Figure 2.2. The ATR reactor manifold consists of (i) a CaF$_2$ window for UV irradiation, (ii) an injection port for liquid phase reactant, and (iii) a gas phase inlet and outlet port. A catalyst thin film was prepared on the ZnSe window from slurry of catalyst powder which was prepared from 10 mg catalyst in 5 ml isopropanol. The catalyst slurry was sonicated for 30 min and allowed to sit stagnant over night. Prior to preparing the thin film the slurry was sonicated for 15 min. Twenty drops (0.1 ml) of slurry solution was deposited onto the ZnSe trough plate. The isopropanol solvent was allowed to evaporate and the procedure was repeated 5 times. After drying (complete evaporation of the solvent) in air at room temperature, the catalyst thin film was ready for isopropanol dehydrogenation studies.

Figure 2.2 ATR reactor system.
2.5 Strategy of Experimentation

Figure 2.3, 2.4, 2.5, and 2.6 illustrate the strategy of experimentation for examining (i) CO₂ and H₂S capture, (ii) SO₂ capture, and (iii) photocatalytic dehydrogenation of isopropanol. The strategy of experimentation includes the application of experimental design which involves planning, conducting, and analyzing the resulting data so valid conclusions may be obtained from our experiments. The goal is to develop a robust process for experimentation which minimizes the possibility of variability of the different factors while maintaining maximum information for efficient realization of our objective. The CO₂, H₂S, and SO₂ capture lend themselves to factorial design due to the nature of the experiment, adsorption and desorption replications are easily performed.

2.5.1 CO₂ / H₂S Experimental Design

A two-factor factorial design was chosen for the design of the CO₂ and H₂S, capture experiments. For the CO₂ and H₂S capture experiments two factors are desired to be investigated. Factor A is related to diffusion limitation of CO₂ through the TEPA thin film and is a function of the thin film thickness. Four thin film thicknesses (4, 182, 364, and 547 µm) were chosen based upon the effective penetration depth of the incident IR beam [2] on the ATR window. The polyethylene glycol (PEG) additive effect lowering the desorption temperature and increasing adsorption capacity for CO₂ and H₂S is of interest, therefore factor B consists of five PEG loading levels (10, 20, 30, 40, and 50 wt% on a 5.37 µmol basis). Each replicate of the experiment contains “ab” treatment
combinations and there will be three replicates at each level of the experiment. With this factorial design we want to answer the following questions:

2.5.2 CO$_2$ / H$_2$S Experimental Questions to be answered

1. Will the addition of PEG promote 100% removal efficiency of CO$_2$ by lowering the desorption temperature?

2. What polyethylene loading will achieve the highest capture capacity?

Figure 2.4 shows an illustration of the experimental plan for CO$_2$ and H$_2$S capture study. Factor A was varied with TEPA thickness layers of 4, 182, 364, and 547 µm. Factor B was studied at the most efficient PEG layer thickness; the levels are 10, 20, 30, 40, and 50 wt % loading onto the TEPA layer. Calibration of the experimental equipment runs in parallel during each planned experiment and replica to ensure reproducibility and reliability of the experimental results. The null hypothesis for this study, PEG will lower the removal efficiency of CO$_2$ lowering its adsorption temperature.

\[ H_0 : \mu_i = \text{lower removal temperature} \]  \hspace{1cm} (2)

2.5.3 SO$_2$ Experimental Design

A two-factor factorial design was chosen for the design of the SO$_2$ capture experiments. For the SO$_2$ capture experiments, two factors are desired to be investigated. A desire to investigate the amine and support effects on SO$_2$ capture led to the assignment of factor A. Factor A varied between the liquid amine layer and amine
supported on SiO$_2$ and Al$_2$O$_3$ support materials. The amine loading on the SiO$_2$ and Al$_2$O$_3$ support materials will effect diffusion and accessibility of the SO$_2$ molecule. Factor B varied the amine loading. Each replicate of the experiment contains “ab” treatment combinations and there will be three replicates at each level of the experiment. With this factorial design we want to answer the following question:

2.5.4 SO$_2$ Experimental Question to be answered

3. Will the di-substituted aromatic amine 1,3-phenylenediamine allow adsorption and release of the acidic SO$_2$ molecule at the proper temperature (i.e. 373 K)?

Figure 2.5 shows an illustration of the experimental plan for SO$_2$ capture study. Factor A has levels of (i) no support, (ii) SiO$_2$, and (iii) Al$_2$O$_3$ supports. Factor B varied 2 and 10 vol % of the amine solution on the SiO$_2$ and Al$_2$O$_3$ supports. Calibration is performed in a parallel fashion during each adsorption experiment and replication to ensure reproducibility and reliability of the experimental results. The null hypothesis for this study is the low basic property of 1,3-phenylenediamine will allow adsorption and release of SO$_2$ below the appropriate temperature. In other words, the release temperature cannot exceed the decomposition temperature (T$_d$) of the amine sorbent.

$$H_0 : \mu_i < T_d$$ (3)
Figure 2.3 Project outline, CO$_2$, H$_2$S, SO$_2$ capture, and photocatalytic dehydrogenation of isopropanol.
Figure 2.4 Experimental plan for CO₂ and H₂S capture study.
Figure 2.5  Experimental plan for SO$_2$ capture.
Figure 2.6  Experimental procedure for photocatalytic reaction.
2.6 Analysis Section

The following sections describe the experimental setup for the analytical equipment, fourier transform infrared spectrometer, mass spectrometer, and gas chromatograph.

2.6.1 IR and Diffuse Reflectance Spectroscopy

A Digilab FTS4000 spectrometer equipped with a Mercury Cadmium Telluride (MCT) detector was used for the photocatalytic experiments. The IR software setup consists of a sampling speed of 20 KHz, filter 5, under sampling ratio (UDR) 1, resolution 4 cm\(^{-1}\), sensitivity 1, and a maximum range of 400 to 6000 cm\(^{-1}\). The speed controls the rate of data collect and interferometer speed. The filter removes the signal frequencies outside the modulation range. The UDR setting sets the sampling range, both sides of the interferogram or only one side of the interferogram can be use for collecting single beam spectra. UDR setting equal to 1 allows sampling on only one side of the interferogram. Sensitivity is a scalar multiplier to amplify the raw single beam data. The spectra is collected and stored on a Dell Optiplex GX270 computer with an intell Pentium 4 2.60 GHz processor and 1 GB RAM running Digilab win-IR Pro 3.4 software. For steady-state transient and transient experiments the spectra consists of 32 co-added scans.

A thermo Nicolet 6700 FTIR equipped with an MCT detector and KBr beam splitter was used to study the CO\(_2\), H\(_2\)S, and SO\(_2\) experiments. The IR software setup consist of resolution 4 cm\(^{-1}\) and sensitivity setting of 8. The spectra collected during steady state and transient experiments are 8 co-added scans.
Harrick Scientific Products, Inc. Praying MantisTM diffuse reflection accessory and reaction chamber diffuse reflectance infrared Fourier transform spectrometry (DRIFTS) is utilized to make spectral measurements under controlled pressures and temperatures. The reaction chamber is a high temperature chamber capable of reaching 673 K and a pressure of several atmospheres. The reaction chamber is manufactured of 316 stainless steel material. The reaction chamber uses ZnSe windows with a spectral range of 4000-650 cm\(^{-1}\). Cooling water is required to prevent the windows from cracking due to thermal expansion. The chamber contains a cup for holding the catalyst that acts as a small simulated packed bed reactor. The temperature is monitored by a K-type thermocouple that enters the back side of the chamber. The reaction temperature is ramped at a maximum of 10 K/min.

Thermo Nicolet Spectra-Tech ARK Attenuated Total Reflectance (ATR) apparatus equipped with the heated top plate, catalog # 0056-100, was used for the liquid amine studies. The ATR cell allows for aqueous and non-aqueous liquid analysis using FTIR while heating the reactor cell during dynamic studies. The volume of the reactor cell is 65 micro liters. The cell is constructed with a custom reactor head and o-ring allowing the analysis at elevated pressures from ambient. The heated plate has an accuracy of +/- 0.1 K at set point temperature using a 110 V, 300 watt heating tape.

2.6.2 Mass Spectrometer (MS)

The reaction effluent is fed to the Pfeifer Omnistar\textsuperscript{TM} mass spectrometer. The gas is fed through a capillary tube into the ionization chamber whose operating pressure is a maximum of 3.0 \times 10^{-6} \text{mbar}. The mass spectrometer is capable of monitoring 24
masses over charge (m/e) ratios as a function of time. The MS setup, one data point is collected in 50 ms and each m/e ratio is carefully selected to prevent overlap between fragmentation species within the ionization chamber. The data is collected by a Gateway Pentium computer with 196MB RAM using Pfeifer QUADSTAR™ software.

2.6.3 GC-MS Analysis

The GC/MS system includes a GC-17A gas chromatograph and mass spectrometer with 145 L/sec turbomolecular pump, one rotary pump and advanced data station with GCMS solution software. The QP5050A system is capable of measuring a mass range of 10-990 m/z and maximum system flow of 5 ml.min. The system can scan up to 50 scans per second or 6750 daltons per second. The MS has two modes, SIM mode and Scan mode. SIM mode allows entering in individual m/z fragment numbers to monitor. The Scan mode allows scanning through a range of m/z fragment numbers.

The stock column that came with the GC unit was a fused silica catalog # 220-94536-01, phase SHR5XLB, dimensions L 30 m, ID 0.25 micron, OD 0.25 micron. The GC operational oven temperature maximum is 723 K. The GCMS included a 6 port 1/16” P type electric actuated valve with 1 cm³ sampling loop. The stock column was replaced with a Carboxene-1010 plot column for separation of permanent gases. The plot column allows separation of oxygen, nitrogen, hydrogen, carbon monoxide, methane, carbon dioxide, acetylene, ethylene, and ethane gases. The GCMS-QP5050A system was further modified to enable the GC portion of the GC/MS to be bypassed so the MS can be used as an MS only system.
Figure 2.3 shows the configuration setup for the GCMS-QP5050A system. Two 4-port valves were configured to allow bypass of the GC column in the GCMS system. Bypassing the column allows the GCMS system to operate as an MS only system. The reactor effluent gas is attached to the 6-port valve in the configuration shown in Figure 2.3. With the 6-port valve in the load position, the reactor effluent gases flow out to the vent line. When the 6-port valve is switch to inject position the reactor gas is switched in line with the injector port. The 6-port valve can be operated in manual mode and by the software method in the GC software. There is a toggle switch for manual operation that is located adjacent to the valve body. To program the valve operation using the GC method use event 91. To place the valve into the inject position set the method to event 91. To place the valve back into load position set the method to event -91. Note, if there is no reactor effluent gases flowing through the 6 port valve there will be a carrier gas leak error notification after a few minutes when the 6-port valve is placed into the inject position. A carrier gas leak might possibly damage the equipment, there needs to be a constant flow to the MS detector during operation and standby mode.
Figure 2.7 Shimadzu GCMS-QP5050A 4-port and 6-port valve configuration setup.
2.6.4 Experimental Techniques (step, pulse, TPR, TPD)

In gas phase reactions, it is imperative to utilize controlled perturbation, from steady-state conditions, in order to study adsorption, desorption, reactions and reactive intermediate species which may lead to steady-state condition. Through the study of transient kinetics, one may obtain information about reaction mechanisms, surface state properties of a catalyst, catalyst activity, selectivity, etc. The following techniques were utilized, (i) step input, (ii) pulse input, (iii) temperature programmed reaction and (iv) temperature programmed desorption which will briefly be discussed.

2.6.4.1 Step Input

A 4-port valve, shown in Figure 2.1, is used to make a switch from one gas flow to another gas flow of different composition. The step is performed from steady-state condition, generally from an inert gas to the reactant composition gases or visa versa. The step input provides transient information via IR active adsorbate species formation as various surface species are formed and consumed to product species monitored by the MS in the reactor effluent. To prevent pressure related fluctuations in the MS spectra the flow rates of gases on either side of the 4-port valve must be identical.

2.6.4.2 Pulse Input

A 6-port valve, shown in Figure 2.1, is used to send a known volume of gas over the catalyst bed at a given reaction temperature. In Figure 2.1, carrier gas A containing a gas composition mixture is flowing into the DRIFTS reactor system. At a specified time, Gas B of known volume, generally 1 cm³, is switched in line with carrier gas A.

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resulting plug of Gas B is carried into the reactor system over the catalyst bed. As a result of the exposure of carrier gas B to the catalyst bed, transient surface and product species may be formed leading to quantitative information about the reaction or catalyst surface. The pulse technique can be used to analyse reaction rates and catalyst poisoning information for a given reaction.

2.6.4.3 Temperature Programmed Reaction (TPR)

The temperature programmed reaction is used to study surface reactions and molecular adsorption on surfaces to discriminate between processes with different activation parameters. Utilizing IR and MS two important pieces of information may be obtained from the TPR study. Under steady-state flow of the reactants, the temperature is increased at a constant rate, generally 10 K/min, and the ensuing catalytic reaction takes place with respect to different temperatures. From the information the lightoff temperature and identification of active and spectator molecular species can be determined. The lightoff temperature is the temperature at which the conversion of the important reactant reaches 50% conversion. The lightoff temperature is very important, it provides a bench mark for a reaction below the lightoff is reaction-controlled which means the reaction represents the overall process. The reaction above the lightoff become diffusion controlled which means the reactants are being consumed at a high rate and the concentration of reactants approach zero near the surface.

The difference between a spectator and active adsorbate is the spectator molecule does not participate in the reaction mechanism toward the product species. The TPR technique can help to elucidate each of these species. Under reaction controlled
conditions (below the lightoff temperature) both active and spectator species will increasingly adsorb on the catalyst surface. Under diffusion controlled conditions (above the lightoff temperature) the spectator species will become the only remaining species during catalytic reaction. The data obtained during the TPR will consist of intensity variation of the absorption peaks of the IR active species and each mass fragment as a function of time / temperature.

2.6.4.4 Temperature Programmed Desorption (TPD)

The temperature programmed desorption technique provides information as how adsorbed species desorbs as a function of temperature. The following information can be obtained from the TPD experiment.

1. The area under a peak is proportional to the amount originally adsorbed or is proportional to the surface coverage of the adsorbed species.

2. The kinetics of desorption provides information on the state of the adsorbed molecule. The MS and IR data will help to distinguish whether the adsorbed species is molecularly adsorbed or dissociative adsorbed.

3. The position of the peak is related to the enthalpy of adsorption and also related to the strength of binding to the surface. If there is more than one binding state for an adsorbing molecule there may be different desorption peaks in the MS spectrum during the TPD experiment.
The TPD experiment is conducted in a similar manner to that of the TPR experiment. The difference being the reactant is first adsorbed upon the catalyst surface at low temperature. Then in an inert gas and after having reached steady state conditions (the system is allowed to equilibrate) the reactor system is heated at a constant rate while collecting the IR and MS data. Also note if there is an occurrence of two desorption peaks this may also be characteristic of the decomposition of a more complex surface species.

2.7 Experimental Difficulties

The major experimental difficulties experienced during each experiment involving the FTIR and MS system are summarized below.

- The custom reactor head for the Thermo Nicolet Heated ARK apparatus required non-destructive leak testing in order to ensure safety of the equipment during the adsorption and desorption of the noxious gases H₂S and SO₂. Nitrogen leak testing was performed using a Perking Elmer Leak detector part number N9306089. The first version of the reactor head caused considerable N₂ leaking. Trouble shooting the system, N₂ was leaking between the heating plates and the o-ring in the reactor head. The N₂ leak between the heating plates was prevented by utilizing liquid copper head gasket sealant and allowing a 24 h cure time. A larger o-ring was replaced into the reactor head to prevent further N₂ leaks.
During the SO$_2$ capture experiments on SiO$_2$ solid support material, the 1,3-phenylenediamine+EtOH solution was injected directly for in situ preparation of the amine sorbent catalyst. The direct injection took place at 373 K into flowing Ar into the DRIFTS reactor. During catalyst preparation, injecting the amine solution into the Ar flow caused a problem by crystallization onto the ZnSe windows. Direct injection of the liquid amine/solvent into Ar at a total flow rate of 150 cm$^3$/min. During the Ar flow significant turbulence occurred in the DRIFTS reactor dome causing a portion of the injected amine solution to crystallize upon the ZnSe windows. The residual amine on the windows caused C-H and amino absorption bands which overlapped with those on the SiO$_2$ support during the SO$_2$ capture experiment causing some difficulty interpreting the IR spectra during the TPD experiment. The windows were cleaned with a cotton swab which removed the residual amine species and the experiment was repeated.

During the photocatalytic experiment with isopropanol, a step change from an oxidizing and reducing environment showed little response to the gas-liquid interface due to diffusion limitations. Injecting 1 cm$^3$ isopropanol resulted in too thick of a liquid layer causing serious diffusion limitations during the experiment. In order to minimize the effects of diffusion limitations the liquid layer thickness was minimized. The liquid layer thickness was dependent upon the evaporation rate of isopropanol; there needed to be sufficient liquid to sustain the reaction.
during the length of the experiment. The layer thickness of 0.1 ml isopropanol allowed an optimum O₂ diffusion during the photocatalytic experiment.

- The Shimadzu GCMS-QP5050A came with two custom valves mounted in the GC oven. The valves were equipped with 448 K polymer rotors allowing a maximum operating temperature of no more than 448 K. We needed to replace the stock fused silica column with a Carboxen 1010 plot column in order to separate the permanent gases for CO₂, H₂S, and SO₂. The problem arises when the Carboxen-1010 column requires 498 K cleaning cycle prior to use. The custom valve rotors would melt at temperature higher than 448 K. The solution was to call Valco Valves Inc. and order 573 K rated rotors and replace the rotors. After replacement of the high temperature rotors, the rotors required pre-treatment and testing for leaks.

2.8 Bibliography


CHAPTER III

IN SITU ATR-IR STUDY ON THE EFFECTS OF POLYMER MODIFIED SORBENT FOR IMPROVED SORBENT CAPACITY DURING CO₂ AND H₂S CAPTURE

3.1 Abstract

The adsorption and desorption of CO₂ and H₂S on tetraethylenepentamine (TEPA) and polyethylene glycol (PEG) has been studied by the step transient technique coupled with in situ infrared (IR), mass spectrometry (MS) and ab initio quantum chemical calculations. CO₂ adsorbs on TEPA/PEG as carbonates and bicarbonates, while H₂S adsorbs as an amine-sulphide \( \text{−}NH\text{−}SH \text{−} \) which also coordinates with the \( −\text{OH} \) from PEG to form an amine-sulphide \( −N\text{−}SH\text{−}O\text{−}\text{H} \) complex. The CO₂ adsorption capacity of the TEPA sorbent was doubled by the addition of PEG and increased by a factor of twelve for the H₂S adsorption. PEG disperses the amine adsorption sites enabling more CO₂ and H₂S molecules to adsorb. A temperature-programmed desorption study on CO₂ and H₂S over TEPA/PEG reveals that PEG offers the unique ability for adjusting the adsorption capacity and desorption temperature (i.e. to 353 K) by modifying the TEPA/PEG blend composition. The removal efficiency was improved by lowering the desorption temperature. These results are attributed to the interactions between the TEPA and PEG additive and CO₂ and H₂S via hydrogen bonding as verified by IR
spectroscopy and ab initio quantum chemistry. The experimental findings demonstrate that additives including amine and hydroxyl group are suitable for modifying the amine based sorbent for CO₂ and H₂S removal.

3.2 Experimental

The experimental section consists of the liquid amine sorbent preparation and characterization, in situ ATR-IR, and theoretical approach used to study CO₂ and H₂S adsorption.

3.2.1 Liquid Amine Preparation and Characterization

The gases supplied by Praxair were N₂ (99.999 vol %), CO₂ (99.995 vol %), and 1% H₂S balance UHP He. A 4 micron liquid layer was prepared from 0.0573 M tetraethylenepentamine (TEPA, Aldrich > 30.0 %) in ethanol (Pharmco-Aaper, 99.98%) solution. The liquid layer was created by adding drop wise 0.1 ml TEPA/ethanol solution upon a ZnSe window. The TEPA liquid layer was allowed to sit stagnant for 30 min for evaporation of the ethanol solvent, and then heated to 373 K at 10 K/min under 100% N₂ flowing at 100 cm³/min to evaporate the remaining solvent and then cooled to 323 K for the adsorption study.

Five additional liquid layer preparations were created by addition of polyethylene glycol (Aldrich, PEG, MW 200) to the TEPA liquid layer, from a 0.00108 M PEG solution, at 9.1, 16.7, 23.0, 29.0, and 33.3 wt % PEG loading. The resulting film was allowed to set stagnant at 323 K for 30 min for complete mixing of the TEPA and PEG.
The liquid layer was further heated to 373 K at 10 K/min under 100 cm$^3$/min N$_2$ flow, held at 373 K for 30 min, and then cooled to 323 K prior to the adsorption study.

3.2.2 In Situ ATR-IR Reaction Studies

The experimental apparatus, shown in Figure 3.1, consists of (i) a reactant metering system (Brooks Instrument 5850 mass flow controllers, (ii) a gas sampling section including a 4-port valve, (iii) a Attenuated Total Reflectance accessory (ATR-IR, Harrick Scientific) and a custom reactor manifold mounted to the ATR-IR top plate mounted inside an Fourier Transform Infrared Spectrometer (FTS6700 FTIR, Thermo-Nicolet), and (iv) a mass spectrometer (MS, Pfeiffer Omnistar™). The 4-port valve allows switching the inlet flow from 100% N$_2$ to 100 % CO$_2$ while maintaining a total flow rate of 100 cm$^3$/min over the liquid sorbent.

The changes in the concentration of IR-observable adsorbates are monitored by FTIR. The IR absorbance spectrum of adsorbed and gaseous species is obtained by $A = -\log\left(P_0/P\right)$ [1], where $P_0$ is the background IR single beam spectrum (32 co-added scans and resolution 4 cm$^{-1}$) of the catalyst under 100% N$_2$ flow and P is the IR single beam spectrum during the adsorption study. The MS responses corresponding to N$_2$ (m/e = 28), CO$_2$ (m/e = 44), and H$_2$S (m/e=34) are monitored for the changes in the ATR-IR reactor effluent concentrations.
Figure 3.1 Experimental Apparatus.
3.2.3 Theoretical Methods

Quantum chemical calculations were performed using GAUSSIAN03 [2] set of programs. The density functional theory used to calculate the infrared vibrational frequencies is the Becke’s three-parameter exchange functional and gradient corrected functional of Lee, Yang, and Parr (B3LYP) [3-5]. Of all the DFT methods, the B3LYP functional is the most widely used [6] for harmonic vibrational frequencies. The 6-31G* basis set [7] has been used as a compromise between accuracy and applicability to large molecules. The smaller basis set (6-31G*) suffice in DFT theory because the basis functions do not have to describe the correlating orbitals [8]. The basis set is modified with the diffuse function (6-31++G*) to improve the accuracy for hydrogen bonded dimmers having electron density at larger distances from the nuclei [9]. Therefore, the TEPA, TEPA/CO₂, TEPA/H₂S, TEPA/PEG/CO₂, and TEPA/PEG/H₂S complexes were optimized using B3LYP/6-31++G* theoretical method. The optimized structures are visualized with GaussView 4.1 [10]. The binding energies for TEPA-PEG with CO₂ or H₂S were obtained from the following equations:

\[
E_b = E[TEPA + CO_2] - E[TEPA] - E[CO_2] \quad (1)
\]

\[
E_b = E[TEPA + PEG + H_2S] - E_b[TEPA] - E[PEG] - E[H_2S] \quad (2)
\]
Where \( E[TEPA+CO_2] \) is the total energy of TEPA with CO\(_2\), \( E[TEPA] \) is the total energy of TEPA and \( E[CO_2] \) is the total energy of the CO\(_2\) molecule, in Eqn. (1). Similarly, in Eqn. (2) the binding energies are determined for H\(_2\)S adsorption.

3.3 Results

The results section describes the interaction effects of TEPA-PEG and CO\(_2\) adsorption over the TEPA, PEG, and blended TEPA/PEG sorbents.

3.3.1 Interactions between TEPA and PEG

Figure 3.2 shows the single beam IR spectra for the pure PEG, TEPA and the blended TEPA/PEG liquid layers. The PEG layer, shown in Figure 3.2(a), exhibit characteristic IR absorption bands for –OH at 3421 cm\(^{-1}\), aliphatic C-H symmetric stretch vibration at 2869 cm\(^{-1}\), C-C-O vibration at 1296 cm\(^{-1}\), and the C-O vibration at 1121 cm\(^{-1}\). The TEPA layer, shown in Figure 3.2(b), show characteristic bands which can be ascribed to the well known group frequencies [11]. The NH\(_2\) group gives a band due to the antisymmetric vibration at 3353 cm\(^{-1}\) and symmetric vibration at 3278 cm\(^{-1}\). The IR adsorption at 1574, 1673, and 3187 cm\(^{-1}\) are assigned to the NH\(_2\) deformation and overtone vibrations respectively. The C-C-N stretch vibration occurs at 1128 cm\(^{-1}\) [11].

Figure 3.2(c-g) compare the IR spectra for 9.1, 16.7, 23.0, 29.0, and 33.3 wt % PEG + TEPA blended liquid layers at 323 K. Blending 9.1% PEG into TEPA, shown in Figure 3.2(c), results in the formation of three distinct N-H absorption bands at 3354, 3282, and 3211 cm\(^{-1}\) along with the appearance of an absorption band at 1672 cm\(^{-1}\) that is assigned to the NH\(_2\) bending mode as compared to the TEPA only in Figure 3.2(b).
Figure 3.2 IR single beam spectra, effect of PEG on the 4 micron TEPA liquid layer. The PEG Loading at 323 K (a) 100 wt% PEG (b) 100 wt% TEPA (c) 9.1 wt% PEG/TEPA (d) 16.7 wt% PEG/TEPA (e) 23.0 wt% PEG/TEPA (f) 29.0 wt% PEG/TEPA (g) 33.3 wt% PEG/TEPA.
The hydroxyl group from the PEG interacts with the amine group through hydrogen bonding consisting of (hydroxyl group of PEG donating hydrogen) $O-H \cdots N$ (nitrogen of the amine accepting hydrogen). The hydroxyl-amine interaction is confirmed from the optimized structure at the B3LYP/6-31++G* level shown in Figure 3.3. Increasing the concentration of PEG in the TEPA liquid layer resulted in the appearance of the NH$_2$ bending vibration at 1672 cm$^{-1}$ and results from PEG dispersing the TEPA molecules on the ZnSe window. Increasing the PEG concentration on TEPA further broadens the N-H stretching region.

3.3.2 CO$_2$ adsorption

The CO$_2$ adsorption process is studied over the TEPA, PEG, and blended TEPA-PEG liquid layers in the absence of the SiO$_2$ support material.

3.3.2.1 TEPA

Figure 3.4 shows the difference IR spectra of the molecular and adsorbed species during CO$_2$ adsorption over the TEPA liquid layer at 323 K. Exposure of TEPA to the CO$_2$ flow led to an increase in IR intensity at 3302 cm$^{-1}$ for N-H stretch, the formation of a broad IR band centred at 2580 cm$^{-1}$ for hydrogen bonding and the formation of carbamate species in the 1600 – 1200 cm$^{-1}$ region. Positive IR peaks for the carbamate species include (i) a shoulder at 1630 cm$^{-1}$ for the R-NH$_2$CO$_2^-$ symmetric stretch [12], (ii) the NCO$_2^-$ asymmetric stretch at 1567 cm$^{-1}$ and, (iii) the monodentate bicarbonate asymmetric vibration at 1463 and symmetric vibration at 1297 cm$^{-1}$ [13-16].
Figure 3.3  Geometry of TEPA/PEG and CO$_2$ at the optimized B3LYP/6-31++G* level.
Figure 3.4  IR absorbance spectra sending CO$_2$ over the 4 micron TEPA liquid layer at 323 K.
Increasing IR intensities for the carbamate species, the N-H stretch vibration at 3302 cm\(^{-1}\) and the broad band at 2580 cm\(^{-1}\) indicate the carbamate species is participating in the IR observable hydrogen bonding effect. Increasing the CO\(_2\) exposure time from 0.00 to 11.13 min did not shift the wavenumber of the IR observable species but caused a variation in IR intensities as a result of greater or lesser amounts of products formed on the TEPA layer.

Figure 3.5 shows the difference IR spectra while sending isotopic \(^{13}\)CO\(_2\) over TEPA liquid layer at 323 K. The presence of isotopic \(^{13}\)CO\(_2\) shows an isotopic shift in the carbamate vibrational frequencies, the NCOO vibration shifted from 1567 cm\(^{-1}\) to 1542 cm\(^{-1}\), and the NCOO skeletal vibration shifted from 1463 cm\(^{-1}\) to 1418 cm\(^{-1}\). The shift in the IR frequencies of carbamates indicates CO\(_2\) is adsorbing at the amine adsorption site. The broad band absorption at 2580 cm\(^{-1}\), attributed to hydrogen bonding of the carbamate species, did not exhibit the isotopic shift effect.

3.3.2.2 PEG liquid layer

Figure 3.6 show the IR absorbance spectra during CO\(_2\) adsorption over PEG liquid layer at 323 K. Exposure of PEG to CO\(_2\) flow caused an increase in IR intensity for (i) the R-CH\(_2\)OHCO\(_2\)^{-} symmetric stretch at 1635 cm\(^{-1}\) and asymmetric stretch at 1565 cm\(^{-1}\), (ii) the monodentate carbonate asymmetric stretch at 1409 cm\(^{-1}\) \([17]\), and (iii) the R-CH\(_2\)-OH wagging at 1290 cm\(^{-1}\). The interaction of CO\(_2\) with PEG also causes spectral changes in the \(\nu_3\) anti-symmetric stretching region producing an intense band at 2338 cm\(^{-1}\) similarly to CO\(_2\) adsorption on polymethyl methacrylate (PMMA) \([18]\).
Figure 3.5  IR absorbance spectra sending $^{13}$CO$_2$ over the 4 micron TEPA liquid layer at 323 K.
Figure 3.6 IR absorbance spectra sending CO$_2$ over PEG (MW 200) liquid layer at 323 K.
The IR adsorption bands at 3390, 3326, and 3245 cm\(^{-1}\) result from the formation of a hydrogen bonded \(\text{CO}_2 \cdots O-H\) complex [19]. Switching the inlet flow to \(\text{N}_2\) from \(\text{CO}_2\), causes the complete desorption of \(\text{CO}_2\) from the PEG layer at 323 K; the weakly adsorbed \(\text{CO}_2\) results in a lower IR intensity (5 times weaker) than that over TEPA.

3.3.2.3 Blended TEPA and PEG liquid layers

Figure 3.7 show the IR difference spectra during \(\text{CO}_2\) adsorption over the blended TEPA and PEG liquid layers at 323 K. Increasing the PEG loading from 9.1 wt\% to 33.3 wt\%, results in the formation of an immiscible PEG layer indicated by the spectral features, at 23.0 wt\% PEG loading, by the formation of (i) the 1409 cm\(^{-1}\) band for \(\text{CO}_2\) adsorption on –OH (the –OH bending mode appears), (ii) the appearance of the v3 antisymmetric band at 2338 cm\(^{-1}\), (iii) the changing IR spectral region of the aliphatic C-H stretching region to resemble that of PEG and (iv) the formation of a hydrogen bonding complex similar to that shown in Figure 3.6.

The TPD study of \(\text{CO}_2\) adsorption over the TEPA/PEG blended sorbent suggests the optimum PEG loading occurs at 16.7 wt\% PEG and TEPA corresponding to 12.83 \(\mu\)mol \(\text{CO}_2\) adsorbed and a \(\text{CO}_2/\text{TEPA}\) ratio of 2.24, shown in Table 3.2. The most important spectral feature during \(\text{CO}_2\) adsorption at 16.7 wt \% PEG loading occurs at the 1409 cm\(^{-1}\) which suggest the slight \(\text{CO}_2\) adsorption at the –OH site. The weak binding energy for \(\text{CO}_2\) and PEG (\(-4.81\) kJ/mol) along with the spectral evidence for PEG forming an immiscible layer over TEPA suggests that PEG offers the unique ability to adjust the \(\text{CO}_2\) desorption temperature.
Figure 3.7 IR absorbance spectra during CO$_2$ adsorption at 323 K over (a) TEPA (b) 9.1 wt% PEG/TEPA (c) 16.7 wt% PEG/TEPA (d) 23.0 wt% PEG/TEPA (e) 29.0 wt% PEG/TEPA (f) 33.3 wt% PEG/TEPA.
Table 3.1  Calculated binding energies for adsorbed species at the B3LYP/6-31++G* and B3LYP/6-31G optimized level.

<table>
<thead>
<tr>
<th>Basis set</th>
<th>PEG + CO&lt;sub&gt;2&lt;/sub&gt; (kJ/mol)</th>
<th>TEPA + CO&lt;sub&gt;2&lt;/sub&gt; (kJ/mol)</th>
<th>TEPA + PEG + CO&lt;sub&gt;2&lt;/sub&gt; (kJ/mol)</th>
<th>TEPA + H&lt;sub&gt;2&lt;/sub&gt;S (kJ/mol)</th>
<th>TEPA + PEG + H&lt;sub&gt;2&lt;/sub&gt;S (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31++G*</td>
<td>-4.81</td>
<td>-23.19</td>
<td>-15.07</td>
<td>-19.86</td>
<td>-17.71</td>
</tr>
<tr>
<td>(6-31G)</td>
<td>(-15.05)</td>
<td>(-45.71)</td>
<td>(-47.23)</td>
<td>(-55.38)</td>
<td>(-36.04)</td>
</tr>
</tbody>
</table>

Table 3.2  CO<sub>2</sub> and H<sub>2</sub>S Temperature Programmed Desorption over TEPA + PEG liquid layer.

<table>
<thead>
<tr>
<th>PEG Loading (wt %)</th>
<th>PEG (µmol)</th>
<th>CO&lt;sub&gt;2&lt;/sub&gt; (µmol)</th>
<th>CO&lt;sub&gt;2&lt;/sub&gt; (µmol)</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;S (µmol)</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;S (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>6.84</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9.1</td>
<td>0.537</td>
<td>8.13</td>
<td>1.41</td>
<td>2.72</td>
<td>0.51</td>
</tr>
<tr>
<td>16.7</td>
<td>1.146</td>
<td>12.83</td>
<td>2.24</td>
<td>5.08</td>
<td>0.95</td>
</tr>
<tr>
<td>23</td>
<td>1.719</td>
<td>6.41</td>
<td>1.12</td>
<td>32.22</td>
<td>6.00</td>
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<tr>
<td>29</td>
<td>2.292</td>
<td>0.49</td>
<td>0.09</td>
<td>9.56</td>
<td>1.78</td>
</tr>
<tr>
<td>33.3</td>
<td>2.865</td>
<td>0.41</td>
<td>0.07</td>
<td>4.76</td>
<td>0.89</td>
</tr>
</tbody>
</table>

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3.3.3 H₂S adsorption

Figure 3.8 shows the IR absorbance spectrum during H₂S adsorption on 23.0 wt% PEG-TEPA layer at 323 K. Exposure of the PEG-TEPA layer to H₂S flow caused an increase in IR intensity (i) at 3222 cm⁻¹ assigned to the N-H deformation of the \( \text{NH}_3^+ \) \[11\] and 1563 cm⁻¹ for the symmetric \( \text{NH}_3^+ \) deformation \[20\], (ii) at 1549 and 1481 cm⁻¹ assigned to the asymmetric and symmetric bending of the TEPA amine (-NH₂) respectively, and (iii) the 1609 cm⁻¹ is assigned to the bending of secondary amines \[21\]. The increase in IR intensity at 1302 cm⁻¹ is assigned to the formation of an amine-sulfide structure (\(-\text{N-S} \cdots \text{O}-)\) from the interaction of –NH₂, -OH, and gaseous H₂S. Interestingly, increasing the PEG loading (to 16.7 and 23.0 wt %), the –CH₂– wagging at 1100 cm⁻¹ and –CH₂-NH₂-SH₂ rocking at 980 cm⁻¹ become very strong (see Figure 3.9) suggesting that PEG disperses the TEPA molecule increasing the number of –NH₂ active sites for H₂S adsorption.

The TPD study of H₂S capture over the TEPA/PEG blended sorbent indicates the optimum PEG loading occurs at 23.0 wt% PEG loading on TEPA corresponding to 32.22 μmol H₂S adsorbed and an H₂S/TEPA ratio of 6.00, shown in Table 3.2. Interestingly, the PEG loading needed to be increased to 23.0 from 16.7 wt % for H₂S (pKa = 6.89) as compared to that for CO₂ (pKa = 6.35) capture even though H₂S is a little more basic than CO₂. The binding energy for the TEPA/PEG-H₂S (-17.71 kJ/mol) did not decrease as significantly as that for the TEPA/PEG-CO₂ (-15.07 kJ/mol) system.
Figure 3.8  IR absorbance spectra showing H$_2$S adsorption over the TEPA + 23.0 wt% PEG liquid layer at 323 K.
Figure 3.9 IR absorbance spectra during H$_2$S adsorption at 323 K over (a) TEPA (b) 9.1 wt% PEG/TEPA (c) 16.7 wt% PEG/TEPA (d) 23.0 wt% PEG/TEPA (e) 29.0 wt% PEG/TEPA (f) 33.3 wt% PEG/TEPA.
3.4 Discussion

CO₂ capture by amine based solid sorbents has been extensively studied [13, 22-30] and vibrational spectroscopy can provide evidence for the various forms of adsorbing CO₂ species [31]. The IR absorbance spectrum presented in Figures 3.4, and 3.5 suggest that CO₂ adsorbs on TEPA, in the absence of H₂O, as carbonate and bicarbonate species. The reaction pathway on the formation of these various species formed from the reaction of CO₂ with the amine functional groups has been understood to occur by a predominant pathway based upon the concentration of available amine sites [32]. In the absence of H₂O, the predominant reaction believed to account for CO₂ removal is the carbamate formation (see Figures 4 and 5) according to the reaction step (1).

\[
\text{CO}_2 + 2R_2NH \rightleftharpoons R_2NH_2^+ + R_2NCOO^- 
\]

For every one mole of amine only 0.5 mole of CO₂ is removed, in Step (1), is generally agreed upon in the literature [22, 28-30]. The formation of bicarbonate species is known to occur in the presence of H₂O according to reaction steps (2-4).

\[
\text{CO}_2 + H_2O \rightleftharpoons H_2CO_3 
\]

\[
\text{CO}_2 + OH^- \rightleftharpoons HCO_3^- 
\]

\[
H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O 
\]
The bicarbonate species may also form directly from the amine plus CO₂ water reaction shown in Eq. (5) and (6).

\[
R_2NCOO^- + 2H_2O + CO_2 \rightleftharpoons R_2NH_2^+ + 2HCO_3^- \quad (5)
\]

\[
CO_2 + R_2NH + H_2O \rightleftharpoons 2NH_2^+ + HCO_3^- \quad (6)
\]

If reaction step (2) is favourable, in the presence of water, one mole of amine is effective in removing two moles of CO₂. Reaction on the surface in the presence of H₂O allows more of the active sites of the material to be available for CO₂ removal. Carbamate formation consumes amine and CO₂ at a stoichiometric ratio of 2:1, whereas bicarbonate formation has a stoichiometry of 1:1. Therefore, systems where carbamate formation dominate will have loadings that are not much higher than 0.5 whereas systems with only bicarbonate formation can have loadings close to 1. Interestingly, in this study, the addition of PEG causes an improvement in the stoichiometric ratio of CO₂ to TEPA in the absence of H₂O.

H₂S capture has been studied primarily for desulfurization through the formation of an M-S species on metal oxides and then its oxidation to SO₂ [33-38] and only a few studies have utilized amine based sorbents [20, 39] for H₂S removal. Under dry conditions, the main reactions between amine and H₂S are shown in Eq. (7) – (9).

\[
H_2S + 2RNH_2 \rightarrow RH_2NH + S - HNH_2R \quad (7)
\]

\[
H_2S + 2R_2NH \rightarrow R_2HNH + S - HNHR_2 \quad (8)
\]
The reaction of H$_2$S with the amine site, shown in Eq. (7) thru (9), suggests each H$_2$S molecule requires two amine sites for its adsorption. The stoichiometry of the reaction indicates for every one mole of amine 0.5 mole of H$_2$S is removed (step (7)). These reactions for H$_2$S adsorption on the amine active sites have been confirmed by the computational studies [25]. Interestingly, the formation of the amine-sulphide complex, in Figures 3.8 and 3.9, suggest that the –OH role in the H$_2$S adsorption process effectively frees up the amine sites for adsorption and increases the stoichiometric ratio to 2:1.

CO$_2$ adsorbs on PEG, shown in Figure 3.6, very weakly at -4.8 kJ/mol (Table 3.2.1) and readily desorbs upon flowing N$_2$ over the PEG film. Comparing Figures 4 and 6, the ratio of the IR intensity in the carbonate region is 5 times weaker on PEG to that on TEPA spectroscopically verifies the theoretical binding energies for PEG-CO$_2$ (-4.81 kJ/mol) and TEPA-CO$_2$ (-23.19 kj/mol) also having a ratio of 5. The experimental IR and theoretical results suggest blending the TEPA and PEG it is possible to lower the binding energy in a TEPA/PEG-CO$_2$ system. The increased CO$_2$ and H$_2$S capacity and lower desorption temperature on addition of PEG supports theoretical investigation on the interaction of TEPA/PEG-CO$_2$ and TEPA/PEG-H$_2$S. The binding energy for TEPA/PEG-CO$_2$ (-15.07 kJ/mol) is in between that of TEPA-CO$_2$ (-23.19 kJ/mol) and PEG-CO$_2$ (-4.81 kJ/mol). Similarly, PEG addition to TEPA lowers the binding energy for the H$_2$S-TEPA adsorption from -19.86 kJ/mol to -17.71 kJ/mol.
Blending PEG with TEPA results in dispersion of the of the TEPA molecule indicated by the IR spectra shown in Figure 3.2. The most striking spectral feature indicating the dispersing effect of PEG occurs on the initial 9.1 wt % PEG loading and the appearance of the –CH₃-NH₂ wagging vibration at 1672 cm⁻¹ suggests PEG frees the amine active site for adsorption of CO₂ or H₂S molecules. The hydrogen bonding broadening effect on the N-H bands at 3282 and 3180 cm⁻¹ further supports the dispersing effect of PEG.

According to these results two different factors have to be taken into account, (i) the molecular mass for an optimal dispersion of the TEPA molecule on the substrate and (ii) the nature and concentration of the active sites suitable for CO₂ capture. The effect of the addition of PEG is to enhance the stability of the overall material through the intermolecular interaction with the TEPA molecule, while enhancing the dispersion effect and the reason for the choice of the 200 MW PEG having approximately the same molecular length as the TEPA molecule.

The dispersion of TEPA by addition of PEG can be attributed to a hydrophilic surfactant effect which explains the immiscible layer formation and could result from a sort of micelle formation around the TEPA molecule. Based upon the results of the IR spectra in Figure 3.2 and during CO₂ adsorption in Figure 3.7, and the theoretical geometry in Figure 3.3, the dispersion phenomena may be interpreted as PEG forming between the TEPA molecules. The hydrogen bonding of the –OH with the –NH₂ active site, the dispersion mechanism can be schematically represented as shown in Figure 3.10.
The weakly bound H$_2$S and CO$_2$ on PEG offers the unique ability for adjusting the adsorption capacity and desorption temperature by modifying the TEPA/PEG blend composition. Thus it is feasible to increase the adsorption capacity and decrease the desorption temperature of CO$_2$ from the TEPA sorbent by controlling the amine active sites through dispersion effects using a hydroxylated polymer such as PEG.

![Dispersion mechanism of TEPA and PEG system.](image)

**Figure 3.10** Dispersion mechanism of TEPA and PEG system.

3.5 Conclusions

CO$_2$ adsorbs on the TEPA/PEG system as carbonates and bicarbonates, while H$_2$S adsorbs as $-NH_2$–$SH_2$ and amine-sulphide ($-N$–$SH_2$⋯$O$–$H$) complex. The CO$_2$ adsorption capacity of the TEPA sorbent was doubled by the addition of PEG and increased by a factor of twelve for the H$_2$S adsorption. H$_2$S adsorption is increased by the formation of the amine-sulphide complex ($N$–$S$⋯$O$–$H$) by freeing one of the amine adsorption sites for another H$_2$S molecule. Dispersion of the TEPA molecule is
important during both CO$_2$ and H$_2$S adsorption processes. PEG disperses the amine adsorption sites enabling more CO$_2$ and H$_2$S molecules to adsorb. A temperature-programmed desorption study of the TEPA/PEG system showed that PEG offers the unique ability for adjusting the adsorption capacity and desorption temperature (i.e. to 353 K) by modifying the TEPA/PEG blend concentration. The desorbing temperature was lowered by lowering the binding energy for between TEPA and CO$_2$ and H$_2$S to -15.07 and -17.71 kJ/mol respectively. These results are attributed to the interactions between the TEPA and PEG additive and CO$_2$ and H$_2$S via hydrogen bonding as verified by IR spectroscopy and ab initio quantum chemistry. The experimental findings demonstrate that additives including amine and hydroxyl group are suitable for modifying and amine based sorbent for CO$_2$ and H$_2$S removal.

3.6 Bibliography


4.1 Abstract

The adsorption and desorption of CO$_2$ on liquid tetraethylenepentamine (TEPA) in the presence of H$_2$O was studied by in situ infrared (IR) and ab initio quantum chemical calculations. Sending CO$_2$ over the dry TEPA liquid layer caused the formation of carbamate species accompanied by a broad band IR absorption at 2580 cm$^{-1}$ indicating the occurrence of hydrogen bonding. Hydrogen bonding plays a crucial role in stabilizing the adsorbing species during the CO$_2$ adsorption process in the presence and absence of H$_2$O. The adsorption of CO$_2$ in the presence of H$_2$O and D$_2$O reveal the the dominant adsorbing species is the bidentate bicarbonate molecule. The D atoms from D$_2$O cause an isotopic shift of the hydrogen bonding broadband spectrum suggesting the reactivity for bicarbonate species is slower than that of carbamate, and carbonate species; however, the bidentate bicarbonate molecule is the dominant adsorbing species during extended CO$_2$ adsorption. The formation of bicarbonate species occurs by a reaction with H$_2$O at the amine adsorption site which is stabilized by hydrogen bonding interaction with neighbouring TEPA molecules. Optimizing the CO$_2$ adsorption process in the
presence of H$_2$O by enhancing hydrogen bonding effects may improve adsorption processes and interaction mechanisms for the adsorbing bicarbonate molecules.

4.2 Experimental

The experimental section describes the liquid amine preparation, in situ ATR-IR, and theoretical approach used to study the CO$_2$ adsorption process.

4.2.1 Liquid Amine Preparation and Characterization

The gases supplied by Praxair were N$_2$ (99.999 vol %) and CO$_2$ (99.995 vol %). A 4 micron liquid layer was prepared from 0.0573 M tetraethylenepentamine (TEPA, Aldrich > 30.0 %) and ethanol (Pharmco-Aaper, 99.98%). The liquid layer was created by adding dropwise 0.1 ml TEPA/ethanol solution upon a ZnSe window. The TEPA liquid layer was allowed to sit stagnant for 30 min. to allow evaporation of the ethanol solvent. The liquid layer was then heated to 373 K at 10 K/min under 100% N$_2$ flowing at 100 cm$^3$/min to evaporate the remaining ethanol solvent and then cooled to 323 K for the adsorption study.

4.2.2 In Situ ATR-IR Reaction Studies

The experimental apparatus, shown in Figure 4.1, consist of (i) a reactant metering system (Brooks Instrument 5850 mass flow controllers), (ii) a gas sampling system including a 4-port valve, (iii) a Attenuated Total Reflectance accessory (ATR-IR, Harrick Scientific) and a custom reactor manifold mounted to the ATR-IR top plate placed inside of an Fourier Transform Infrared Spectrometer (FTS6700 FTIR, Thermo-
Nicolet), and (iv) a mass spectrometer (MS, Pfeiffer Omnistar™). The 4-port valve allows switching the inlet flow from 100% N₂ to 100 % CO₂ while maintaining a total flow rate of 100 cm³/min over the 4 micron TEPA liquid layer.

Changes in the concentration of IR observable adsorbates are monitored by in situ ATR-IR. The IR absorbance spectrum of adsorbed and gaseous species is obtained by

\[ A = -\log \left( \frac{I_o}{I} \right) \]

where \( I_o \) is the background IR single beam spectrum (32 co-added scans and resolution 4 cm⁻¹) of the clean TEPA liquid layer and \( I \) is the IR single beam spectrum during the CO₂ adsorption reaction. The MS responses corresponding to N₂ (m/e = 28) and CO₂ (m/e = 44) are monitored for the changes in the ATR-IR reactor effluent concentrations.
Figure 4.1 Experimental apparatus.
4.2.3 Theoretical Methods

Quantum chemical calculations were performed using GAUSSIAN03 [2] set of programs. The density functional theory used to calculate the infrared vibrational frequencies is the Becke’s three-parameter exchange functional and gradient corrected functional of Lee, Yang, and Parr (B3LYP) [3-5]. Of all the DFT methods, the B3LYP functional is the most widely used [6] for harmonic vibrational frequencies. The 6-31G* basis set [7] has been used as a compromise between accuracy and applicability to large molecules. The smaller basis set (6-31G*) suffice in DFT theory because the basis functions do not have to describe the correlating orbitals [8]. The basis set is modified with the diffuse function (6-31++G*) to improve the accuracy for hydrogen bonded dimers having electron density at larger distances from the nuclei [9]. Therefore, the TEPA, TEPA/CO₂, and TEPA/carbonate structures were optimized using B3LYP/6-31++G* theoretical method. Harmonic vibrational frequencies were computed at the same level to confirm the convergence to minima on the potential surface and to evaluate the zero-point vibrational energies. The binding energies for TEPA with CO₂ or carbonate species were obtained from the following equations:

\[
E_b = E[TEPA + CO_2] - E[TEPA] - E[CO_2] \tag{1}
\]

\[
E_b = E[TEPA + carbonate species] - E_b[TEPA] - E[carbonate species] \tag{2}
\]

Where \( E[TEPA + CO_2] \) is the total energy of TEPA with CO₂, \( E[TEPA] \) is the total energy of TEPA and \( E[CO_2] \) is the total energy of the CO₂ molecule, in Eqn. (1).
Similarly, in Eqn. (2) the binding energies were calculated where carbonate species is the carbonate, monodentate bicarbonate, or bidentate bicarbonate molecular species.

4.3 Results

The results section describes the CO₂ adsorption over the liquid TEPA thin film and the interaction effects in the presence of H₂O and D₂O.

4.3.1 TEPA thin film

Figure 4.2 shows the IR spectra of the 4 micron liquid TEPA layer and the theoretical IR normal modes of vibration. The infrared adsorptions, in Figure 4.2(a), for TEPA can be ascribed to the well known group frequencies [10]. The NH₂ group produced an antisymmetric vibration at 3353 cm⁻¹ and symmetric vibration at 3278 cm⁻¹. The IR adsorption at 1673 and 3187 cm⁻¹ are assigned to the NH₂ deformation and overtone vibrations respectively. The antisymmetric stretch vibration for C-C-N occurs at 1128 cm⁻¹.

The stick spectrum representing the IR normal modes of vibration for TEPA are obtained from the optimized structure at the B3LYP/6-31++G* level, shown in Figure 4.2(b). A scaling factor of 0.9945 is used to bring the fundamental vibrational frequencies closer to the experimental data due to their over estimation from anharmonicity [6, 11] in the theoretical calculation.
The simulated spectrum for the N-H stretch and NH$_2$ deformation slightly differ from the experimentally observed bands however the trend in the variation in Figure 4.2 is consistent with the experimental observations on G-L transition of ammonia. During the G-L transition for NH$_3$ there is a noticeable shift in the IR adsorption spectrum; the stretching bands for NH$_3$ shift to lower frequencies whereas the bands for deformation shift to higher frequencies [12]. Similarly, the simulated spectrum for N-H stretching (v$_{as}$ 3642 cm$^{-1}$, v$_s$ 3434 cm$^{-1}$, and v$_{δ}$ 3378 cm$^{-1}$), shown in Figure 4.2(b), are shifted higher than that observed in experiment (v$_{as}$ 3353, v$_s$ 3278, and v$_{δ}$ 3187 cm$^{-1}$) for liquid TEPA.
4.3.2 H₂O / D₂O adsorption over TEPA liquid layer

The IR spectra of the molecular and adsorbed species during 3.1% H₂O/N₂ vapour adsorption on the TEPA liquid layer at 323 K is shown in Figure 4.3. Exposure of TEPA to the H₂O/N₂ flow led to the formation of an intense IR broad band for the O-H stretch at 3173 cm⁻¹, a less intense IR broad band centred at 2446 cm⁻¹, the δ_H₂O scissoring mode at 1652 cm⁻¹. The broad band absorption at 3173 cm⁻¹ is consistent with that of hydrogen bonding between H₂O molecules. The less intense broad band at 2446 cm⁻¹ is assigned to \( N-H \cdots O-H \) intermolecular hydrogen bonding between the H₂O molecules and TEPA.

The IR spectra of the molecular and adsorbed species during 3.1% D₂O/N₂ vapour adsorption on the TEPA liquid layer at 323 K is shown in Figure 4.4. Flowing D₂O/N₂ over TEPA led to the formation of an intense IR broad band for the O-D stretch at 2446 cm⁻¹, a less intense IR broad band at 3173 cm⁻¹, and the absorption band at 1549 cm⁻¹ for \( \nu_8 \) of D₂O.

The less intense IR broad band at 3173 cm⁻¹ indicates an H₂O impurity in the D₂O vapour phase. The broad band adsorption for the O-D stretch at 2446 cm⁻¹ obscures observation of \( N-H \cdots O-D \) intermolecular hydrogen bonding between the D₂O molecules and TEPA.
Figure 4.3 Difference spectra sending N$_2$/H$_2$O over TEPA liquid layer at 323 K.
Figure 4.4  Difference spectra sending N$_2$/D$_2$O over TEPA liquid layer at 323 K.
4.3.3 CO₂ adsorption over TEPA, TEPA/H₂O, and TEPA/D₂O

Figure 4.5 shows the difference IR spectra of the molecular and adsorbed species during CO₂ adsorption on the TEPA liquid layer at 323 K. Flowing CO₂ over TEPA led to an increase in IR intensity at 3302 cm⁻¹ for the N-H vibration, the formation of a broad IR band centred at 2580 cm⁻¹ for hydrogen bonding and the formation of carbamate species in the 1600 – 1200 cm⁻¹ region. Positive IR peaks for the carbamate species include (i) a shoulder at 1630 cm⁻¹ for the R-NH₂ bending mode, (ii) a NCOO vibration at 1567 cm⁻¹ and, (iii) a NCOO skeletal vibration at 1463 and 1297 cm⁻¹ [13-16]. Increasing the CO₂ exposure time from 1.52 to 11.13 min did not shift the wavenumber of IR observable species but further increased the IR intensity as a result of a greater amount of carbamate species adsorbing in the TEPA liquid layer. Temperature programmed desorption (TPD) results show 6.8 µmol CO₂ desorbed from the TEPA liquid layer at 100 °C, shown in Table 4.1.

The binding energy for TEPA and CO₂, calculated at the B3LYP/6-31++G* level, was determined to be -23.19 kJ/mol, shown in Table 4.2. The broadband adsorption at 2580 cm⁻¹ suggests the geometry of TEPA and CO₂ are influenced by hydrogen bonding interaction. Hydrogen bonded compounds have significant electron density at large distances from the nuclei [9]. To investigate the hydrogen bonding effect on the binding energy, the TEPA and CO₂ molecular structures were optimized at the B3LYP/6-31G level. The binding energy for TEPA and CO₂ (B3LYP/6-31G level) was determined to be -21.60 kJ/mol. Without the stabilizing effects from hydrogen bonding (i.e. no diffuse and polarization terms) the binding energy increases from -23.19 to -45.71 kJ/mol. The
increase in binding energy along with the IR observations indicates that hydrogen bonding stabilization on CO\textsubscript{2} plays an important role in the adsorption process.

Figure 4.5 Difference spectra of 4 micron TEPA liquid layer during CO\textsubscript{2} adsorption at 323 K.
Table 4.1  The amount of CO$_2$ desorption in the absence and presence of H$_2$O and D$_2$O.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>CO$_2$ ($\mu$mol)</th>
<th>CO$_2$/TEPA ($\mu$mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$/N$_2$</td>
<td>6.8</td>
<td>1.19</td>
</tr>
<tr>
<td>CO$_2$/H$_2$O/N$_2$</td>
<td>9.4</td>
<td>1.65</td>
</tr>
<tr>
<td>CO$_2$/D$_2$O/N$_2$</td>
<td>11.3</td>
<td>1.97</td>
</tr>
</tbody>
</table>

Table 4.2  Calculated binding energies for adsorbed species at the B3LYP/6-31++G* and B3LYP/6-31G optimized level.

<table>
<thead>
<tr>
<th>Basis set</th>
<th>TEPA + CO$_2$ (kJ/mol)</th>
<th>Carbonate (kJ/mol)</th>
<th>Monodentate bicarbonate (kJ/mol)</th>
<th>Bidentate bicarbonate (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31++G*</td>
<td>-23.19</td>
<td>-9.93</td>
<td>-54.07</td>
<td>-1835.38</td>
</tr>
<tr>
<td>(6-31G)</td>
<td>(-45.71)</td>
<td>(-50.22)</td>
<td>(-105.49)</td>
<td>(-1864.59)</td>
</tr>
</tbody>
</table>

Figure 4.6 shows the difference IR spectra for the molecular and absorbed species during H$_2$O/CO$_2$ adsorption on the TEPA liquid layer at 323 K. Sending H$_2$O/CO$_2$ over TEPA produced an intense IR broad band centred at 2580 cm$^{-1}$, bidentate bicarbonate at 1624 cm$^{-1}$, monodentate bicarbonate at 1485 and 1414 cm$^{-1}$, and monodentate carbonate at 1337 cm$^{-1}$ [17-20]. The characteristic IR vibrations of these carbonate species on TEPA are also consistent with adsorbed CO$_2$ species on the metal oxides and zeolites in the literature [21-24]. Initial CO$_2$ exposure at 0.34 min show IR bands at 1567, 1485, and 1297 cm$^{-1}$ correspond to the initial adsorption and formation of carbamate species.
Increasing CO₂ exposure to 10.28 min shifts the wavenumber of the IR observable species resulting from the formation of the monodentate and bidentate bicarbonate species. TPD results show more CO₂ molecules desorbed in the presence of H₂O (9.4 µmol) as compared to that in the absence of H₂O (6.8 µmol), shown in Table 4.1.

Figure 4.6  Difference spectra, sending CO₂ over the hydrated (w/H₂O) TEPA liquid layer at 323 K.
The increasing broad band adsorption at 2580 cm\(^{-1}\), resulting from hydrogen bonding of the adsorbed species in Figure 4.6, is similar in shape to that for CO\(_2\) adsorption in the absence of H\(_2\)O (see Figure 4.5). Interestingly the peak intensity is greater in the presence of H\(_2\)O than that in its absence suggesting H\(_2\)O plays an important role enhancing the hydrogen bonding effect. Figure 4.7 shows the optimized structures at the B3LYP/6-31++G* level for CO\(_2\) adsorption including the carbonate, monodentate bicarbonate, and bidentate bicarbonate species. By inspection of the optimized structures, the differences in hydrogen bonding intensities appear to be related to differences in the local geometry such as distances and mutual orientation (conformations) of the interacting species. In the presence of H\(_2\)O, CO\(_2\) forms bicarbonate species. The binding energies (optimized at B3LYP/6-31++G*) determined for TEPA and carbonate, monodentate bicarbonate, and bidentate bicarbonate species are -9.93, -54.07, and -1835.38 kJ/mol respectively. The binding energies at the B3LYP/6-31G level, in Table 4.2, also show a increase in energy suggesting hydrogen bonding has a significant role in stabilizing the adsorbing molecular species. It is interesting the binding energy for the carbamate species is lower than that for CO\(_2\) adsorption on TEPA. The binding energy for bidentate bicarbonate is also significantly higher than that of the other adsorbing species (i.e. carbonate and monodentate bicarbonate). The stronger interaction energy suggests this species will more favourably adsorb on the TEPA sorbent as compared to the carbonate and monodentate bicarbonate species.

Figure 4.8 shows the difference IR spectra during D\(_2\)O/CO\(_2\) adsorption over TEPA liquid layer at 323 K. The D\(_2\)O/CO\(_2\) and TEPA interaction produced an IR broad
Figure 4.7  Geometry of TEPA (a) CO₂ (b) Carbonate (c) Monodentate bicarbonate (d) Bidentate bicarbonate (298 K, 1 atm) at the optimized B3LYP/6-31++G* level.
Figure 4.8  Difference spectra sending CO$_2$ over hydrated (w/D$_2$O) TEPA liquid layer at 323 K.
band having two peaks, one centred at 2530 cm\(^{-1}\) and the other at 2271 cm\(^{-1}\). The occurrence of two peaks is related to two adsorbing species, (i) the carbamate species and (ii) the bicarbonate species. Initial CO\(_2\) adsorption at 0.89 min show carbamate IR adsorption bands similarly to that in Figure 4.6, in the presence of H\(_2\)O. Increasing CO\(_2\) exposure from 0.22 min to 10.07 min resulted in a shift in the wavenumber from 2271 to 2126 cm\(^{-1}\) for hydrogen bonding, along with an increase in IR intensity corresponding to a greater amount of adsorbing species responsible for the shift (see Figure 4.8).

The normalized IR intensity of adsorbed CO\(_2\) species in the presence of H\(_2\)O and D\(_2\)O as a function of time is shown in Figure 4.9. In the presence of H\(_2\)O, CO\(_2\) adsorption led to the rapid increase in IR intensity for carbamate species (1542, 1485, 1414, and 1297 cm\(^{-1}\)) with a peak maximum at 1.18 min leading the formation of the monodentate and bidentate bicarbonate species. Interestingly, the IR intensity at 2580 cm\(^{-1}\) for hydrogen bonding follows the IR intensity for bidentate bicarbonate species at 1624 cm\(^{-1}\) suggesting this species is a major contributor to the peak intensity at 2580 cm\(^{-1}\). The normalized intensities for CO\(_2\) adsorption in the presence of D\(_2\)O, shown Figure 4.9(b), follow a similar trend as that in Figure 4.8(a), (i) the initial exposure of CO\(_2\) led to the rapid formation of carbamate species, (ii) the prolonged exposure to CO\(_2\) led to the formation of deuterated carbonate species, and (iii) the hydrogen bonding intensity at 2126 cm\(^{-1}\) follows the bidentate bicarbonate species IR intensity profile at 1526 cm\(^{-1}\). The increase and decrease in IR intensities are consistent with the increases in binding energies of the bicarbonate species. The higher binding energies for monodentate (-54.07 kJ/mol) and bidentate bicarbonate (-1835.38 kJ/mol) result in substitution of the less stable carbamate (-23.19 kJ/mol) and carbonate species (-4.69 kJ/mol).
Figure 4.9  IR intensity data for adsorbed species (a) CO$_2$/H$_2$O (b) CO$_2$/D$_2$O.
Figure 4.10  Mechanism of carbonate formation (a) in the presence of H$_2$O (b) in the presence of D$_2$O.
The process of CO$_2$ adsorption upon TEPA induces a transformation of less stable species to the more stable species which. The infrared spectra during CO$_2$/H$_2$O adsorption along with the calculated IR normal modes for the various absorbing species, shown in Figure 4.11, illustrates the complexity of molecular aggregation and multiple adsorption sites affecting the IR bands. The relative IR intensities for the normal modes indicate the extent of molecular perturbation; therefore, the important IR bands for discussion are indicated by an asterisk next to the band in Figure 4.11.

The observed spectra of liquid TEPA saturated with CO$_2$ in the presence or absence of H$_2$O is shown in Figure 4.5 and 3.6 and the calculated IR spectra for the various absorbing species are shown in Figure 4.11. The observed and calculated IR wavenumbers for the adsorbate species are listed in Table 4.3. The IR spectrum for liquid TEPA saturated with CO$_2$ in the presence of H$_2$O shows a very strong C=O vibration at 1567 cm$^{-1}$ for both carbonate and monodentate bicarbonate and slightly shifted lower C=O vibration at 1537 cm$^{-1}$ for bidentate bicarbonate species. The band assignment, for the C=O stretching vibration of carboxylate, is in agreement with the accepted region of 1550-1610 cm$^{-1}$ [25]. A very strong band at 1624 is also observed and is assigned to the carboxyl group in the 1650-1740 cm$^{-1}$ region. By comparison with the calculated frequencies in Table 4.3 along with the relative intensities shown in Figure 4.11, evidence is provided for the formation of multiply adsorbed carbonate species having overlapping IR bands. Another interesting feature is the calculated IR bands at 2092 and 2616 cm$^{-1}$ for bidentate bicarbonate species resulting from hydrogen bonding. This provides strong evidence that the bidentate bicarbonate species is in fact a major contributor to the IR observable hydrogen bonding interaction. Other important spectral
features during CO₂ adsorption on liquid TEPA is the increase in IR intensity at 3310 and 3401 cm⁻¹ due to the N-H stretching vibration from the perturbing carbonate species. The bidentate carbonate species also resulted in adsorption bands at 3229, 3333, and 3397 cm⁻¹; the calculated values for the N-H stretching vibration are in good agreement with the observed wavenumbers shown in Table 4.3.

Table 4.3 Observed and calculated vibrational wavenumbers of carbonate, monodentate bicarbonate, and bidentate bicarbonate adsorption on TEPA.

<table>
<thead>
<tr>
<th></th>
<th>Carbonate (cm⁻¹)</th>
<th>Monodentate bicarbonate (cm⁻¹)</th>
<th>Bidentate bicarbonate (cm⁻¹)</th>
<th>B3LYP/6-31++G*</th>
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<td>Carbonate (cm⁻¹)</td>
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<td>Bidentate bicarbonate (cm⁻¹)</td>
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<td>-</td>
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Figure 4.11 TEPA with CO$_2$/H$_2$O and the calculated IR spectra at B3LYP/6-31++G* level (a) IR spectra of liquid TEPA (b) TEPA, (c) TEPA and CO$_2$ (d) TEPA with carbonate (e) TEPA with monodentate bicarbonate (f) TEPA with bidentate bicarbonate.
4.4 Discussion

The IR absorbance spectrum presented in Figures 4.5, 4.6, and 4.8 suggest the adsorption of gaseous CO\textsubscript{2} onto TEPA in the absence and presence of H\textsubscript{2}O is quite complex resulting from the simultaneous adsorption of multiple species (i.e. carbamate, carbonate, monodentate and bidentate bicarbonate). The reaction pathway on the formation of these various species from gaseous CO\textsubscript{2} with basic amine functional groups has been understood to occur by two pathways: (i) a minor path via CO\textsubscript{2} reaction with hydroxide ion and (ii) a predominant pathway based upon the concentration of available amine sites [26]. In the absence of H\textsubscript{2}O, the predominant reaction believed to account for CO\textsubscript{2} removal is the carbamate formation (Figure 4.5) by the reaction step (1).

\[ CO_{2} + 2R_{2}NH \rightleftharpoons R_{2}NH^{+} + R_{2}NCOO^{-} \]  \hspace{1cm} (1)

Step (1) shows for every one mole of amine, only 0.5 mole of CO\textsubscript{2} is removed and is generally agreed upon in the literature [27-30]. In the presence of H\textsubscript{2}O, the carbamate ion may react to form bicarbonate species. The formation of bicarbonate from CO\textsubscript{2} and H\textsubscript{2}O is a well known reaction in chemistry having three related mechanisms, shown in reaction steps (2-4).

\[ CO_{2} + H_{2}O \rightleftharpoons H_{2}CO_{3} \]  \hspace{1cm} (2)
\[ CO_{2} + OH^{-} \rightleftharpoons HCO_{3}^{-} \]  \hspace{1cm} (3)
\[ H_{2}CO_{3} + OH^{-} \rightleftharpoons HCO_{3}^{-} + H_{2}O \]  \hspace{1cm} (4)
The bicarbonate species may also form directly from the amine plus CO₂ water reaction in Eq. (5) and (6).

\[ R_{2}NCOO^{-} + 2H_{2}O + CO_{2} \rightleftharpoons R_{2}NH_{2}^{+} + 2HCO_{3}^{-} \quad (5) \]

\[ CO_{2} + R_{2}NH + H_{2}O \rightleftharpoons 2NH_{2}^{+} + HCO_{3}^{-} \quad (6) \]

If reaction step (2) is favourable, in the presence of water, one mole of amine is effective in removing two moles of CO₂. Reaction on the surface in the presence of H₂O allows more of the active sites of the material to be available for CO₂ removal. Carbamate formation consumes amine and CO₂ at a stoichiometry of 2:1, whereas bicarbonate formation has a stoichiometry of 1:1. Therefore, systems where carbamate formation dominate will have loadings that are not much higher than 0.5 whereas systems with only bicarbonate formation can have loadings close to 1.

A striking feature of the spectrum, in Figure 4.5, and the most important finding is the broad band centred at about 2580 cm⁻¹, which arises when both CO₂ and TEPA are present. The intense absorption at 2580 cm⁻¹ along with an increase in IR intensity at 3302 cm⁻¹ indicate \textit{N–H} \cdots \textit{O} hydrogen bonding, the broadness of the band at 2580 cm⁻¹ is consistent with such an interpretation. Water at the interface can be excluded as its origin since the TEPA liquid layer has not been exposed to moisture.

In the literature [13, 27-35], the CO₂ adsorption mechanisms are proposed for the carbamate the bicarbonate formation. The formation of the carbamate and bicarbonate species is discussed however; there is an absence of discussion on the preferential
adsorption of either adsorbed species. Comparison of the IR intensity profiles for CO$_2$
adsorption in the presence of H$_2$O and D$_2$O, in Figures 4.6 and 4.8, led to the proposed
reaction Figure 4.10(a) and 4.10(b) respectively. The IR band shift (from 2217 to 2126
cm$^{-1}$), in Figure 4.8, during the D$_2$O isotopic study provides insight into the formation
sequence of the adsorbing species. In the presence of H$_2$O (or D$_2$O), CO$_2$ adsorbs
according to the following sequence: CO$_2$ activation $\rightarrow$ carbamate ion $\rightarrow$
monodentate bicarbonate $\rightarrow$ bidentate bicarbonate. The isotopic shift and intense absorption at 2126
cm$^{-1}$ provides definitive evidence that the major adsorbing species is bidentate
bicarbonate. This observation (D$_2$O shift data) is, to the best of our knowledge, the first
direct spectroscopic indication of an interaction, such as the one depicted in Figures
4.10(a), which is proposed to play an important role in the reaction and adsorption of CO$_2$
on this amine sorbent. Furthermore, the bidentate bicarbonate species having a
significantly higher binding energy (1835.38 kJ/mol) as compared to the other adsorbing
species indicates the species is more likely to occupy the adsorption sites which are in
agreement with the IR isotopic shift in Figure 4.8.

The formation of bidentate bicarbonate shifts the equilibrium of the adsorbing
carbamate and monodentate bicarbonate adsorbate becoming the dominant adsorbing
species on the TEPA sorbent. This observed relationship between chemical equilibrium
and kinetics of the adsorbing species has implications in the search for a more effective
sorbent. Improving the hydrogen bonding effect can improve the effectiveness of a CO$_2$
sorbent. Hydrogen bonding stabilization should be considered as an important factor for
the design and improvement of CO$_2$ capture catalysts.
4.5 Conclusion

This study presents a novel approach using the IR observable hydrogen-bonding interaction between CO$_2$ and TEPA to elucidate the adsorption mechanism during CO$_2$ capture on TEPA. In the presence of H$_2$O, CO$_2$ adsorbs in the sequence, (i) CO$_2$ activation, (ii) carbamate ion, (iii) monodentate bicarbonate, and (iv) bidentate bicarbonate, where bicarbonate bidentate becomes the dominant adsorbing species on the TEPA sorbent. When the carbonate and bicarbonate species desorb, they desorb as CO$_2$ giving a peak temperature at 373 K. Optimizing the hydrogen bonding during CO$_2$ adsorption may improve the adsorption and desorption processes during CO$_2$ capture. The molecular level information for the catalytic G-L interface could be obtained by the combination of ATR-IR spectroscopy and ab initio theoretical methods.

4.6 Bibliography


CHAPTER V

IN SITU INFRARED STUDY OF SO$_2$ CAPTURE OVER
1,3-PHENYLENEDIAMINE/SIO$_2$ SORBENT

5.1 Abstract

The adsorption and desorption of SO$_2$ over 1,3-phenylenediamine/SiO$_2$ sorbent has been studied by the step transient response technique coupled with in situ infrared (IR) and mass spectrometry (MS). Flowing 3300 ppm SO$_2$/He over 1,3-phenylenediamine/SiO$_2$ sorbent produces adsorbed species in the form of sulphite and monodentate sulphate. Adsorbing sulphite at the amine adsorption site disrupts the 1,3-phenylenediamine adsorbate layer on the SiO$_2$ surface. During adsorption, the mobile adsorbate layer along with the adsorbate-adsorbate interaction results in agglomeration of the amine active sites lowering the SO$_2$ adsorption capacity. Polyethylene glycol (PEG) effectively disperses and immobilizes the aromatic amine during SO$_2$ adsorption.

5.2 Experimental

The experimental section describes the preparation procedure and characterization of the liquid amine and solid amine sorbents for SO$_2$ capture.
5.2.1 Preparation and Characterization of the Sorbents

The gases used in this study supplied by Praxair were \( \text{N}_2 \) (99.999 vol %), \( \text{O}_2 \) (99.993 vol %), \( \text{Ar} \) (99.998 vol %), and \( \text{SO}_2 \) (99.9 vol %). The 2 and 10% 1,3-phenylenediamine/SiO\(_2\) were prepared by depositing 1,3-phenylenediamine (Aldrich) onto SiO\(_2\) (CABOT) by the incipient wetness impregnation method. The solid sorbents were prepared from 0.148 M and 0.195 M 1,3-phenylenediamine and ethanol solutions on 5 g of SiO\(_2\). The resulting slurry was stirred at room temperature for 30 min. The solution was then heated at 353 K to evaporate the excess ethanol solvent. The resulting sorbent is further dried for 12 h in air at 353 K. The 1,3-phenylenediamine thin film was created by adding dropwise 0.1 ml of 0.116 M 1,3-phenylenediamine/ethanol solution on a ZnSe window. The thin film was allowed to sit stagnant for 15 min and the ZnSe window was then heated to 373 K at 10 K/min under 100% \( \text{N}_2 \) flowing at 100 cm\(^3\)/min to evaporate the ethanol solvent completely and then cooled to 323 K for the adsorption study.

The experimental apparatus, shown in Figure 5.1, consist of (i) a reactant metering system (Brooks Instrument 5850 mass flow controllers), (ii) a gas sampling system including a 4-port and 6-port valves, (iii) a Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS, HVC-DRP, Harrick Scientific) reactor containing
Figure 5.1 Experimental Apparatus.
33 mg catalyst or a Attenuated Total Reflectance accessory (ATR-IR, Harrick Scientific) and a custom reactor manifold mounted to the ATR-IR top plate placed inside of an Fourier Transform Infrared Spectrometer (FTS6700 FTIR, Thermo-Nicolet), and (iv) a mass spectrometer (MS, Pfeiffer Omnistar™). The 4-port valve allows switching the inlet flow from 100% N₂ to 0.33 % SO₂ while maintaining a total flow rate of 100 cm³/min over the sorbent. The 6-port valve is used to pulse 1 cm³ SO₂/N₂ into N₂ flow for calibration purposes. The UV-Visible diffuse reflectance spectra of the sorbents were recorded by a Hitachi U-3010 Spectrometer with a Harrick Scientific (HVC-DRP) diffuse reflectance accessory.

Changes in the concentration of IR observable adsorbates are monitored by in situ DRIFTS and ATR-IR. The IR absorbance spectrum of adsorbed and gaseous species is obtained by $A = -\log \left( \frac{I_o}{I} \right) [1]$, where $I_o$ is the background IR single beam spectrum (32 co-added scans and resolution 4 cm⁻¹) of the clean TEPA liquid layer and I is the IR single beam spectrum during the CO₂ adsorption reaction. The MS responses corresponding to N₂ (m/e = 28), O₂ (m/e = 32), and SO₂ (m/e = 64) are monitored for the changes in the DRIFTS and ATR-IR reactor effluent concentrations.

5.3 Results and Discussion

The experimental results are reported and discussed in the following sections for NO and SO₂ adsorption over the 1,3-phenylenediamine sorbent.
5.3.1 NO Adsorption on 1,3-phenylenediamine

Figure 5.2 shows the IR absorbance spectrum during NO adsorption over 1,3-phenylenediamine/SiO2 sorbent. Flowing gaseous NO over the sorbent results in the formation of a nitrosamine species from the interaction of NO with 1,3-phenylenediamine [2-4]. Exposure of NO to 1,3-phenylenediamine results in an increase in IR intensity for (i) N-H vibration at 3442, (ii) deformation band $\nu_\delta$ for $-\text{NH}_2$ at 3141 cm$^{-1}$, (iii) di-nitrosyl (N$_2$O$_4$) species at 2117 cm$^{-1}$ [5, 6], (iv) adsorbed nitryl NO$_2^-$ at 1662 and 1540 cm$^{-1}$ for $\nu_{as}$ and $\nu_{s}$ vibrations [2] respectively, and (v) $-\text{CH}_2\text{NH}_2\text{NO}$ vibration at 1436 cm$^{-1}$ [4]. The appearance of the overtone deformation vibration at 3141 cm$^{-1}$ suggests the IR adsorption at 1662 cm$^{-1}$ may also be assigned to that of $-\text{NH}_2$ deformation during adsorption. The formation sequence of N$_2$O$_4$, NO$_2^-$, and nitrosamine species suggest the NO adsorption process follows the following reaction steps.

\begin{align*}
NO(g) + M-O & \rightarrow NO_2^-M \\
NO_2^-M & \rightarrow M + NO_2 \\
2NO_2^-M & \rightarrow 2M + N_2O_4 \\
NO_2^-M & \rightarrow M + NO_2^-NH_2^-
\end{align*}

(1) \quad (2) \quad (3) \quad (4)
Figure 5.2 IR absorbance spectra during NO adsorption on 1,3-phenylenediamine/SiO2 at 323 K.

Gaseous NO adsorbs on the oxide surface and is oxidized to adsorbed nitryl $\text{NO}_2^-$ in step (1). Adsorbed $\text{NO}_2^-$ then desorb to gaseous NO2 (step 2) or combine to form N2O4 species in step (3). Adsorbed $\text{NO}_2^-$ may further react with an amine active site to form the nitrosamine species in step (4). The formation of $\text{NO}_2^-$ and N2O4 suggest SiO2 support plays an important role in the NO adsorption process. NO adsorption and formation of $\text{NO}_2^-$ suggest the amine sites are more reactive for the nitryl species than that of gaseous NO.
5.3.2 SO₂ adsorption over 1,3-phenylenediamine/SiO₂

Figure 5.3 show the IR absorbance spectra during SO₂ adsorption over 1,3-phenylenediamine thin film and 1,3-phenylenediamine/SiO₂ at 323 K. Exposure of SO₂ flow to the 1,3-phenylenediamine thin film, in Figure 5.3(a), result in (i) a decrease in IR intensity for N-H vibration at 3420 and 3334 cm⁻¹ and the overtone for –NH₂ deformation at 3210 cm⁻¹, (ii) a increase in IR intensity for hydrogen bonding broadband in the 3200 – 2000 cm⁻¹ region centered at 2905 cm⁻¹, and (iii) a increase in IR intensity at 1531 cm⁻¹ for –NH₂ deformation vibration. SO₂ interacts with the amine functional group at 1408 cm⁻¹, adsorbed sulfite at 1277 cm⁻¹, gaseous sulfite at 1098 cm⁻¹, and monodentate sulfate at 1000 and 941 cm⁻¹ [7, 8].
Figure 5.3 SO$_2$ adsorption over (a) 1,3-phenylenediamine thin film (ATR-IR) (b) 1,3-phenylenediamine/SiO$_2$ (DRIFTS) at 323 K.
The assignment of adsorbed SO\textsubscript{2} as sulfite structure is in agreement with adsorption on Y-type zeolites at around 1240 cm\textsuperscript{-1} and on Al\textsubscript{2}O\textsubscript{3} at 1070 cm\textsuperscript{-1} \cite{9}.

Figure 5.3(b) shows the IR absorbance spectra during SO\textsubscript{2} adsorption over 1,3-phenylenediamine/SiO\textsubscript{2} supported sorbent at 323 K. Introduction of SO\textsubscript{2} over the sorbent results in an increase in IR intensity at 3147, 1617, and 922 cm\textsuperscript{-1} indicating the SO\textsubscript{2} adsorption on the amine adsorption site similar to that in Figure 5.3(a). The adsorption band at 1349 cm\textsuperscript{-1} is assigned to the asymmetric vibration for gaseous SO\textsubscript{2} \cite{10}. The
Sulfite adsorbate species are weakly adsorbed at 1089 cm\(^{-1}\). SO\(_2\) adsorption on 1,3-phenylenediamine/SiO\(_2\) sorbent proceeds by the following reaction steps.

\[
SO_2(g) + M - O \longrightarrow SO_3^{2-} - M \quad (5)
\]

\[
SO_2(g) + M - OH \longrightarrow HSO_3^{-} - M \quad (6)
\]

\[
SO_3^{2-} - M + NH_2 - \longrightarrow M + SO_3^{2-} - NH_2^{-} \quad (7)
\]

\[
HSO_3^{-} - M + NH2 - \longrightarrow M + HSO_3^{-} - NH_2^{-} \quad (8)
\]

SO\(_2\) reacts with oxygen on the oxide surface to form sulfite SO\(_3^{2-}\) and bisulfate HSO\(_3^{-}\) products [11, 12], steps (5) and (6), followed by adsorption to the amine active site in steps (7) and (8). The reaction scheme is in agreement with that observed during the NO adsorption study, the surface oxidation of NO to NO\(_2^{-}\) with the appearance N\(_2\)O\(_4\) followed by absorption at the amine active site (NO\(_2^{-}\)-NH\(_2^{-}\)).

5.3.3 UV-Vis Spectra of 1,3-phenylenediamine

Figure 5.5 presents the UV-Visible diffuse reflectance spectra of (a) ethanol, (b) 2 vol % 1,3-phenylenediamine, and (c) 10 vol % 1,3-phenylenediamine solution. A broadband at 400-550 nm, in the visible region, for the 2 vol % 1,3-phenylenediamine solution is due to \(\pi\) electron conjugation in adjacent aromatic molecules [13-15]. The 10
vol % solution shows an increase in the broadband absorbance intensity, in Figure 5.5(c), corresponding to a greater amount of conjugated π electrons in solution. The linear increase in absorbance intensity shows the proportionality of intensity to concentration and can be used as a measure for the presence of a highly conjugated molecular structure [16].

Figure 5.6 shows the UV-Visible diffuse reflectance spectra during the adsorption of CO₂, NO, and SO₂ gases on 1,3-phenylenediamine/SiO₂ sorbent at 323 K. The UV-Visible absorbance spectrum was placed in Kubelka-Munk units to investigate the changes in the adsorbate surface concentrations during the adsorption process [17]. The basis for the choice of the Kubelka-Munk function is to highlight the changes in surface concentration of an “adsorbate on a solid” system which would have otherwise not visible in the UV-Visible diffuse reflectance absorbance spectrum.
Figure 5.5 UV-Visible diffuse reflectance spectra of (a) ethanol (b) 2 vol % 1,3-phenylenediamine/ethanol solution (c) 10 vol % 1,3-phenylenediamine/ethanol solution.
Figure 5.6 UV-Visible diffuse reflectance spectra of 1,3-phenyleldiamine/SiO$_2$ during adsorption at 373 K of (a) CO$_2$ (b) NO (c) SO$_2$. 
Flowing CO₂ (pKₐ = 6.35) over the sorbent, in Figure 5.6(a), results in a slight increase in K-M absorbance intensity. The slightly lower reflectivity (i.e. increase in K-M absorbance intensity) is attributed to weak CO₂ and 1,3-phenylenediamine interaction on the SiO₂ surface. Flowing gaseous NO and SO₂ (pKₐ = 1.81) over the sorbent results in a strong broadband adsorption between 400-650 nm after 5 min exposure time to gaseous NO and 10 min exposure to SO₂. The increase in absorbance intensity and broadening is attributed to the effects of adsorption (cation formation) and a higher concentration of 1,3-phenylenediamine on the SiO₂ surface from agglomeration of newly formed adsorbate surface species [18]. Adsorbing NO exhibits a higher rate of agglomeration evidenced by the large and broader intensity after 5 min exposure time in comparison to SO₂ shown in Figure 5.6b-c. The observations suggest the 1,3-phenylenediamine sorbent becomes mobile on the SiO₂ surface in the cationic state in the presence of an acidic reactant gas.

The adsorption of aromatic amine on SiO₂ result from the interactions of the π-electrons with the terminal SiO₂ silanol groups thus heterocyclic molecules such as 1,3-phenylenediamine are bound less strongly on silica than on alumina [19]. The heat of adsorption of aromatic hydrocarbons is decreased with increasing adsorbate loading [20] and at the higher 1,3-phenylenediamine loading, observed 1,3-phenylenediamine behavior in the presence of gaseous NO and SO₂ suggest the adsorbate layer becomes mobile through agglomeration. Low adsorbate coverage minimizes adsorbate-adsorbate interactions and thus adsorbate mobility is reduced.
The 0.0026 wt % 1,3-phenylenediamine/SiO₂ sorbent adsorbed 1260 μmol/g of SO₂, shown in Figure 5.4. Interestingly, increasing the amine loading on SiO₂ results in a decrease in adsorption capacity; the limitation in SO₂ adsorption may be related to the (i) low surface area of the support material and poor dispersion of 1,3-phenylenediamine, and (ii) deactivation by SO₂ poisoning. The poisoning effects were investigated using ATR-IR spectroscopy by depositing 4 μm amine thin film on a ZnSe window. The SO₂ TPD study show for each adsorption/desorption cycle there is a decrease in SO₂ capture capacity from 16.0 to 8.52 μmol SO₂ after the fourth cycle, shown in Table 5.1. Redissolving the amine thin film in ethanol resulted in an increase in adsorption capacity to 14.6 μmol SO₂ (see Table 5.1). The enhancement effect on SO₂ capture by ethanol suggests that the 1,3-phenylenediamine is re-dispersed on the ZnSe window. The apparent poisoning effect on SO₂ adsorption may be the result of agglomeration of the amine active sites deactivating the adsorption capacity of the sorbent.

Regeneration of the 1,3-phenylenediamine thin film and SiO₂ supported sorbent resulted in deactivation of the SO₂ adsorption capacity, shown in Table 5.1 and Figure 5.4 respectively, as a result of agglomeration of the 1,3-phenylenediamine molecules. The addition of PEG to the 1,3-phenylenediamine/SiO₂ sorbent enhanced SO₂ adsorption capacity. In the presence of PEG, increased 1,3-phenylenediamine loading resulted in an increase in SO₂ adsorption capacity, shown in Table 5.2. Increasing the PEG content from 0.1 to 3.3 wt % increased SO₂ adsorption capacity from 0.26 to 2.22 mmol/g, a factor of 8.5 times.
SO₂ liberation from an absorbent as well as SO₂ capture is an important step for SO₂ management by adsorption in the power generation sector. PEG limits the migration area providing a barrier to the preferential migration mechanism for agglomeration and resulting deactivation. The sorbents capture capacity increased during PEG addition; PEG effectively disperses the 1,3-phenylenediamine on the SiO₂ surface as depicted in Figure 3.7.

Table 5.1 SO₂ adsorption on 4 µm think film of 1,3-phenylenediamine.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>SO₂ (µmol)</th>
<th>SO₂/amine (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.0</td>
<td>0.82</td>
</tr>
<tr>
<td>2</td>
<td>14.2</td>
<td>0.73</td>
</tr>
<tr>
<td>3</td>
<td>10.1</td>
<td>0.58</td>
</tr>
<tr>
<td>4</td>
<td>8.52</td>
<td>0.42</td>
</tr>
<tr>
<td>Add ethanol</td>
<td>14.6</td>
<td>0.75</td>
</tr>
</tbody>
</table>

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Table 5.2  SO$_2$ adsorption on 1,3-phenylenediamine+PEG/SiO$_2$ sorbent.

<table>
<thead>
<tr>
<th>1,3-phenylenediamine (wt %)</th>
<th>PEG (wt %)</th>
<th>SO$_2$ (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.1</td>
<td>0.26</td>
</tr>
<tr>
<td>30</td>
<td>0.1</td>
<td>0.67</td>
</tr>
<tr>
<td>50</td>
<td>0.1</td>
<td>0.80</td>
</tr>
<tr>
<td>10</td>
<td>3.3</td>
<td>2.22</td>
</tr>
<tr>
<td>30</td>
<td>3.3</td>
<td>2.10</td>
</tr>
<tr>
<td>50</td>
<td>3.3</td>
<td>2.30</td>
</tr>
</tbody>
</table>

Figure 5.7  Proposed surface adsorbate scheme during SO$_2$ adsorption (a) agglomeration of aromatic amine (b) immobilization of aromatic amine by polyethylene glycol.
5.4 Conclusion

Changes in the adsorbate layer by agglomeration of the aromatic amine molecules were observed during SO$_2$ adsorption process. Under high amine loadings, agglomeration of the amine active sites results in a decrease in SO$_2$ adsorption capacity. The optimum SO$_2$ sorbent preparation with the 1,3-phenylenediamine on SiO$_2$ is achieved by dispersing and immobilizing the amine active sites. Improving the 1,3-phenylenediamine sorbent is achieved by preventing agglomeration of the amine active sites by the use of PEG as an effective dispersing agent.

5.5 Bibliography


CHAPTER VI

IN SITU IR STUDY OF ADSORBED SPECIES DURING PHOTOCATALYTIC OXIDATION OF 2-PROPANOL OVER AU/TiO₂, PD/TiO₂, AND TiO₂ CATALYSTS

6.1 Abstract

The reaction pathway for the photocatalytic oxidation of 2-propanol on Au/TiO₂, Pd/TiO₂, and TiO₂ at 303 K has been studied by in situ infrared (IR) spectroscopy. Exposure of 2-propanol/TiO₂ to UV illumination lead to the formation of acetone (\(CH₃COCH₃_{ad}\)) and \(H₂O_{ad}\), followed by C-C bond cleavage and the formation of acetate (\(CH₃COO⁻_{ad}\)), and formate (\(HCOO⁻_{ad}\)). The C-C bond breakage and subsequent production of \(CH₃COO⁻_{ad}\) and \(HCOO⁻_{ad}\) on TiO₂ and Pd/TiO₂ led to \(CH₃COCH₃_{ad}\) site blocking. The acidic acetate and basic acetone adsorbate species coupled with in situ IR offers a unique ability to observe the competitive adsorption of these product species through the hydrogen bonding interaction with \(H₂O_{ad}\). Addition of Au on TiO₂ lowered the catalytic activity of the catalyst but improved the selectivity to acetone compared to TiO₂. The improved selectivity is attributed to a dual reaction pathway as a result of Au unique ability to produce the reactive surface oxygen species during UV illumination.
6.2 Experimental

The experimental section describes the catalyst preparation and in situ IR setup for investigating the adsorbing species during the photocatalytic dehydrogenation of 2-propanol.

6.2.1 Catalyst Preparation

The 1 wt % Pd/TiO$_2$ catalyst was prepared by the incipient wetness impregnation of $Pd(\text{NO}_3)_2 \cdot H_2O$ (Aldrich) on TiO$_2$ (Degussa P25) and dried at 298 K. The catalyst was calcined in air at 673 K (heating rate 10 K/min) for 30 min. The gold reference catalyst (1.49 wt% Au/TiO$_2$) was obtained from the World Gold Council. The reaction studies were carried out, over the TiO$_2$, Pd/TiO$_2$ and Au/TiO$_2$ catalysts, (i) after calcination and (ii) after reduction at 673 K in 5% H$_2$/Ar flow (35 cm$^3$/min) for 30 min. The catalysts were characterized by X-ray Diffraction (XRD) Philips Analytical X-Ray PW1710 diffractometer using Cu k$_\alpha$ radiation operating at 49 kV and 35 mA.

6.2.2 In Situ IR Reaction Studies

The experimental apparatus, shown in Figure 6.1, consist of (i) a reactant metering system (Brooks Instrument 5850 mass flow controllers), (ii) a gas sampling system with 4-port valve, (iii) a Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS, Harrick Scientific) reactor containing 89.6 mg catalyst and placed inside a Fourier Transform Infrared Spectrometer (FTIR, Varian Inc. FTS-4000), and (iv) a 350 W mercury lamp (Oriel 6286) with light condenser (Oriel 77800) used for irradiating the catalyst surface. The 4-port valve allows switching the inlet flow from
100% Ar to 100% O₂ or 5% H₂/Ar while maintaining a total flow rate of 35 cm³/min over the TiO₂, Au/TiO₂ or Pd/Al₂O₃ catalysts.

Figure 6.1 Experimental Apparatus (i) reactant metering system (ii) gas sampling system (iii) analysis section (iv) UV-lamp.
The changes in the concentration of IR-observable adsorbates are monitored by FTIR. The IR absorbance spectrum of adsorbed and gaseous species is obtained by

\[ A = -\log\left( \frac{I_o}{I} \right) \] [1], where \( I_o \) is the background IR single beam spectrum (32 co-added scans and resolution 4 cm\(^{-1}\)) of the catalyst under 100% Ar flow and \( I \) is the IR single beam spectrum during the reaction studies.

6.3 Results

The catalyst characterization from XRD and the in situ IR results during UV irradiation of Au/TiO\(_2\), Pd/TiO\(_2\), and TiO\(_2\) are reported in the following sections.

6.3.1 XRD Characterization

Figure 6.2 shows the XRD patterns for the Au/TiO\(_2\) catalyst before and after the photocatalytic studies. The XRD peaks for the anatase phase of TiO\(_2\) occur at 25.4\(^o\), 37.9\(^o\), 48.0\(^o\), 54.0\(^o\), and 55.0\(^o\), the rutile phase of TiO\(_2\) occur at 27.5\(^o\), 36.0\(^o\), 39.8\(^o\), 41.3\(^o\), and 56.6\(^o\) [2]. The peaks for Au at 38.0\(^o\), and 43.8\(^o\) were observed on the Au/TiO\(_2\) catalyst [3]. The peaks for PdO at 33.9\(^o\) [4], Pd(111) at 40.4\(^o\), and Pd(200) at 46.4\(^o\) were observed on the Pd/TiO\(_2\) catalyst [5]. XRD analysis shows that the photocatalytic reaction did not result in any serious structural modifications for the Au/TiO\(_2\) catalyst. After reduction of the Pd/TiO\(_2\) catalyst, the PdO peak was not observed. The Au particle size 3.6 nm for Au/TiO\(_2\) was determined by TEM [6]. The Pd particle size 5.8 nm for Pd/TiO\(_2\) was determined by XRD using the Scherer equation from line broadening [7].
Figure 6.2  XRD analysis of Au/TiO$_2$ catalyst before and after photo-catalytic reaction.
6.3.2 $\text{H}_2\text{O}_{\text{ad}}$ and $-\text{OH}$ on the Au/TiO$_2$, Pd/TiO$_2$, and TiO$_2$ catalysts

Figure 6.3 shows the IR single beam and absorbance spectra during 2-propanol adsorption and temperature programmed reduction (TPR) of the TiO$_2$, Au/TiO$_2$, and Pd/TiO$_2$ catalysts. The adsorption of 2-propanol on TiO$_2$, shown in Figure 6.3(a), displaced $\text{H}_2\text{O}_{\text{ad}}$ on the catalyst surface. Displacement of $\text{H}_2\text{O}_{\text{ad}}$ produced a corresponding negative IR intensity at 3725 cm$^{-1}$ for isolated $-\text{OH}$ [8], and at 3696 and 3632 cm$^{-1}$, for the linearly and triply bonded $-\text{OH}$ [9-11] respectively. The addition of Au on TiO$_2$ suppressed the formation of the isolated $-\text{OH}$ at 3725 cm$^{-1}$. The shape of the $-\text{OH}$ species show a narrower bandwidth on Au/TiO$_2$, which suggests that the localized $-\text{OH}$ species are more strongly hydrogen bonded in the presence of Au. Loading Pd on TiO$_2$, also suppressed the formation of the isolated $-\text{OH}$ at 3725 cm$^{-1}$ on TiO$_2$. A weaker IR intensity at 3696 and 3632 cm$^{-1}$ suggests that Pd lowers the amount of $\text{H}_2\text{O}_{\text{ad}}$ on the TiO$_2$ surface and is in agreement with studies that have shown increasing Pt loading on TiO$_2$ block the $-\text{OH}$ adsorption sites [2].

After 2-propanol adsorption, the single beam spectra indicates that the bridging $-\text{OH}$ remains to be strongly adsorbed on the TiO$_2$ surface, shown in Figure 6.3(d). The Au/TiO$_2$ catalyst (see Figure 6.3b) exhibit negative IR intensities for linear $-\text{OH}$ at 3696 cm$^{-1}$, for bridged $-\text{OH}$ at 3669 cm$^{-1}$, and for triply bonded $-\text{OH}$ at 3632 cm$^{-1}$ indicating these species are still present on the catalyst surface. The broadband adsorption in the
Figure 6.3  Infrared single beam spectra of Au/TiO₂, Pd/TiO₂, and TiO₂ catalysts during (a) 2-propanol adsorption (b) Au/TiO₂ (c) Pd/TiO₂ (d) TiO₂ reduced in 5% H₂/Ar from 303 – to – 673 K.
3500-3000 cm\(^{-1}\) region for TiO\(_2\), Au/TiO\(_2\), and Pd/TiO\(_2\) results from hydrogen bonding between the adsorbed 2-propanol species which are subsequently removed on reduction at 673 K. Further 2-propanol adsorption displaces the remaining H\(_2\)O\(_{ad}\) on the reduced catalysts, shown in Figure 6.3(a). Interestingly, after reduction, the IR spectra of the Au/TiO\(_2\) catalyst show an IR intensity for the isolated –OH species at 3725 cm\(^{-1}\). The appearance of the isolated –OH suggest that the isolated –OH formation depends on the H\(_2\)O\(_{ad}\) surface coverage.

Figure 6.4 shows the IR absorbance spectra during 2-propanol adsorption over Au/TiO\(_2\), Pd/TiO\(_2\), and TiO\(_2\) catalysts at 303 K. The 2-propanol adsorption on Au/TiO\(_2\), in Figure 6.4(a), show an increase in IR intensity for aliphatic C-H stretch at 2973 and 2888 cm\(^{-1}\), the OH stretch for C\(_3\)H\(_8\)O\(_{ad}\) at 1307 cm\(^{-1}\), δ\(_{ad}(\text{CH}_3)\) at 1465 cm\(^{-1}\), δ\(_s(\text{CH}_3)\) at 1383, and ν(\text{C-C}) at 1161 and 1132 cm\(^{-1}\) [12]. The IR spectra (see Figure 6.4 a-c) indicate that the primary adsorbing species is molecular 2-propanol. The coverage of 2-propanol is difficult to control; increasing the coverage of 2-propanol results in a higher IR intensity from hydrogen bonding in the 3500-3000 cm\(^{-1}\) region. The higher IR intensity at 3500-3000 cm\(^{-1}\) on TiO\(_2\) during adsorption indicates the presence of a larger amount of 2-propanol coverage on the TiO\(_2\) surface.

6.3.3 UV Irradiation of calcined Au/TiO\(_2\), Pd/TiO\(_2\), and TiO\(_2\)

Figure 6.5 shows the difference spectrum during UV-irradiation of adsorbed 2-propanol on TiO\(_2\), Au/TiO\(_2\), and Pd/TiO\(_2\) at 303 K. The difference spectra were obtained by subtracting the spectrum at 0 min (i.e. before UV-irradiation) from the spectra.
Figure 6.4  IR absorbance spectra during 2-propanol adsorption at 303 K over (a) Au/TiO$_2$ (b) Pd/TiO$_2$ (c) TiO$_2$ catalysts.
Figure 6.5  UV irradiation of adsorbed 2-propanol at 30 °C (a) IR difference spectra, IR intensity data on (b) TiO₂ (c) Au/TiO₂ (d) Pd/TiO₂ (e) normalized IR intensity data Au/TiO₂ catalysts.
following exposure to UV. The UV-irradiation of 2-propanol saturated TiO$_2$ surface, shown in Figure 6.5(a), resulted in an increase in IR intensity for (i) surface –OH at 3500 – 3000 cm$^{-1}$ region, (ii) CO$_2$ at 2350 cm$^{-1}$, (iii) C=O of acetone at 1706 cm$^{-1}$ [13], (iv) acetate (CH$_3$COO$_{ad}^-$) at 1590 cm$^{-1}$, (v) formate (HCOO$_{ad}^-$) at 1427 cm$^{-1}$, and (vi) methoxy at 1357 cm$^{-1}$, shown in Figure 6.5(a). The ratio of IR intensity for CH$_3$COO$_{ad}^-$/CH$_3$COCH$_3$$_{ad}$ and HCOO$_{ad}^-$/CH$_3$COCH$_3$$_{ad}$, indicates that CH$_3$COO$_{ad}^-$ (1590 cm$^{-1}$) grew to a maximum as the dominant surface species after 27.78 min. The increase in IR intensity at 1590 and 1428 cm$^{-1}$ may also be attributed to the presence of the mesityl oxide (O)CH=C(CH$_3$)$_2$ [14, 15] species. Table 6.1 shows the apparent first-order reaction-rate constant (k$_{app}$) for acetone formation over TiO$_2$ was determined to be 7.75 X 10$^{-3}$ min$^{-1}$.

The addition of Au onto TiO$_2$ lowered the apparent k$_{app}$ to 4.27 X 10$^{-3}$ min$^{-1}$ for acetone formation and modified the selectivity to acetone. UV-irradiation of the Au/TiO$_2$ surface resulted in a broadband IR adsorption in the 3000-1000 cm$^{-1}$ region (see Figure 6.5a) suggesting that Au may block the sites for electron and hole recombination leading to an accumulation of the electrons in the conduction band. Au blocking property on electron and hole recombination may also contribute to the lower apparent k$_{app}$ for acetone formation. The IR intensity profile, shown in Figure 6.5(b), suggests that acetone formation led the acetate and formate formation on Au/TiO$_2$. The ratio of IR intensity for CH$_3$COO$_{ad}^-$/CH$_3$COCH$_3$$_{ad}$ and HCOO$_{ad}^-$/CH$_3$COCH$_3$$_{ad}$, indicate that CH$_3$COCH$_3$$_{ad}$ (1706 cm$^{-1}$) is the dominant surface species on the Au/TiO$_2$ catalyst.
Table 6.1 The apparent first-order reaction-rate constants for acetone formation over the calcined catalysts, reduced catalysts, and during O₂ introduction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Calcined k (min⁻¹)</th>
<th>Reduced k (min⁻¹)</th>
<th>Introducing O₂ k (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/TiO₂</td>
<td>4.27 X 10⁻³</td>
<td>7.38 X 10⁻³</td>
<td>0.12</td>
</tr>
<tr>
<td>Pd/TiO₂</td>
<td>1.99 X 10⁻³</td>
<td>5.00 X 10⁻⁵</td>
<td>0.76</td>
</tr>
<tr>
<td>TiO₂</td>
<td>7.75 X 10⁻³</td>
<td>7.11 X 10⁻³</td>
<td></td>
</tr>
</tbody>
</table>

Adding Pd to TiO₂ decreases the apparent $k_{app}$ value to 1.99 X 10⁻³ min⁻¹, shown in Table 6.1. Exposure of Pd/TiO₂ to UV radiation caused the formation of product species similar to that on Au/TiO₂, however $CH_3COO^{-}_{ad}$ was the dominant product species, shown in Figure 6.5(c). The absence of a broadband adsorption on Pd/TiO₂ suggests that the addition of Pd onto TiO₂ does not lead to the accumulation of photogenerated electrons as compared to Au. The XRD spectra of the calcined Pd/TiO₂ catalyst (see Figure 6.2) indicate that Pd-O is present on the surface of the catalyst. The presence of Pd-O may consume the photogenerated electrons on UV-irradiation. Thus, removing these Pd-O sites may improve the catalytic activity for acetone formation.

The normalized intensities of IR observable adsorbates with time for Au/TiO₂, shown in Figure 6.5(e), reveal the time when the species reach their maximum IR intensities. At 2.00 min, following UV-irradiation, the IR observable species intensities...
increased in the order: (i) photo-generated e\(^-\), (ii) \(CH_3COCH_3\text{_{ad}}\), (iii) \(CH_3COO\text{_{ad}}^-\), (iv) methoxy, and (v) \(HCOO\text{_{ad}}^-\). The formation sequence of the product species was similar on the TiO\(_2\) catalyst. If the photocatalytic oxidation of 2-propanol follows a series (i.e. \(A \rightarrow B \rightarrow C \cdots \rightarrow E\) etc) reaction pathway, then the reaction proceeds through \(CH_3COCH_3\text{_{ad}} \rightarrow CH_3COO\text{_{ad}}^- \rightarrow \text{methoxy} \rightarrow HCOO\text{_{ad}}^-\) according to the maximum intensity of each IR observable species at the 2.00 min time period \([16]\). The trend of the IR intensity curves at 1590 cm\(^{-1}\) (\(CH_3COO\text{_{ad}}^-\)) and 1427, 1357 cm\(^{-1}\) (\(HCOO\text{_{ad}}^-\), methoxy) suggest that it is likely the C\(_2\)-oxygenated (\(CH_3COO\text{_{ad}}^-\)) and C\(_1\)-oxygenated (\(HCOO\text{_{ad}}^-\)) species are formed from parallel pathways in the photocatalytic oxidation of 2-propanol over the TiO\(_2\) and Au/TiO\(_2\) catalysts.

### 6.3.4 UV Irradiation of reduced Au/TiO\(_2\), Pd/TiO\(_2\), and TiO\(_2\)

Figure 6.6 shows the difference spectra and IR intensity profiles while flowing O\(_2\) over the adsorbed 2-propanol on reduced TiO\(_2\), Au/TiO\(_2\), and Pd/TiO\(_2\) catalysts at 303 K. Flowing O\(_2\) over TiO\(_2\), shown in Figure 6.6(a), did not result in any spectral changes. Flowing O\(_2\) over the Au/TiO\(_2\) catalyst resulted in an increase in IR intensity for acetone at 1706 cm\(^{-1}\), for acetate at 1590 cm\(^{-1}\), for formate at 1427 cm\(^{-1}\), and for methoxy at 1357 cm\(^{-1}\). Acetone formation, in the absence of UV radiation, is attributed to the TPR pretreatment of the Au/TiO\(_2\) catalyst. It has been shown that oxygen does not readily dissociatively adsorb on Au \([17-20]\), therefore, the catalytic activity may be attributed to the TPR (i) producing free electrons in the TiO\(_2\) conduction band and (ii) removing oxygen from the TiO\(_2\) lattice. The conduction band electrons and oxygen vacancies in
the TiO$_2$ lattice may facilitate O$_2$ dissociation producing a reactive surface oxygen species. Exposure of O$_2$ and formation of a reactive oxygen species lead to an increase in the apparent rate constant for acetone formation ($k_{app} = 0.12$ min$^{-1}$).

The Pd/TiO$_2$ catalyst exhibited strikingly different behavior in the IR difference spectrum upon exposure to O$_2$, shown in Figure 6.6. Flowing O$_2$ over the reduced Pd/TiO$_2$ catalyst resulted in a negative broadband IR intensity resembling that of the broadband adsorption during UV-irradiation and subsequent formation of photo-generated electrons. Pd, known for its ability to dissociatively adsorb O$_2$, may help to facilitate the consumption of electrons trapped in the conduction band.
Figure 6.6  IR difference spectra introducing O$_2$ over the 2-propanol-Au/TiO$_2$, Pd/TiO$_2$, TiO$_2$ catalysts.
Figure 6.7 IR difference spectra during UV irradiation of adsorbed 2-propanol at 30 °C over Au/TiO₂, Pd/TiO₂, and TiO₂ catalysts.
The negative broadband IR intensity suggest that the electrons in the conduction band recombine with O$_{2, \text{ad}}$ on the TiO$_2$ surface to produce oxygen ions (O$_2^-$) by the $O_{2, \text{ad}} + e^- \rightarrow O_2^-$ reaction [2]. Pd effect on promoting the consumption of conduction band electrons, further increased the apparent rate constant for acetone formation to 0.76 min$^{-1}$ (see Table 6.1). The increased activity for acetone during O$_2$ exposure over Au/TiO$_2$ and Pd/TiO$_2$ compared to TiO$_2$ suggests that Au and Pd are a necessary requirement for promoting the consumption of conduction band electrons on the TiO$_2$ support in the absence of UV-irradiation.

Reducing the catalyst did not change the formation sequence of the product species but affected the activity of the TiO$_2$, Au/TiO$_2$, and Pd/TiO$_2$ catalysts on UV-irradiation. Reducing Au/TiO$_2$ increased the apparent k$_{\text{app}}$ value to 7.38 X 10$^{-3}$ min$^{-1}$, whereas the activity decreased on Pd/TiO$_2$ (1.99 X 10$^{-3}$ min$^{-1}$) and TiO$_2$ (7.11 X 10$^{-3}$ min$^{-1}$). The increased activity for Au/TiO$_2$ may be related to Au ability to block the recombination of the photo-generated e$^-$ and h$^+$ evidenced by the broadband adsorption shown in Figure 6.7(a). Our direct IR observations of the evolution of adsorbed species during the 2-propanol reaction result in the postulation of a parallel/series pathway for the conversion of 2-propanol to acetone and other product species, shown in Figure 6.8. The reaction pathway shows that CH$_3$COHCH$_3$$_{\text{ad}}$ can undergo oxidation by either $\ddagger$OH or O$_2^-$ to produce the transient C$_2$-oxygenated intermediate species which rapidly decompose to acetone, acetate, methoxy, formate, and H$_2$O$_{\text{ad}}$ product species.
The IR spectral position, intensity, and bandwidth reflect the amount of adsorbed product species and extent of hydrogen bonding on the catalyst surface. An interesting spectral feature occurs by the adsorbed product species perturbation on the \(-\text{OH}\) (3500 – 3000 cm\(^{-1}\)) region. The IR spectra shows that the adsorbed acetone produces a flattened spectral feature whereas adsorbed acetate produces a rounded spectral feature in the \(-\text{OH}\) region (see Figure 6.7a). In the presence of both acetone and acetate adsorbate species (near a 1:1 ratio), the spectra exhibits a transition feature resembling a triangular shape on Au/TiO\(_2\) (see Figure 6.5a). Three forces are involved in the acetone-H\(_2\)O\(_{\text{ad}}\) interaction on the catalyst surface: (i) dipole-dipole interactions, (ii) hydrogen bonding interactions, and (iii) hydrophobic interactions [21, 22]. The hydrogen bonding, between H\(_2\)O\(_{\text{ad}}\), acetone, and acetate species, is observed on the \(-\text{OH}\) bands with increasing H\(_2\)O\(_{\text{ad}}\) and product species surface coverage. As the reaction proceeds, there is no shift in the vibrational frequency for the C=O with the appearance of the hydrogen bonding spectral features,
suggesting that hydrogen bonding is stronger than the dipole-dipole interactions between acetone, acetate, and H$_2$O$_{ad}$ surface species.

6.4 Discussion

Vibrational spectroscopy has provided evidence for the initiating species responsible for the photocatalytic oxidation of alcohols; the key species that initiate the photocatalytic oxidation have been identified in the literature as $\bullet OH$ and h$^+$ initiating [23-31] and occur according to the following reaction steps.

$$TiO_2 + hv \rightarrow h^+ + e^-$$ (1)

$$H_2O_{ad} \rightarrow OH^- + H^+$$ (2)

$$OH^- + h^+ \rightarrow \bullet OH$$ (3)

$$O_{2,ad} + e^- \rightarrow O_2^-$$ (4)

$$O_2^- + 2H_2O_{ad} \rightarrow 2\bullet OH + 2OH^- + O_2$$ (5)

Researchers agree on the elementary steps, the holes produced from UV-irradiation may react with H$_2$O$_{ad}$ to produce $\bullet OH$ whereas the electrons react through two steps, (i) the transfer of electrons from the TiO$_2$ surface to adsorbed oxygen ($O_{2,ad}$) (step 4) and (ii) the reaction of $O_2^-$ with H$_2$O$_{ad}$ to produce $\bullet OH$ (step 5).

The proposed mechanisms differ however on the involvement of $\bullet OH$ and h$^+$ in the photocatalytic oxidation of 2-propanol. Two reaction pathways have been proposed
describing the oxidation process [32, 33]. One reaction pathway suggests that the process begins with the $\cdot OH$ species following the steps (6 - 12) [33].

\[
\begin{align*}
CH_3COHCH_{3,ad} + \cdot OH & \rightarrow CH_3C\cdot OHCH_3 + H_2O_{ad} \quad (6) \\
CH_3C\cdot OHCH_{3,ad} & \rightarrow CH_3COCH_{3,ad} + H^+_{ad} + e^- \quad (7) \\
CH_3C\cdot OHCH_{3,ad} + O_2 & \rightarrow CH_3COO\cdot OHCH_{3,ad} \quad (8) \\
CH_3COO\cdot OHCH_{3,ad} & \rightarrow CH_3OCH_{3,ad} + H^+_{ad} + O^2_- \quad (9) \\
CH_3C\cdot OHCH_{3,ad} + H\cdot O_{2,ad} & \rightarrow CH_3COOHOHCH_{3,ad} \quad (10) \\
CH_3COOHOHCH_{3,ad} & \rightarrow CH_3COCH_{3,ad} + H_2O_{2,ad} \quad (11) \\
\cdot OH + H\cdot O_2 & \rightarrow H_2O + O_2 \quad (12)
\end{align*}
\]

UV-irradiated TiO$_2$ produces the $\cdot OH$ radical (step 3) that is reactive with adsorbed 2-propanol resulting in a radical species and H$_2$O$_{ad}$ (step 6). The 2-propanol radical is reactive on the surface producing adsorbed acetone (step 7) or reacting with O$_2$ to form a C$_2$-oxygenate species (step 8). The C$_2$-oxygenate species and the active oxygen containing species further react to form the stable products acetone, H$_2$O, and O$_2$ (steps 9 - 12).

Studies have also suggested a reaction pathway that is initiated by h$^+$ and adsorbed 2-propanol [32] according to steps (13) through (15).

\[
h^+ + CH_3COHCH_{3,ad} \rightarrow CH_3COH^+CH_3_{ad} \quad (13)
\]
\[ CH_3CHOH^+CH_{3,ad} + O_{ad}^{2-} \rightarrow CH_3CHOCH_{3,ad} + OH \] (14)

\[ CH_3CHOCH_{3,ad} + OH \rightarrow CH_3COCH_{3,ad} + H_2O + e^- \] (15)

The hole initiated process forms a charged adsorbed 2-propanol species (step 13) that is claimed to have a lower energy barrier for removing lattice oxygen from TiO\(_2\) surface (step 14). The formation of acetone and H\(_2\)O results from the loss of the OH species (step 14 and 15). The oxygen lattice pathway studies have shown that the photocatalytic oxidation of 2-propanol may occur with UV activated lattice oxygen [34-37] in the absence of O\(_2\). The lattice oxygen may then be replaced in the absence of UV-irradiation for the subsequent reactivation by UV-irradiation. The initial step for 2-propanol oxidation has also been proposed to react with the \(O_2^-\) species [38] on the surface of the TiO\(_2\) catalyst by steps 16 and 17.

\[ O_2^- + CH_3COHCH_{3,ad} \rightarrow CH_3COOHCH_{3,ad} \] (16)

\[ CH_3COOHCH_{3,ad} \rightarrow HO^- + CH_3COCH_{3,ad} \rightarrow CH_3COCH_{3,ad} \] (17)

The \(O_2^-\) anion may react with an adjacent 2-propanol molecule to form a reactive radical species (step 16). The 2-propanol radical then dehydrates to form acetone on the surface of the catalyst (step 17). Regardless of the active species involved in the dehydrogenation of 2-propanol, the removal of acetone and H\(_2\)O from the catalyst surface results in the completion of the photocatalytic cycle.
In this study, the presence of H$_2$O$_{ad}$ would lower the possibility of h$^+$ initiated reaction (step 13) and make OH available for initiating the reaction according to reaction pathway A in Figure 6.8. It has been demonstrated that OH is able to desorb from TiO$_2$, oxidizing the species that is not directly adsorbed on the TiO$_2$ surface [29, 30]. Therefore, OH could attack the hydrogen on both the $\alpha$- and $\beta$-carbon in CH$_3$COHCH$_3$, as shown in Figure 6.8. The observation of acetate, methoxy, and formate product species on TiO$_2$ and Pd/TiO$_2$ suggest that the pathway A is mainly initiated by abstraction of hydrogen from the $\beta$-carbon via OH. This reaction leads to the formation of CH$_3$COO$^-$OHCH$_3$, intermediate which can undergo C-C bond scission to the acetate and formate product species. The product formation sequence suggest that initial selectivity favors acetone formation however, at an extended reaction time, the acetate species becomes the dominant product species over the TiO$_2$ and Pd/TiO$_2$ catalysts. The selectivity change, on extended reaction time, is attributed to acetate (kPa = ~4.76) more strongly adsorbing blocking the acetone (kPa = 24.2) formation.

The reaction pathway for the photocatalytic oxidation of 2-propanol is dependent upon the coverage of H$_2$O$_{ad}$, acetone, and acetate. In situ IR studies have shown that these adsorbing species interact on the surface of the catalyst. These interactions may be further elucidated by observing the interaction between H$_2$O$_{ad}$ and the adsorbate species by the changing molecular orientation of water molecules on the surface of the TiO$_2$ catalyst during the photocatalytic oxidation reaction. Studies have shown [8] that pH effects the structure and orientation of water molecules at an organic-H$_2$O interface exhibiting a distinct change in the spectrum resulting from a change in the average –OH orientation. Thus, the acidic acetate and basic acetone adsorbate species coupled with in
situ IR offers a unique ability to observe the competitive adsorption of these product species through the hydrogen bonding effect in the –OH region.

The IR spectra exhibits a flattened feature in the –OH region (see the Au/TiO₂ in Figures 6 and 7) when acetone is the dominant surface adsorbate, and a rounded feature (see the TiO₂ in Figures 5 and 7) when acetate is the dominant surface species. Interestingly, the addition of Au on TiO₂ resulted in a change in selectivity to acetone and exhibits a fascinating spectral feature. The IR spectra on Au/TiO₂, shown in Figure 6.5, exhibits a transition feature resembling a triangular shape suggesting the presence of two competing reaction pathways on the Au/TiO₂ catalyst. The competing reaction pathways A and B are elucidated by the spectral shape during the photocatalytic oxidation of 2-propanol. The selectivity change is attributed to the formation of a reactive $O_2^-$ ion on the Au/TiO₂ catalyst during UV irradiation. It has been reported in Au oxidation catalysis (i.e. CO oxidation), that during UV-irradiation of Au/TiO₂, adsorbed oxygen may form three types of reactive oxygen ions (i.e. $O_2^-$, $O_3^-$, and $O_3^{2-}$) [39] which readily react with CO to form CO₂. The interfacial hypothesis suggests that the active site of the catalyst is located at the junction between the gold particle and the transition series metal oxide support. [40-45]. Due to the inability of IR spectroscopy of the $O_2^-$ species, its involvement in the oxidation cannot be ruled out and has to be inferred from the dynamic behavior of the oxidation intermediate species which contain C=O and COO⁻. The proposed $O_2^-$ initiated oxidation step leads to higher selectivity and activity for acetone formation as compared to $\cdot OH$ initiated oxidation.
6.5 Conclusion

The reaction pathway for the photocatalytic oxidation of 2-propanol is strongly dependent on the coverage of H$_2$O$_{ad}$. Exposure of 2-propanol/TiO$_2$ to UV illumination lead to the formation of acetone (CH$_3$COCH$_{3,ad}$) and H$_2$O$_{ad}$, followed by C-C bond cleavage and the formation of acetate (CH$_3$COO$_{ad}^-$), and formate (HCOO$_{ad}^-$). The C-C bond breakage and subsequent production of CH$_3$COO$_{ad}^-$ and HCOO$_{ad}^-$ on TiO$_2$ and Pd/TiO$_2$ led to CH$_3$COCH$_{3,ad}$ site blocking. The acidic and basic properties of acetate and acetone offer a unique ability to observe the completive adsorption of the product species on the reaction pathway. Acetate behaves as the dominant adsorbate on TiO$_2$ and Pd/TiO$_2$ catalysts. The addition of Au to TiO$_2$ improves the selectivity for acetone formation and lowers acetates ability to inhibit the acetone formation. The improved selectivity is attributed to a dual reaction pathway as a result of Au unique ability to produce the reactive surface oxygen species during UV illumination.

6.5 Bibliography


7.1 Abstract

Photocatalytic dehydrogenation of 2-propanol to acetone occurred on Au/TiO₂ which exhibited a higher activity for the generation of photogenerated electron than the photocatalytic inactive Pd/TiO₂ and Pd/Al₂O₃ at 298 K.

7.2 Introduction

Catalytic dehydrogenation of alcohol is an important process for the production of aldehyde and ketone. [1] The majority of these dehydrogenation processes occur at the liquid-metal interface. The liquid phase catalytic reaction presents a challenge for identifying reaction intermediates and reaction pathways due to the strong overlapping infrared absorption of the solvent molecules. The objective of this study is to explore the feasibility of photocatalytic alcohol dehydrogenation.

In this paper, we examined the isopropyl alcohol dehydrogenation on Au/TiO₂, Pd/Al₂O₃ and Pd/TiO₂ under UV-irradiation using attenuated total reflection infrared spectroscopy (ATR-IR) in the presence and absence of UV-irradiation as well as in the presence of hydrogen. Hydrogen is used for limiting further conversion of aldehyde to
acid. The ATR-IR technique allows monitoring the change in the concentration of adsorbed species in the liquid environment under reaction conditions where UV is used to initiate the reaction. [2-3] Au/TiO₂ is used for its unique activity and selectivity of partial oxidation; it may exhibit the unique activity for oxidative dehydrogenation. Pd/Al₂O₃ and Pd/TiO₂ are used for their activities for alcohol dehydrogenation at 323 K. [4-5]

7.3 Experimental Section

1 wt% Pd/TiO₂ and 1wt % Pd/Al₂O₃ catalysts were prepared by depositing Pd onto Degussa P25 TiO₂ and Al₂O₃ (STREM) using the incipient wetness impregnation method. The aqueous solution prepared from Pd(NO₃)₂ (Aldrich) onto 2 g of TiO₂ and Al₂O₃ was stirred at room temperature for 30 min. then heated to 373 K and held until complete evaporation of the solvent. The resulting catalyst is further dried in air at 353 K for 24 h and then calcined in air at 673 K for 30 min.

1 wt% Au/TiO₂ was prepared by depositing Au onto TiO₂ using the homogeneous deposition-precipitation method. A 200 ml of aqueous solution is prepared from 0.15 g H AuCl₄ (Aldrich), 1 g TiO₂, 2.65 g urea and vigorously stirred at 353 K for 8 h. The resulting solid catalyst is separated by centrifugation using 353 K deionized water. This procedure is repeated five times to remove residual Cl⁻ ions as well as any non-interacting Au particles. The Au/TiO₂ catalyst is further dried in air at 373 K for 24 h.

The experimental apparatus consists of a gas flow system with a four port valve, a multi-reflection Attenuated Total Reflection (ATR) accessory (Pike Technologies), and a custom reactor manifold which mounts to the ATR top plate shown in Figure 7.1. The
ATR reactor manifold consists of (i) a CaF$_2$ window for UV irradiation, (ii) an inlet and outlet port, and (iii) an injection port for the liquid phase reactant.

Thin-film was prepared from a slurry of catalyst powder which is prepared from 10 mg catalyst in 5 ml of 2-propanol. The catalyst slurry was sonicated for 30 min. and allowed to sit stagnant over night. Before preparing the films, the slurry was sonicated for 15 min., 20 drops of 0.1 ml were added onto a ZnSe trough plate internal reflection element (022-2010-45, Pike Technologies). The solvent was allowed to evaporate, the procedure is repeated a total of five times. After drying in air at room temperature the catalyst thin-film is ready for 2-propanol dehydrogenation studies.

Figure 7.1 ATR Reactor System.
7.4 Results and Discussion

Irradiating a catalyst thin-film with ultraviolet (UV) radiation causes the excitation of trapped electrons producing adsorption in the mid-IR region. [6-7] Figure 7.2(a), (b), and (c) show the development of changes in the single beam IR spectra for Pd/TiO₂, Pd/Al₂O₃, and Au/TiO₂ catalysts during UV-irradiation. The single beam spectra show residual 2-propoanol from the preparation of the catalyst thin film converted to acetone. To highlight the change in IR absorption of the catalyst thin film due to UV-irradiation, the difference spectra, obtained by subtracting the single beam spectrum at 0.00 min before UV-irradiation from those after UV-irradiation at times after 0.01 min, are shown in Fig (d), (e), and (f). The shape of the broad absorption varies depending upon the catalyst suggesting strong dependence of IR adsorption behavior on the catalyst composition. Figure 7.2(d) shows there is an inflection point around 2700 cm⁻¹ on Pd/TiO₂ catalyst, indicating IR adsorption at lower wavenumbers results from Pd metal and the higher wavenumbers results from the TiO₂ support. Figure 7.2(e) show the absence of the IR adsorption at high wavenumber, 3500 - 6000 cm⁻¹ on the Pd/Al₂O₃ catalyst, indicating the lack of the reduced Pd metal on the Al₂O₃ support as compared to the interaction with the semiconductor TiO₂. Figure 7.2(f) shows the background shift occurs around 4000 cm⁻¹ on the Au/TiO₂ catalyst. The intensity of the Au/TiO₂ adsorption is four times greater than for the Pd/TiO₂ and Pd/Al₂O₃ catalysts. The results suggest that Au/TiO₂ could be a more effective photocatalyst than Pd catalysts due to its ability to produce more photogenerated electrons.

Injecting 0.5 ml 2-propanol onto the catalyst thin-film produced the characteristic bands [8] at (i) νOH band at 3330 cm⁻¹, (ii) νC-H stretching bands at 2973 and 2883 cm⁻¹,
(iii) δ\textsubscript{a-CH\textsubscript{3}} bending mode at 1469 cm\textsuperscript{-1}, (iv) δ\textsubscript{s-CH\textsubscript{3}} bending mode at 1379 cm\textsuperscript{-1}, (v) δ\textsubscript{OH} band at 1299 cm\textsuperscript{-1}, (vi) υ\textsubscript{C-C} band at 1152 cm\textsuperscript{-1}, and (vii) r\textsubscript{CH\textsubscript{3}} at 951 cm\textsuperscript{-1}, shown in Figure 7.3(a).

Figure 7.2  ATR single beam spectrum of a catalyst thin-film on ZnSe crystal under argon upon UV-irradiation (a) Pd/TiO\textsubscript{2} catalyst (b) Pd/Al\textsubscript{2}O\textsubscript{3} catalyst (c) Au/TiO\textsubscript{2} catalyst; difference spectra reveals the background shift on (d) Pd/TiO\textsubscript{2} catalyst (e) Pd/Al\textsubscript{2}O\textsubscript{3} catalyst (f) Au/TiO\textsubscript{2} catalyst.
Figure 7.3  ATR difference spectrum of catalyst thin-film on ZnSe crystal in contact with 2-propanol (a) Pd/TiO$_2$ catalyst (b) Pd/Al$_2$O$_3$ catalyst (c) Au/TiO$_2$ catalyst.
The difference spectra for 2-propanol dehydrogenation are shown in Figure 7.3(b), (c), and (d). UV-irradiation of the catalyst caused the disappearance of the characteristic bands for 2-propanol on all of the catalysts. The disappearance of the 2-propanol bands on the Au/TiO₂ catalyst corresponded with the emergence of C=O band at 1712 cm⁻¹ indicating the dehydrogenation of 2-propanol to acetone. The Pd/TiO₂ and Pd/Al₂O₃ catalysts in Figure 7.3(b) and (c) were not active for dehydrogenation evidenced by the missing C=O band. Turning off the UV-irradiation causes the reappearance of the characteristic bands for 2-propanol on both Pd catalysts indicating Pd catalysts was not effective for the reaction. In contrast, Au/TiO₂ catalyst, acetone is hydrogenated to 2-propanol upon removal of UV-light.

7.5 Conclusion

The Au/TiO₂ catalyst shows the activity for photocatalytic dehydrogenation of 2-propanol at 298 K. The activity of Au/TiO₂ is attributed to its unique capability for producing IR-observable photogenerated electrons, causing the rise of IR background during UV-irradiation.

7.6 Bibliography


CHAPTER VIII

CONCLUDING REMARKS

The in situ infrared and mass spectrometric technique were used to study novel solid sorbents prepared using TEPA, 1,3-phenylenediamine, PEG, and SiO$_2$ and the photocatalytic oxidation of 2-propanol. It was hypothesized that the addition of PEG as an additive may improve the CO$_2$ and H$_2$S adsorption capacity of TEPA on SiO$_2$. The use of PEG improved the CO$_2$ and H$_2$S adsorption capacity as discussed in chapters 3 and 4 of this dissertation. It was also hypothesized that the low basic property may allow the development of a reusable amine based sorbent for SO$_2$ removal. A reusable sorbent was developed from 1,3-phenylenediamine and PEG on SiO$_2$ as discussed in chapter 5. Chapters 6 and 7 list the studies of the oxidative dehydrogenation of 2-propanol in the gas-solid and liquid-solid reactions, respectively. Based on the experimental observations and theoretical analysis, the major results are summarized on each of the three topics covered in this work, followed by suggestions for future study.

8.1 Catalytic behavior of PEG and TEPA during CO$_2$ and H$_2$S capture

The TEPA/PEG system provides an ideal remedy for CO$_2$ and H$_2$S capture. CO$_2$ adsorbs on the TEPA/PEG as carbonates and bicarbonates, while H$_2$S adsorbs as $-\text{NH}_2\text{SH}_2$ and an amine-sulphide ($-\text{N-SH}_2\cdots\text{O-H}$) complex. PEG allowed the CO$_2$
adsorption capacity of the TEPA to increase by a factor of two and for H2S by a factor of twelve. PEG enhances the adsorption capacity by dispersing the TEPA adsorption sites. At the optimum PEG loading 16.7 wy%, the desorption temperature was decreased from 373 K to 353 K. These results are attributed to the interactions between the TEPA and PEG additive and PEG’s low binding energy for CO2 and H2S molecules. The experimental findings demonstrate that additives including amine and hydroxyl group are suitable for modifying and amine based sorbent for CO2 and H2S removal.

8.2 Catalytic behavior of 1,3-phenylenediamine during SO2 capture

1,3-phenylenediamine basic property allowed the efficient adsorption and desorption of SO2. IR spectroscopy revealed that SO2 adsorbed as sulphite and monodentate sulphate on the amine adsorption sites. Exposure of 1,3-phenylenediamine to SO2 resulted in agglomeration of the adsorption sites reducing the adsorption capacity of the sorbent. Under high 1,3-phenylenediamine loadings, increasing agglomeration of the amine adsorption sites results in a further decrease in SO2 adsorption capacity. PEG effectively dispersed and immobilized the aromatic amine during SO2 adsorption improving the adsorption capacity of the solid sorbent. Improving the 1,3-phenylenediamine sorbent is achieved by preventing agglomeration of the amine active sites by the use of PEG as an effective dispersing agent.

8.3 Photocatalytic dehydrogenation of 2-propanol

The reaction pathway during G-S photocatalytic dehydrogenation of 2-propanol is strongly dependent on the coverage of H2Oad. In situ IR studies under high coverage
H$_2$O$_{ad}$ suggest that $\cdot$OH initiated reaction appears to be present on Pd/TiO$_2$ and TiO$_2$ catalyst, whereas H$^+$ or $O_2^-$ initiated reaction occurs on the Au/TiO$_2$. The $O_2^-$ initiating 2-propanol dehydrogenation reaction produced more acetone than the $\cdot$OH initiating process suggesting the parallel process for the formation of $\cdot$OH is more favorable however it becomes the rate limiting step during the photocatalytic reaction in the presence of H$_2$O$_{ad}$. In the presence of H$_2$O$_{ad}$, during UV-irradiation, the buildup of photogenerated electrons prior to the acetone formation on Au/TiO$_2$ suggests that Au blocks the electron and hole recombination sites. Au and Pd on the TiO$_2$ surface promote the formation of $O_2^-$ from photogenerated electrons and are required for the formation of the $O_2^-$ reactive species in the absence of UV-irradiation. Lowering the coverage of H$_2$O$_{ad}$ shifts the reaction from $\cdot$OH initiating to $O_2^-$ initiating.

The reaction pathway during L-S photocatalytic dehydrogenation of 2-propanol was difficult to determine. The photo-reaction was strongly O$_2$ diffusion limited. The Au/TiO$_2$ catalyst exhibited a greater amount of photogenerated electrons evidenced by the larger broadband adsorption compared to the Pd/TiO$_2$ and Pd/Al$_2$O$_3$ catalysts. The Au/TiO$_2$ catalyst was active catalyst for 2-propanol dehydrogenation is in agreement with that of the G-S reaction study.

8.4 Future study

Future study is expected to focus upon the size of the alcohol additive for improving the adsorption capacity of TEPA. The use of 200 MW PEG may yet block a portion of the amine active sites, and thus a study on larger (500-600 MW PEG) and
smaller (< 200 MW PEG) molecules will help to elucidate any inhibiting adsorption effects PEG may have during the CO₂ and H₂S adsorption processes. A similar study may be performed on the 1,3-phenylenediamine sorbent for improving the adsorption capacity. The use of a lower MW PEG may facilitate higher adsorption capacities while maintaining its immobilizing properties.

Future study of the L-S photocatalytic process is expected to focus upon creating a thinner liquid layer upon the catalyst thin film to improve O₂ diffusion to the catalyst surface. The dehydrogenation process in the L-S reaction slower reaction is attributed to the diffusion limitation of O₂ to the catalyst surface. The activity of Au/TiO₂ is attributed to its unique capability for producing photogenerated electrons thus further improvement in the generation of electrons from the conduction band by doping the TiO₂ support with nitrogen would increase the dehydrogenation process. Nitrogen doping may be achieved through high temperature calcinations during ammonia adsorption.
APPENDICES
Nitrogen oxides are serious pollutants in the earth’s atmosphere and are toxic to the human body as well as harmful to the environment. The removal of NOx is one of the key research projects targeting the protection of our environment. Though NOx removal has been studied for many years (i.e. direct decomposition and selective catalytic reduction (SCR)) its removal remains complicated especially in the presence of oxygen. The presence of oxygen results in a series of fast competing reactions producing nitrogen dioxide or nitrous oxide species. This appendix has been organized in the following way. First, it is advantageous to look at the symmetry considerations involving the adsorbing nitrate and nitrite species to gain an understanding why in the literature only two vibrational modes are reported for each adsorbing nitrate species. Section A.1, titled “Symmetry Considerations of Adsorbed nitrates” helps to elucidate the number of infrared active modes of vibration during gaseous NO adsorption and subsequent formation of nitrate and nitrite species on the catalyst surface. The sections that follow are A.2 In Situ Infrared Study of NO Reduction over Pd/Al2O3 and Ag-Pd/Al2O3 Catalysts under H2-Rich and Lean-burn Conditions, section A.3 The Effect of O2 on the NO-CO reaction over Ag-Pd/Al2O3: an In Situ Infrared Study, and section A.4 Pulse Transient Responses of NO Decomposition and Reduction with H2 on Ag-Pd/Al2O3
A.1 Symmetry Considerations of Adsorbed nitrates

The symmetry and geometry of a molecule can be used to determine the number of fundamental frequencies, the degeneracy of the vibrations, and the selection rules for the allowed infrared and Raman spectra of a given molecule. The internal motions of a vibrating molecule are the result of a number of relatively simple vibratory motions known as the normal modes of vibration. Calculation of the number of fundamental normal mode vibrations is straightforward. The number of normal modes of vibration is calculated for nonlinear molecules $3N-6$ and for linear molecules $3N-5$ where $N$ is the number of atoms in the molecule.

The bridging nitrate molecule will be used to demonstrate how to determine the number of infrared active normal mode vibrations for adsorbed nitrate. The free nitrate molecule has $D_{3h}$ symmetry, but attaching two oxygen's (bridging bidentate nitrate) lowers the symmetry of nitrate to $C_{2v}$. In order to find out how many genuine normal modes of vibration occur in the infrared for an adsorbed nitrate or nitrite molecule we need to find each irreducible representation of the molecular symmetry group for the molecule in question. We begin by creating a displacement matrix for the model shown in Figure A.1(a). The dimensions of the displacement matrix is $3N = 12$, therefore each matrix representation will be a $12 \times 12$ matrix. Next we apply the operations of the symmetry group to the molecule to the set of Cartesian displacement vectors which represent the centers of the atoms in the adsorbed nitrate. The symmetry operations, including the matrix representation are shown in Figure A.2, A.3, and A.4. This gives directly the symmetry types of the genuine and non-genuine modes, infrared/Raman and translation/rotation respectively.
All of the properties of the group representations and their characters can be derived from these matrix representations using what is called the Great Orthogonality Theorem (GOT). The character $\chi(R)$ of each symmetry operation can be determined by summing the diagonal of each matrix shown in Figure A.2, A.3, and A.4. The process of finding the characters of the reducible representation is greatly simplified by recognizing that none of the vectors which are shifted to a different location by a symmetry operation makes any contribution to the value of the character of the matrix corresponding to this operation. The resulting characters for each symmetry operation are listed in Table A.1. Utilizing the GOT we can calculate the list of irreducible representations of the molecular symmetry group using the character of each symmetry operation shown in Equations (1)-(4).

\[
a_i = \frac{1}{4} \left(1(1)(1) + 1(1)(-2) + 1(1)(2) + 1(1)(4)\right) = 4
\]

\[
a_i = \frac{1}{4} \left(1(1)(1) 21(1)(-2) + 1(-1)(2) + 1(-1)(4)\right) = 1
\]

\[
a_i = \frac{1}{4} \left(1(1)(1) 21(-1)(-2) + 1(1)(2) + 1(-1)(4)\right) = 3
\]

\[
a_i = \frac{1}{4} \left(1(1)(1) 21(-1)(-2) + 1(-1)(2) + 1(1)(4)\right) = 4
\]

From the GOT we obtain a list of the irreducible representations of the molecular symmetry group shown in Equation (5).
Equation (5) lists the contributions from vibrational, translational and rotational motions of the bridging bidentate nitrate molecule. We are only interested in the normal modes of vibration, and by inspection of the $C_{2v}$ group table in Table A.1, the rotational contribution is $R_x = B_2$, $R_y = B_1$, and $R_z = A_1$, the translational contribution is $x = B_1$, $y = B_2$, and $z = A_1$. Therefore the irreducible representation can be reduced to Equation (6).

\[
\Gamma = 2A_1 + A_2 + B_1 + 2B_2
\]  

(6)

The number of normal mode vibrations that is possible for the bridging nitrate molecule is calculated to be $3N-6 = 6$ which agrees with Equation (6). The list of normal mode vibrations in Equation (6) contains both Raman and infrared contributions. By inspection of Table A.1 the Raman and infrared active vibrations can be separated into Equations (7) and (8) respectively.

Raman: \[ \Gamma = A_1 + A_2 + B_1 + B_2 \]  

(7)

Infrared: \[ \Gamma = A_1 + B_2 \]  

(8)
Equation (7) illustrates four vibrations are Raman active, while Equation (8) shows only two vibrations are infrared active. Thus, only two infrared vibrations are listed in the literature shown in Table A.2, A.3, A.4.

Figure A.1 Proposed models for adsorbed nitrate and nitrite (a) bridging bidentate nitrate (b) monodentate nitrate (c) bridging nitrite (d) chelating bidentate nitrate (e) free nitrate (f) monodentate nitrite (g) linear NO (h) linear nitrite (i) coordinated NO.
Figure A.2  The effect of $E$ operation on bridging nitrate molecule and its matrix representation.
Figure A.3  The effect of $C_2$ operation on bridging nitrate molecule and its matrix representation.
Figure A.4  The effect of $\sigma(xy)$ operation on bridging nitrate molecule and its matrix representation.

$$D(\sigma(xy)) = \begin{bmatrix}
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 
\end{bmatrix}$$
Table A.1  C2v group table with the character $\chi(R)$ for bridging nitrate molecule.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>E</th>
<th>C2</th>
<th>$\sigma(\sigma_{xy})$</th>
<th>$\sigma(\sigma_{yz})$</th>
<th>Infrared</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>z</td>
<td>$x^z$, $y^z$, $z^z$</td>
</tr>
<tr>
<td>A2</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$R_z$</td>
<td>xy</td>
</tr>
<tr>
<td>B1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$x$, $R_y$</td>
<td>xz</td>
</tr>
<tr>
<td>B2</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$y$, $R_x$</td>
<td>yz</td>
</tr>
<tr>
<td>$\chi(R)$</td>
<td>12</td>
<td>-2</td>
<td>2</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table A.2  IR band assignments (cm$^{-1}$) of adsorbed nitrite and nitrate species on metal oxides / γ-Al$_2$O$_3$ catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp. (K)</th>
<th>N=O</th>
<th>NO$_2$ as</th>
<th>N=O</th>
<th>NO$_2$ as</th>
<th>NO$_2$ sy</th>
<th>NO$_2$ sy</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Al$_2$O$_3$</td>
<td>300</td>
<td>1645</td>
<td>1580</td>
<td>1525</td>
<td>1764</td>
<td>1710</td>
<td></td>
<td>[1]</td>
</tr>
<tr>
<td>Ga$_2$O$_3$-Al$_2$O$_3$</td>
<td>573</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[2]</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>473</td>
<td></td>
<td></td>
<td></td>
<td>1586</td>
<td>1248</td>
<td>1234</td>
<td>[3]</td>
</tr>
<tr>
<td>Pt/BaO/Al$_2$O$_3$</td>
<td>373 to 673</td>
<td>1625</td>
<td>1265</td>
<td>1292</td>
<td>1397</td>
<td>1343</td>
<td>1464</td>
<td>1319</td>
</tr>
<tr>
<td>BaO/Al$_2$O$_3$</td>
<td>323</td>
<td></td>
<td></td>
<td></td>
<td>1579</td>
<td>1260</td>
<td>1429, 1429</td>
<td>[5]</td>
</tr>
<tr>
<td>Pt/Al$_2$O$_3$</td>
<td>523</td>
<td>1610</td>
<td>1210</td>
<td>1297</td>
<td>1550</td>
<td>1257</td>
<td>1380</td>
<td>[6]</td>
</tr>
<tr>
<td>Pd/Al$_2$O$_3$</td>
<td>473</td>
<td>1629</td>
<td>1562</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[7-8]</td>
</tr>
<tr>
<td>Th-Pt/Al$_2$O$_3$</td>
<td>303</td>
<td>1625</td>
<td></td>
<td>1558</td>
<td>1550</td>
<td></td>
<td></td>
<td>[9]</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>298</td>
<td>1610</td>
<td>1204</td>
<td>1364</td>
<td>1176</td>
<td>1520</td>
<td>1245</td>
<td>[10]</td>
</tr>
<tr>
<td>Pt/BaCO$_3$/Al$_2$O$_3$</td>
<td>523</td>
<td></td>
<td>1544</td>
<td>1436</td>
<td>1337</td>
<td></td>
<td></td>
<td>[11]</td>
</tr>
<tr>
<td>γ-Al$_2$O$_3$</td>
<td>296</td>
<td>1628</td>
<td>1264</td>
<td>1564</td>
<td>1302</td>
<td>1539</td>
<td>1327</td>
<td>[12]</td>
</tr>
</tbody>
</table>

Notes:

a  Reduced prior to adsorption study
b  Oxidized prior to adsorption study
Table A.3  IR band assignments (cm$^{-1}$) of adsorbed nitrite and nitrate species on metal oxides / $\gamma$-Al$_2$O$_3$ catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp (K)</th>
<th>N=O NO$_2$,as</th>
<th>N=O NO$_2$,as</th>
<th>NO$_2$,as NO$_2$,sy</th>
<th>NO$_2$,sy</th>
<th>NO$_2$,sy</th>
<th>NO$_2$,sy</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga$_2$O$_3$/Al$_2$O$_3$</td>
<td>623</td>
<td>1580</td>
<td>1240</td>
<td>1552</td>
<td>1294</td>
<td></td>
<td></td>
<td>[13]</td>
</tr>
<tr>
<td>La$_2$O$_3$/Al$_2$O$_3$</td>
<td>1617</td>
<td>1228</td>
<td>1558</td>
<td>1252</td>
<td>1508</td>
<td>1318</td>
<td>1950</td>
<td>1461</td>
</tr>
<tr>
<td>Ag/Al$_2$O$_3$</td>
<td>423</td>
<td>1615</td>
<td>1560</td>
<td>1250</td>
<td>1720</td>
<td>1980</td>
<td></td>
<td>1470</td>
</tr>
<tr>
<td>MnOx/Al$_2$O$_3$</td>
<td>323</td>
<td>1620</td>
<td>1220</td>
<td>1555</td>
<td>1290</td>
<td></td>
<td>1835</td>
<td>1415</td>
</tr>
<tr>
<td>Pt/Al$_2$O$_3$</td>
<td>298</td>
<td>1660</td>
<td>1250</td>
<td>1570</td>
<td>1290</td>
<td>1500</td>
<td>1400</td>
<td>[17]</td>
</tr>
<tr>
<td>SiO$_2$/Al$_2$O$_3$</td>
<td></td>
<td>1598</td>
<td>1589</td>
<td>1303</td>
<td>1550</td>
<td>1249</td>
<td></td>
<td>[18]</td>
</tr>
<tr>
<td>Pt or Pd/Al$_2$O$_3$</td>
<td></td>
<td>1620</td>
<td>2298</td>
<td>1592</td>
<td>1294</td>
<td></td>
<td>1365</td>
<td>[19]</td>
</tr>
<tr>
<td>BaO/Al$_2$O$_3$</td>
<td>300</td>
<td>1620</td>
<td>1250</td>
<td>1570</td>
<td>1300</td>
<td></td>
<td>1425</td>
<td>[20]</td>
</tr>
<tr>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>298</td>
<td>1610</td>
<td>1296</td>
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<td></td>
<td>1465</td>
<td>[21-22]</td>
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<td>$\gamma$-Al$_2$O$_3$</td>
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<td>1625</td>
<td>1587</td>
<td>1565</td>
<td></td>
<td>1313</td>
<td>1230</td>
<td>[23]</td>
</tr>
</tbody>
</table>

Notes:

a  Reduced prior to adsorption study
b  Oxidized prior to adsorption study
Table A.4  IR band assignments (cm⁻¹) of adsorbed nitrite and nitrate species on metal oxides / $\gamma$-Al₂O₃ catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp. (K)</th>
<th>N=O</th>
<th>NO₂,as</th>
<th>N=O</th>
<th>NO₂,as</th>
<th>NO₂,sy</th>
<th>NO₂,sy</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>298</td>
<td>1652</td>
<td>1261</td>
<td>1565</td>
<td></td>
<td>1461</td>
<td>1318</td>
<td>[24]</td>
</tr>
<tr>
<td>Ag-Pd/Al₂O₃</td>
<td></td>
<td>1614</td>
<td>1579</td>
<td>1300</td>
<td>1550</td>
<td>1248</td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>BaO/Al₂O₃</td>
<td>90</td>
<td></td>
<td>1440</td>
<td>1340</td>
<td></td>
<td></td>
<td>1225</td>
<td>[5, 26-27]</td>
</tr>
<tr>
<td>KBr-Ag/Al₂O₃</td>
<td>473</td>
<td>1614</td>
<td>1585</td>
<td>1304</td>
<td>1556</td>
<td></td>
<td></td>
<td>[28]</td>
</tr>
<tr>
<td>Ag/Al₂O₃</td>
<td>473</td>
<td>1612</td>
<td>1583</td>
<td>1302</td>
<td>1560</td>
<td>1250</td>
<td></td>
<td>[29]</td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>298</td>
<td>1630</td>
<td>1592</td>
<td>1552</td>
<td></td>
<td>1477</td>
<td>1340</td>
<td>1230 [30]</td>
</tr>
</tbody>
</table>

Notes:

a  Reduced prior to adsorption study
b  Oxidized prior to adsorption study
A.2 In Situ Infrared Study of NO Reduction over Pd/Al₂O₃ and Ag-Pd/Al₂O₃ Catalysts under H₂-Rich and Lean-burn Conditions.

Catalytic reduction of NO under H₂-rich and lean-burn conditions over Pd/Al₂O₃ and Ag-Pd/Al₂O₃ has been studied by temperature programmed reaction (TPR) coupled with in situ infrared (IR) and mass spectrometry (MS) techniques. Under H₂-rich conditions, Pd/Al₂O₃ produces, Pd-NCO, Pd-NO⁺, Pd⁰-NO, and adsorbed nitrate at temperatures below 398 K; N₂ and adsorbed NH₃ are produced at temperatures above 400 K. Addition of Ag to Pd/Al₂O₃ suppresses the Pd-NO⁺ formation and lowers the formation temperature of NH₃ species to 373 K. Under lean-burn conditions, Pd/Al₂O₃ produces Pd-NCO, Pd-NO⁺, Pd⁰-NO, and adsorbed nitrate at temperatures below 373 K, while the addition of Ag suppresses the Pd-NCO and Pd-NO⁺ formation, and enhances the Pd⁰-NO formation. Infrared results reveal that oxygen under lean-burn conditions does not oxidize Pd⁰ sites to Pd⁺ on the Ag-Pd/Al₂O₃ catalyst. Addition of Ag enhances NO₂ formation and shifts the N₂ formation to lower temperatures, suggesting that NO₂ is effectively reduced to N₂.

A.2.1 Introduction

Lean burn and diesel engines provide the advantages of low hydrocarbon emissions and high fuel efficiency, but present a challenge in control of NO + NO₂ (NOₓ) emission. The catalytic technologies for the removal of NOₓ under lean-burn conditions includes (i) selective catalytic reduction (SCR) by NH₃ or urea [31-35], (ii) SCR with hydrocarbon and hydrogen reductant [36-39], and (iii) direct decomposition of NO [9,
Hydrogen has been suggested to be a promising agent for reducing NO\textsubscript{x} to N\textsubscript{2} under lean burn conditions in the 400 – 500 K temperature region \[43-45\]. Under practical conditions (H\textsubscript{2}:CO ratio of 1:3) the use of H\textsubscript{2} as a reductant provides the advantage of high activity and N\textsubscript{2} selectivity in the NO/CO/O\textsubscript{2} reaction \[46\]. Pd/Al\textsubscript{2}O\textsubscript{3} catalysts with V\textsubscript{2}O\textsubscript{5} and TiO\textsubscript{2} additives have been shown to increase the activity for NO reduction and N\textsubscript{2} yield \[45-46\]. However, the lack of understanding of the specific role of each component makes the preparation of highly active and selective catalyst very empirical.

The objective of this study is to investigate (i) the role of Ag as a promoter and (ii) the nature of adsorbed species on Pd/Al\textsubscript{2}O\textsubscript{3} and Ag-Pd/Al\textsubscript{2}O\textsubscript{3} under hydrogen-rich and lean-burn conditions using in situ infrared coupled with mass spectrometry. Ag is used for its high oxidation activity \[47\] and its role in breaking up the ensemble surface of Pd on supported Pd catalysts \[48\]. The nature of adsorbed species on Pd/Al\textsubscript{2}O\textsubscript{3} and Ag-Pd/Al\textsubscript{2}O\textsubscript{3} determined by in situ IR as well as the activity and selectivity results obtained from MS provide the basis for elucidation of the reaction pathway and the role of Ag in specific reaction steps.

A.2.2 Experimental

The experimental section describes the preparation of Pd/Al\textsubscript{2}O\textsubscript{3} and Ag-Pd/Al\textsubscript{2}O\textsubscript{3}, reactor setup and data analysis method used during this study.
A.2.2.1. Catalyst preparation

The 5 wt% Pd/Al₂O₃ catalyst was prepared by incipient wetness impregnation of Pd(NO₃)₂·H₂O (Aldrich) solution on α-Al₂O₃ (Aldrich). The 5% Ag-5% Pd/Al₂O₃ catalyst is prepared by incipient wetness co-impregnation of Pd(NO₃)₂·H₂O (Aldrich) and Ag(NO₃) (Aldrich) solution onto α-Al₂O₃ (Aldrich). After impregnation, each catalyst was filtered and rinsed with deionized water. The Pd/Al₂O₃ and Ag-Pd/Al₂O₃ catalysts were then dried and calcined at 773 K in air at a heating rate of 10 K/min. The catalysts were characterized by X-ray Diffraction (XRD) Philips Analytical X-Ray PW1710 diffractometer using Cu Kα radiation operating at 40 kV and 35 mA.

A.2.2.2. Reaction Studies

Figure A.5 shows the experimental apparatus, which consists of (i) a gas flow section with mass flow controllers (Brooks Instrument 5850), (ii) a Diffuse Reflectance Infrared Fourier Transfer Spectroscopy (DRIFTS, Harrick Scientific) cell placed inside a FTS-4000 Fourier transform infrared spectrometer (FTIR, Varian Inc.), and (iii) a Omnistar™ quadrupole mass spectrometer (MS, Pfeiffer). The catalyst (150 mg) was placed inside the DRIFTS cell with an IR path length of 1.5 cm and reduced under 5% H₂ in helium balance while heating at a rate of 10 K/min from 298 to 723 K. After maintaining the temperature at 723 K for 30 min, 100% He was sent to the reactor and the background IR spectra were collected while cooling the catalyst from 723 to 298 K. The H₂-rich mixture was prepared by flowing [NO/H₂/CO/O₂/He] (1/6/2/2/59.7 cm³/min), and the lean-burn mixture was prepared by flowing [NO/H₂/CO/O₂/He] (1/2/0.5/10/57.2 cm³/min) to give a GHSV of 107,156 hr⁻¹ at a total flow rate of 70.7
cm³/min. The temperature-programmed reaction (TPR) was carried out by flowing either the H₂-rich mixture or lean-burn mixture over the catalysts at a heating rate of 10 K/min from 298 to 723 K while collecting the IR spectra every 10 K. The infrared absorbance spectrum was obtained by taking the logarithmic ratio of the single beam spectrum of the catalyst with flowing reactants to the background spectrum free of the reactants. The reactor effluent was analyzed by MS. FTIR along with gas chromatograph (SRI Instruments Inc. 8610C) equipped with a TCD detector were utilized to cross check the MS concentration profiles developed from the Data Analysis of the MS data.

Figure A.5 Experimental apparatus.
A.2.2.3. Data Analysis

The effluent of the DRIFTS cell contains nitrogen dioxide (NO\(_2\)), nitrogen (N\(_2\)), carbon dioxide (CO\(_2\)), and unreacted NO and CO. Overlapping MS fragmentation patterns present a problem in determining the composition of N\(_2\), CO, CO\(_2\), and N\(_2\)O in the reactor effluent. To separate the overlapping signals, a matrix inversion technique was used to derive the MS intensities that correspond to known concentrations of each gaseous species.

The MS measures the total intensity derived from the contributions of all gaseous species in the reaction. The total intensity measured at each mass number (amu) is a linear combination of all the contributions from different compounds (\(I_{amu}^X\)) multiplied by a constant (\(\alpha_{amu}^X\)), plus the background intensity shown in Eq. (1).

\[
I_{amu}^{total} = \sum_{1}^{n} \alpha_{amu}^X \cdot I_{amu}^X + I_{amu}^{background}
\]  

For each gaseous species X, the \(\alpha_{amu}^X\) values are determined from separate calibration experiments. Calibration of the MS and DRIFTS (loaded with KBr) was carried out by switching the flow between different concentrations of the pure gaseous species. It is assumed that the \(\alpha_{amu}^X\) values for a species X are constant in a given experiment. The \(\alpha_{amu}^X\) values are calculated by normalizing the fragment intensities for each species with respect to the most abundant MS fragment (the base peak assigned a relative intensity value of 100), shown in Eq. (2).
Expanding the total mass balance, shown in Eq. (1), the individual contributions of each overlapping species can be written in Eqs. (3) – (8). The resulting six linearly dependent equations are then arranged into a 6 X 6 matrix shown in Eq. (9).

\[ \alpha_{amu}^X = \frac{I_{amu}^X}{I_{amu}^{100}} \] (2)

\[ I_{14}^{total} = 0 \cdot I_{28}^{CO} + 0 \cdot I_{44}^{CO_2} + \alpha_{14}^{N_2} \cdot I_{28}^{N_2} + \alpha_{14}^{N_4O} \cdot I_{44}^{N_4O} + \alpha_{14}^{NO} \cdot I_{30}^{NO} + \alpha_{14}^{NO_2} \cdot I_{46}^{NO_2} \] (3)

\[ I_{16}^{total} = \alpha_{16}^{CO} \cdot I_{28}^{CO} + \alpha_{16}^{CO_2} \cdot I_{44}^{CO_2} + 0 \cdot I_{28}^{N_2} + \alpha_{16}^{N_4O} \cdot I_{44}^{N_4O} + \alpha_{16}^{NO} \cdot I_{30}^{NO} + \alpha_{16}^{NO_2} \cdot I_{46}^{NO_2} \] (4)

\[ I_{28}^{total} = \alpha_{28}^{CO} \cdot I_{28}^{CO} + \alpha_{28}^{CO_2} \cdot I_{44}^{CO_2} + \alpha_{28}^{N_2} \cdot I_{28}^{N_2} + \alpha_{28}^{N_4O} \cdot I_{44}^{N_4O} + 0 \cdot I_{30}^{NO} + 0 \cdot I_{46}^{NO_2} \] (5)

\[ I_{30}^{total} = 0 \cdot I_{28}^{CO} + 0 \cdot I_{44}^{CO_2} + 0 \cdot I_{28}^{N_2} + \alpha_{30}^{N_4O} \cdot I_{44}^{N_4O} + \alpha_{30}^{NO} \cdot I_{30}^{NO} + \alpha_{30}^{NO_2} \cdot I_{46}^{NO_2} \] (6)

\[ I_{44}^{total} = 0 \cdot I_{28}^{CO} + \alpha_{44}^{CO_2} \cdot I_{44}^{CO_2} + 0 \cdot I_{28}^{N_2} + \alpha_{44}^{N_4O} \cdot I_{44}^{N_4O} + 0 \cdot I_{30}^{NO} + 0 \cdot I_{46}^{NO_2} \] (7)

\[ I_{46}^{total} = 0 \cdot I_{28}^{CO} + 0 \cdot I_{44}^{CO_2} + 0 \cdot I_{28}^{N_2} + 0 \cdot I_{44}^{N_4O} + 0 \cdot I_{30}^{NO} + \alpha_{46}^{NO_2} \cdot I_{46}^{NO_2} \] (8)
The MS intensities for the individual species were determined using matrix multiplication and inversion functions. This approach allows separation of the MS intensities for N₂, N₂O, NO₂, NO, CO, and CO₂ concentration profiles for each reactant and product in the rich and lean-burn experiments. The MS concentration profiles of N₂O, NO₂, NO, CO, CO₂, and N₂ were cross checked with FTIR and GC calibration experiments.

A.2.3. Results

The XRD characterization and temperature programmed reaction under H₂-rich and lean-burn conditions are reported in the following sections.

A.2.3.1. XRD Characterization

Figure A.6 shows the XRD patterns for Pd/Al₂O₃ and Ag-Pd/Al₂O₃ catalysts. The XRD peaks for Pd(111) at 40.4°, Pd(200) at 46.4°, Ag-Pd at 38.9° and 45.1° were observed on these catalysts. The presence of Ag-Pd peaks indicate the existence of an Ag-Pd alloy phase [49] and may explain the absence of the Pd peaks on the Ag-Pd/Al₂O₃ catalyst. The XRD reflections at 35.1°, 43.3°, 52.5°, 57.4° are for α-Al₂O₃ and agree with
those in the literature [50-52]. An average Pd particle size of 6 nm for Pd/Al₂O₃ was calculated using the Scherer equation from line broadening [53].

A.2.3.2. TPR under H₂-rich conditions

The temperature programmed reaction under a hydrogen rich atmosphere is studied over Pd/Al₂O₃ and Ag-Pd/Al₂O₃ catalysts and reported in the following sections.

A.2.3.2.1 Pd/Al₂O₃

Figures A.7 and A.8 show the infrared spectra of gas phase and adsorbed species, the MS concentration profile, and the IR intensity during the H₂-rich TPR over Pd/Al₂O₃. Flowing the H₂-rich reactant mixture over the catalyst at 298 K produced (i) an intense Pd-NCO band at 2176 cm⁻¹ [54], (ii) a Pd-NO⁺ at 1828 cm⁻¹, (iii) a linear NO (Pd⁰-NO) at 1746 cm⁻¹ [55-56], (iv) a chelating nitro at 1282 cm⁻¹, a chelating bidentate nitrate at 1527 cm⁻¹, and a nitrate at 1330 cm⁻¹ on the Al₂O₃ surface [36], and (v) gaseous CO₂ at 2350 cm⁻¹ and NO₂ at 1633 cm⁻¹. Assignment of adsorbed species on Pd and Al₂O₃ is consistent with those reported in the literature [7-8]. NO₂ could be produced from the gas phase reaction of NO with O₂ in the H₂-rich mixture. The absence of this reaction was verified by passing the H₂-rich reactant mixture over the blank IR cell.
Figure A.6 XRD of Pd/Al₂O₃ and Ag-Pd/Al₂O₃ pretreated by reduction at 673 K.
Figure A.7  IR spectra of adsorbed species and gaseous reactants/products during TPR over Pd/Al₂O₃ catalyst under H₂-rich condition.
Figure A.8  Concentration profiles of reactants and products during TPR over Pd/Al₂O₃ catalyst under H₂-rich condition.

Chelating bidentate nitrate at 1527 cm⁻¹, produced from adsorption of NO₂/O₂ on Al₂O₃, was the most prominent IR band at 298 K [36]. A significant decrease in the intensity of nitrate and nitro species occurred around 398 K where a sharp increase in the concentration of adsorbed NH₃ at 3221, 1633, 1446, and 1218 cm⁻¹ took place. At temperatures above 400 K, adsorbed NH₃ is the dominant surface species while gaseous CO₂ and N₂ are the major products. The N₂ formation profile in Figure A.8 showed a
maxima at 470 K where NO conversion approached 16.4% (see Table A.5) and adsorbed NH₃ remained a dominant surface species, suggesting that N₂ formed at this temperature is a result of the NOₓ reaction with NH₃. As the temperature increased to 500 K, the N₂ profile reached a minimum, indicating the temperature dependence of NOₓ SCR with NH₃. The pronounced decrease in the N₂ formation suggests that adsorbed NH₃ was oxidized rather than involved in NO reduction lowering its availability for reducing NOx to N₂ in this temperature range.

A.2.3.2.2 Ag-Pd/Al₂O₃

Figures A.9 and A.10 show the infrared spectra of gas phase and adsorbed species, the MS concentration profile, and the IR intensity during the H₂-rich TPR over Ag-Pd/Al₂O₃. Comparison of IR spectra of adsorbed species at 298 K on Ag-Pd/Al₂O₃ in Figure A.9 and on Pd/Al₂O₃ in Figure A.7 shows that the addition of Ag to Pd suppresses the formation of Pd⁰-NO at 1746 cm⁻¹ as well as Pd-NO⁺ at 1828 cm⁻¹. MS analysis of gaseous products in Figure A.10 shows that the rate of NO₂ formation over Ag-Pd is significantly higher than that of NO₂ over Pd in Figure A.8. The effect of Ag on the reaction under H₂-rich condition can be further discerned by careful comparison of the MS profiles in Figs. 4 and 6.

While both Ag-Pd/Al₂O₃ and Pd/Al₂O₃ catalysts show a similar light-off behavior for CO oxidation, both catalysts exhibit a different behavior in NO reduction after light-off. The addition of Ag causes the following (i) an increase in N₂ selectivity between 450 and 700 K, (ii) a decrease in the N₂O selectivity, and (iii) an increase in the H₂ conversion after CO₂ light-off.
Table A.5  Conversion and selectivity summary for Pd/Al₂O₃ and Ag-Pd/Al₂O₃ catalysts under rich and lean-burn conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant Ratio w.r.t. NO</th>
<th>Temp. (K)</th>
<th>( S_{N_2}^a )</th>
<th>( S'_{N_2}^b )</th>
<th>( X_{\text{NOx}}^c )</th>
<th>( X_{\text{CO}} )</th>
<th>( X_{\text{H}_2} )</th>
<th>( r_{N_2} ) (mol hr⁻¹ g⁻¹)</th>
<th>GHSV (hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂-Rich</td>
<td></td>
<td>373</td>
<td>1.2</td>
<td>0.5</td>
<td>4.1</td>
<td>15.0</td>
<td>1.3</td>
<td>4.0 x 10⁻⁶</td>
<td>107156</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>1 2 2 6</td>
<td>423</td>
<td>82.7</td>
<td>67.5</td>
<td>12.9</td>
<td>43.8</td>
<td>3.7</td>
<td>8.8 x 10⁴</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>473</td>
<td>71.3</td>
<td>60.7</td>
<td>16.8</td>
<td>62.5</td>
<td>6.1</td>
<td>9.9 x 10⁴</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>523</td>
<td>45.4</td>
<td>36.3</td>
<td>9.8</td>
<td>70.0</td>
<td>6.4</td>
<td>3.6 x 10⁴</td>
<td></td>
</tr>
<tr>
<td>Ag-Pd/Al₂O₃</td>
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<td>89.0</td>
<td>43.9</td>
<td>14.4</td>
<td>25.0</td>
<td>6.4</td>
<td>1.0 x 10⁻³</td>
<td>107156</td>
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<tr>
<td>Pd/Al₂O₃</td>
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<td>423</td>
<td>85.3</td>
<td>73.9</td>
<td>16.5</td>
<td>25.0</td>
<td>12.7</td>
<td>1.2 x 10⁻³</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>473</td>
<td>85.8</td>
<td>82.4</td>
<td>36.9</td>
<td>75.0</td>
<td>14.6</td>
<td>2.6 x 10⁻³</td>
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</tr>
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<td></td>
<td></td>
<td>523</td>
<td>88.4</td>
<td>88.3</td>
<td>44.2</td>
<td>75.0</td>
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</tr>
<tr>
<td>Lean-burn</td>
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<td>4.0 x 10⁻⁶</td>
<td>107156</td>
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<tr>
<td>Pd/Al₂O₃</td>
<td>1 0.5 10 2</td>
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</tr>
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<td>5.1</td>
<td>100.0</td>
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<td>1.7 x 10⁻⁴</td>
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</tr>
<tr>
<td></td>
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<td>100.0</td>
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<tr>
<td>Ag-Pd/Al₂O₃</td>
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<td>98.3</td>
<td>3.6</td>
<td>2.3</td>
<td>36.4</td>
<td>4.6</td>
<td>2.3 x 10⁻⁴</td>
<td>107156</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
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<td>423</td>
<td>99.0</td>
<td>7.1</td>
<td>5.6</td>
<td>51.1</td>
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<td>4.1 x 10⁻⁴</td>
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<tr>
<td></td>
<td></td>
<td>473</td>
<td>99.3</td>
<td>10.4</td>
<td>7.1</td>
<td>75.5</td>
<td>13.7</td>
<td>5.8 x 10⁻⁴</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>523</td>
<td>99.6</td>
<td>23.4</td>
<td>15.5</td>
<td>100.0</td>
<td>25.3</td>
<td>1.1 x 10⁻³</td>
<td></td>
</tr>
</tbody>
</table>

a  Calculating \( S_{N_2} \) selectivity: 
\[
S_{N_2} = \frac{[N_2]}{[N_2] + [N_2O]} \times 100
\]

b  Calculating \( S'_{N_2} \) Selectivity 
\[
S'_{N_2} = \frac{[N_2]}{[N_2] + [N_2O] + [NO_2]} \times 100
\]

c  Calculating NOx conversion: 
\[
x_{\text{NOx}} = 1 - \frac{[NO_2] + [NO]}{[NO_2]_{in} + [NO]_{in}}
\]
Figure A.9  IR spectra of adsorbed species and gaseous reactants/products during TPR over Ag-Pd/Al₂O₃ catalyst under H₂-rich condition.
Figure A.10  Concentration profiles of reactants and products during TPR over Ag-Pd/Al$_2$O$_3$ catalyst under H$_2$-rich condition.
A.2.3.3 TPR under lean-burn Conditions

The temperature programmed reaction under a lean-burn atmosphere is studied over Pd/Al₂O₃ and Ag-Pd/Al₂O₃ catalysts are reported in the following sections.

A.2.3.3.1 Pd/Al₂O₃

Figures A.11 and A.12 show the infrared spectra of gas phase and adsorbed species, the MS concentration profile, and the IR intensity during the lean-burn TPR over Pd/Al₂O₃. At 298 K, the adsorbed species observed resemble those in Figure A.7. Surprisingly, lean-burn conditions, which are characterized by an excess of O₂ in the reactant stream, produced a higher intensity Pd⁰-NO than that in the case of H₂-rich conditions shown in Figure A.7. The high intensity of Pd⁰-NO prior to light-off in Figure A.11 suggests that (i) the rate of its conversion to other species is lower under lean-burn than that under H₂-rich and (ii) the Pd surface remains in the reduced state under lean-burn condition.

The CO light-off occurred at 335 K where Pd⁰-NO was observed as shown in Figure A.12, suggesting that CO oxidation occurred on Pd⁰ site under the lean-burn condition. Emergence of N₂ at 475 K with a sharp decrease in NO₂ formation and absence of adsorbed NH₃ in Figure A.11 suggests that the pathway for reduction of NO₂ to N₂ under lean-burn condition differs from that under H₂-rich condition.
Figure A.11  IR spectra of adsorbed species and gaseous reactants/products during TPR over Pd/Al₂O₃ catalyst under lean-burn condition.
Figure A.12  Concentration profiles of reactants and products during TPR over Pd/Al₂O₃ catalyst under lean-burn condition.
A.2.3.3.2 Ag-Pd/Al₂O₃

Figures A.13 and A.14 show the infrared spectra of gas phase and adsorbed species, the MS concentration profile, and the IR intensity during the lean-burn TPR over on Ag-Pd/Al₂O₃. The dominant species observed on the catalyst surface was Pd⁰-NO at 1746 cm⁻¹. The assignment of 1746 cm⁻¹ band to N₂O₄ [57] may be ruled by its third intense 1520 cm⁻¹ band was not observed and this species can only be formed at low temperatures [58]. Flowing 100% He over the Pd/Al₂O₃ catalyst did not remove adsorbed Pd⁰-NO and chelating bidentate nitrate from the catalyst surface. Interestingly, Ag inhibited the formation of Pd-NO⁺ species that was observed on Pd/Al₂O₃, indicating that Ag kept the Pd surface in the reduced state. Both lean-burn and H₂-rich conditions show that Ag promoted the reaction of NO with O₂ to produce NO₂ at 298 K. Figure A.14 shows the CO light-off occurred on Ag-Pd/Al₂O₃ at 370 K, which was in the same range as Pd/Al₂O₃ except that the light-off curve is more gradual on Ag-Pd/Al₂O₃ than on Pd/Al₂O₃. A similar gradual trend is observed for the H₂ light-off shown in Figure A.14.

Table A.5 lists the N₂ selectivity and NOₓ conversion on Pd and Ag-Pd at 373, 423, 473, and 523 K. The N₂ selectivity was calculated by two methods using (i) N₂ and N₂O and (ii) N₂, N₂O, and NO₂ as a basis. N₂ selectivity has been calculated in the literature on the basis of N₂ and N₂O products excluding NO₂, shown in Table A.6 [43, 45-46]. Although the concentration of NO used in this study (Table A.5) is significantly higher than those reported in Table A.6, the NOₓ conversions obtained from this study generally fall in the same range as those in literature. [43-46, 59-60]
Table A.6  Literature review of conversion and selectivity data for Pd catalysts under lean-burn conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NO</th>
<th>O₂</th>
<th>CO</th>
<th>O₂/H₂/HC</th>
<th>GHSV (hr⁻¹)</th>
<th>Refs</th>
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</thead>
<tbody>
<tr>
<td>0.5 wt% Pd/Al₂O₃</td>
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<td>1</td>
<td>0</td>
<td>1</td>
<td>100</td>
<td>45, 59</td>
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<tr>
<td>1.5 wt% Pd/Al₂O₃</td>
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<td>2.5</td>
<td>7.5</td>
<td>0.5</td>
<td>100</td>
<td>42.8</td>
</tr>
<tr>
<td>2.5 wt% Pd/Al₂O₃</td>
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<td>1</td>
<td>100</td>
<td>60</td>
<td>7.5</td>
<td>45.4</td>
</tr>
<tr>
<td>3.0 wt% Pd/Al₂O₃</td>
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<td>0.5</td>
<td>5</td>
<td>30</td>
<td>476190</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
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<td>1</td>
<td>100</td>
<td>7</td>
<td>7.5</td>
<td>476190</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
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<td>1</td>
<td>100</td>
<td>7</td>
<td>8</td>
<td>476190</td>
</tr>
<tr>
<td>Pd/Al₂O₃/Al₂O₃</td>
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<td>1</td>
<td>100</td>
<td>7</td>
<td>8</td>
<td>476190</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
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<td>100</td>
<td>7</td>
<td>8</td>
<td>476190</td>
</tr>
<tr>
<td>CuO/Al₂O₃</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>60</td>
<td>2</td>
<td>25.9</td>
</tr>
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<td>25.9</td>
</tr>
<tr>
<td>CuO/Al₂O₃</td>
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<td>1</td>
<td>0</td>
<td>83.3</td>
<td>2</td>
<td>25.9</td>
</tr>
<tr>
<td>CuO/Al₂O₃</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>83.3</td>
<td>2</td>
<td>25.9</td>
</tr>
<tr>
<td>CuO/Al₂O₃</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>2.5</td>
<td>0</td>
<td>25.9</td>
</tr>
</tbody>
</table>

Xₙₗₙₜ

<table>
<thead>
<tr>
<th>Reactant Ratio w.r.t. NO</th>
<th>373</th>
<th>423</th>
<th>473</th>
<th>523</th>
<th>583</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xₙₗₙₜ</td>
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<td>1.5</td>
<td>2.5</td>
<td>3.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

GHSV (hr⁻¹)
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant Ratio w.r.t. NO</th>
<th>$X_{NOx}$</th>
<th>GHSV (hr$^{-1}$)</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NO  CO  O$_2$  H$_2$/HC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag/Al$_2$O$_3$</td>
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<td>0  0  0  2</td>
<td>285840</td>
<td>[63]</td>
</tr>
<tr>
<td>BaO/Al$_2$O$_3$</td>
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<td>25  32  47  68</td>
<td>31400</td>
<td>[64]</td>
</tr>
<tr>
<td>Ag/Al$_2$O$_3$</td>
<td>1  0  100  5</td>
<td>13  86  88</td>
<td>75000</td>
<td>[65]</td>
</tr>
<tr>
<td>Ag/Al$_2$O$_3$</td>
<td>1  0  100  1</td>
<td>17  30</td>
<td>30000</td>
<td>[66]</td>
</tr>
</tbody>
</table>
Figure A.13  IR spectra of adsorbed species and gaseous reactants/products during TPR over Ag-Pd/Al₂O₃ catalyst under lean-burn condition.
Figure A.14 Concentration profiles of reactants and products during TPR over Ag-Pd/Al₂O₃ catalyst under lean-burn condition.
A.2.4 Discussion

Control of NO\textsubscript{x} emissions from lean-burn and diesel engines requires an effective catalyst for selective reduction of NO and NO\textsubscript{2} to N\textsubscript{2} in the presence of excess oxygen and other potential poisons in the 298 – 673 K temperature range for cold start and normal operating conditions [67]. An effective catalyst must possess the activity for N-O bond scission, selective removal of adsorbed oxygen from dissociated NO, and N-N bond formation. The nature of adsorbed species and active sites for these bond formation and scission steps may be unraveled from the analysis of the gaseous products produced and IR spectra of adsorbed species observed during the temperature-programmed reaction.

NO can adsorb on reduced Pd\textsuperscript{0} as linear NO (Pd\textsuperscript{0}\textendash NO) and on oxidized Pd\textsuperscript{+} as Pd\textendash NO\textsuperscript{+} exhibiting IR bands at 1746 cm\textsuperscript{-1} and 1828 cm\textsuperscript{-1}, respectively [7-8]. CO adsorbs on Pd\textsuperscript{0} as linear CO (Pd\textsuperscript{0}\textendash CO) at 2065 cm\textsuperscript{-1} [7-8, 68]. Oxidation of Pd\textsuperscript{0} to Pd\textsuperscript{+} shifts the linear CO to 2120 cm\textsuperscript{-1}; oxidation of Pd\textsuperscript{+} to Pd\textsuperscript{2+} further shifts linear CO to 2156 cm\textsuperscript{-1} [69]. The observation of the prominent Pd\textsuperscript{0}\textendash NO at 1746 cm\textsuperscript{-1} during the reaction indicates (i) the presence of Pd\textsuperscript{0} sites and (ii) the initial rate of Pd\textsuperscript{0}\textendash NO formation was greater than its disappearance rate. The lack of variation of Pd\textsuperscript{0}\textendash NO wavenumber with its intensity in Figs. 3, 5, 7, and 9 indicates that there is no dipole-dipole coupling between neighboring Pd\textsuperscript{0}\textendash NO. Adsorbed Pd\textsuperscript{0}\textendash NO may be surrounded by other species such as adsorbed oxygen, hydrogen, and NO\textsubscript{2}.

The absence of adsorbed CO at 298 K suggests that the majority of the Pd surface possesses the characteristic of a Pd(111) surface, which adsorbs significantly more Pd\textsuperscript{0}\textendash NO at 1735-1745 cm\textsuperscript{-1} [56, 70] than Pd\textsuperscript{0}\textendash CO and bridged CO. This is indeed not surprising for the 5 wt% Pd/Al\textsubscript{2}O\textsubscript{3} since the size of its Pd particle is about 6 nm and the
Pd(111) is the dominant surface structure of Pd/Al₂O₃ as shown in Figure A.6. The observation of Pd⁰–NO on Ag-Pd/Al₂O₃ in Figures A.9 and A.10 also indicates that the majority of the Pd surface remains in the reduced Pd(111) form even when the surface is decorated with Ag atoms and is exposed to excess oxygen under lean-burn conditions. The unique characteristic of Pd remaining in the reduced state could be related to a weak Pd-Al bonding and fewer PdO formation on α-alumina [71], which was confirmed by the absence of PdO in the XRD results shown in Figure A.6.

Reduced Pd surface can adsorb oxygen on the metal surface as atomic oxygen (Pd⁰-O). Although Pd⁰-O cannot be observed by infrared spectroscopy, the CO oxidation light-off on Pd/Al₂O₃ and on Ag-Pd/Al₂O₃ under lean-burn and H₂-rich conditions, provides indirect evidence of the presence of Pd⁰-O. Adsorbed oxygen on the metal surface (M-O) has been observed to participate in the CO₂ formation where the reaction rate is proportional to the concentration of adsorbed oxygen [72]. It has been reported that H₂O participates in CO₂ formation by the low-temperature gas-water-shift (WGS) reaction in the 463 – 513 K region [73]. However, the low activity for CO oxidation in the WGS reaction [74] and the low CO light-off temperature in the present study suggest that CO oxidation depends on the concentration of adsorbed oxygen, CO, NO, and NO₂ as well as the surface state of Pd. Thus, lean-burn conditions are expected to lower the light-off temperature for CO₂ formation compared to that of hydrogen-rich conditions due to abundance of Pd⁰-O. In contrast to CO oxidation, NO oxidation occurs readily at room temperature as shown by significant formation of NO₂ in Figs. 3 to 10, which decreased with temperature due to its low thermodynamic equilibrium constants at high temperatures [75].
In addition to oxidation of CO to CO$_2$ and oxidation of NO to NO$_2$, Pd$^0$-O could play a role in controlling the concentration of Pd$^0$-NO at 1746 cm$^{-1}$. Mechanistic studies of the NO-CO reaction have shown that the concentration of Pd$^0$-NO at 1746 cm$^{-1}$ was increased during the O$_2$ addition to NO-CO reaction [7-8]. The IR intensity for Pd$^0$-NO is expected to depend on the rate of NO bond scission and the removal of oxygen from the NO dissociation sites. Thus, the observed high concentration (i.e. intensity) of Pd$^0$-NO under lean-burn condition can be attributed to slowing down the N-O band scission by high concentration of adsorbed oxygen, which is resulted from excess gaseous oxygen molecules.

The observed high concentration of Pd$^0$-NO on Ag-Pd/Al$_2$O$_3$ compared to that on Pd/Al$_2$O$_3$ (Figs. 3, 5; 7 and 9) can also be attributed to Ag inhibition effect on the N-O bond scission. Since Ag does not modify NO adsorption sites, the Ag-inhibiting effect could be related to its activity to activate adsorbed oxygen, increasing the concentration of adsorbed oxygen on the catalyst surface. Inhibiting NO dissociation by Ag and adsorbed O$_2$ is also manifested by the low intensity of Pd-NCO at 2176 cm$^{-1}$ that produced from the reaction of adsorbed N and adsorbed CO, under lean-burn conditions on Ag-Pd/Al$_2$O$_3$ catalyst.

The possible pathways for N$_2$ formation include (i) recombination of adsorbed atomic N and atomic N from dissociated NO, (ii) hydrolysis of NCO, and (iii) reaction of adsorbed NH$_3$ with adsorbed NO$_2$ [43-46]. The absence of the direct correlation between the N$_2$ MS profile and the IR intensity of adsorbed NO and NCO suggests that the pathways (i) and (ii) did not play a significant role in N$_2$ formation on Pd/Al$_2$O$_3$ and Ag-Pd/Al$_2$O$_3$ catalysts under reaction condition of this study. The presence of adsorbed NH$_3$
and formation of N$_2$ on Pd/Al$_2$O$_3$ in the 400 – 600 K range in Figure A.7 under H$_2$-rich condition suggests that the selective reduction of NO to N$_2$ by NH$_3$ is a favorable pathway. NH$_3$ produced by successive hydrogenation of atomic N was reacted with Brønsted acid sites to form NH$_4^+$. Adsorbed NH$_4^+$ has been recognized to play a key role in selective reduction of NO to N$_2$ on Pd-V$_2$O$_5$-TiO$_2$-Al$_2$O$_3$, 423 K under lean-burn condition [46]. The symmetric and asymmetric bending modes of NH$_4^+$ have been assigned to 1460 and 1680 cm$^{-1}$ [46, 76]. These bands are similar to the adsorbed NH$_3$ at 1446 and 1633 cm$^{-1}$ observed in Figure A.7 under H$_2$-rich conditions, further supporting that adsorbed ammonia as NH$_4^+$ could play a role in the selective reduction of NO to N$_2$ at low temperature on Pd.

Ag on Al$_2$O$_3$ has been extensively studied as a hydrocarbon SCR catalyst [63, 65-66, 77]. Ag$^+$ and partial positive charge of Ag have been proposed to be responsible for the selective reduction of NO to N$_2$ [61]. Comparison of TPR results on Pd/Al$_2$O$_3$ and Ag-Pd/Al$_2$O$_3$ shows that Ag increases the NO$_2$ formation and light-off temperature of CO and H$_2$ under lean-burn condition, but lowered the light off temperature for CO and H$_2$ under H$_2$-rich condition. The enhancement of oxidation of CO and H$_2$ under H$_2$-rich condition can be attributed to the presence of Ag$^0$ that promotes the total oxidation. Under lean-burn condition, Ag could be in the form of Ag$^+$, which slowed down the total oxidation, but promotes the reaction of adsorbed NO with adsorbed oxygen to produce NO$_2$. A 1:1 feed ratio of NO:NO$_2$ has been shown to give the highest efficiency for the selective conversion of NO/NO$_2$ to N$_2$ with NH$_3$ on a V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst [78].
A.2.5 Conclusion

Both Pd/Al₂O₃ and Ag-Pd/Al₂O₃ exhibit activity for the reduction of NO and NO₂ in H₂-rich and lean-burn conditions. NO adsorbed as Pd⁰-NO and Pd-NO⁺ on Pd/Al₂O₃ and as Pd⁰-NO on Ag-Pd/Al₂O₃. Adsorbed NO dissociates on the Pd surface, producing Pd-NCO at 373 K and N₂O at 400 K. Reduction of NO and NO₂ to N₂ under H₂-rich condition occurs at 400 K over Pd/Al₂O₃ and at 373 K over Ag-Pd/Al₂O₃. Ag promotes NO₂ formation and further shifts the NH₃ and N₂ formation to lower temperature under lean-burn conditions over the Ag-Pd/Al₂O₃ catalyst.

Excess oxygen under lean-burn conditions does not oxidize the Pd sites to Pd⁺ on Ag-Pd/Al₂O₃, as evidenced by the presence of Pd⁰-NO. During lean-burn, NO₂ is reduced to N₂ in the absence of adsorbed NH₃ in contrast to NO reduction in the H₂-rich environment. The presence of Ag inhibits the formation of Pd-NO⁺. The NOₓ reduction activity of Ag-Pd/Al₂O₃ under lean-burn conditions can be related to its ability to maintain the Pd sites in a reduced state.

A.3 The Effect of O₂ on the NO-CO reaction over Ag-Pd/Al₂O₃: an In Situ Infrared Study

The effect of O₂ on the NO-CO reaction over Pd/Al₂O₃ and Ag-Pd/Al₂O₃ has been studied by in situ infrared (IR) spectroscopy coupled with the O₂ pulse technique at 373 - 573 K. Pulsing O₂ into the NO-CO flow at 373 K causes the oxidation of Pd⁺-NO to gaseous NO₂ over Pd/Al₂O₃ and the emergence of Pd⁰-NO on Ag-Pd/Al₂O₃. The formation of Pd⁰-NO during the O₂ pulse over Ag-Pd/Al₂O₃ catalyst suggests that (i) O₂ disrupts the Ag overlayers on the Pd surface, allowing the Pd surface to be exposed to
NO; and (ii) Ag species is able to keep the Pd surface in reduced state in the presence of 
O₂. Increasing the temperature to 573 K does not lead to the formation of Pd⁺-NO, over 
Ag-Pd/Al₂O₃ further supporting the unique ability of Ag to keep Pd in the reduced state 
in an oxidizing environment. Ag enhances NO oxidation and slows CO oxidation on 
Pd/Al₂O₃. Adsorbed oxygen on Ag-Pd/Al₂O₃ exhibits two distinctly different 
reactivities: (i) a more active adsorbed oxygen reacting with NO, giving a sharp NO₂ 
response and (ii) a less active one, respect to NO, oxidizing CO, giving a trailing CO₂ 
response. Ag is unable to alleviate the negative impact of O₂ on the NO-CO reaction 
over Pd/Al₂O₃. Keeping Pd in the reduced state is not a necessary condition for 
nullifying the impact of O₂ on the NO-CO reaction.

A.3.1 Introduction

NOₓ (NO and NO₂) pollution from automobile and diesel exhausts, their control 
and release, has driven the search for an active and selective catalyst [79-82]. Pt/Rh-
based catalysts have been used in the catalytic converter to reduce the emission of NOₓ 
and other pollutants [83-84]. Successful development of Pd-based catalysts has been 
considered as an alternative to the Pt/Rh-based catalysts for low temperature activity of 
Pd and excellent durability at high temperatures [85]. Further improving the catalytic 
performance of Pd catalysts through mechanistic understanding has been attempted by 
spectroscopic studies of chemisorbed NO and CO on Pd single crystal [56, 86] and 
supported metal catalysts [7-8, 87]. NO chemisorbs upon Pd/Al₂O₃ as cationic (Pd-
NOδ⁺), linear (Pd⁰-NO), and bent (Pd-NOδ⁻) [88]. Previous studies have shown that Pd⁰-
NO act as active precursors involved in the formation of N₂ from NO [8].
O$_2$ behaves as a poison to the NO-CO reaction over Pd/Al$_2$O$_3$ catalyst [8]. The possible effects of O$_2$ include (i) oxidation of the Pd$^0$ site to Pd$^+$ site, (ii) blockage of NO dissociation site, and (iii) oxidation of NO to NO$_2$ [89-90]. In contrast, O$_2$ plays a key role in selective catalytic reduction of NO on Pd [91-92]. In the present work, we have studied the effect of oxygen on (i) dynamic behavior of adsorbed NO and (ii) gaseous CO$_2$ and NO$_2$ formation upon Pd/Al$_2$O$_3$ and Ag-Pd/Al$_2$O$_3$ by an in situ infrared method coupled with the O$_2$ pulse into the steady state NO-CO flow. Ag, known for its resistance to oxidation [93], may alleviate the negative impact of O$_2$ on Pd catalyst for the NO-CO reaction. Ag has also been shown to play an important role in selective catalytic reduction of NO$_x$ with hydrocarbons [94]. Although the behavior of adsorbed oxygen cannot be monitored by infrared spectroscopy, the effect of adsorbed oxygen can be elucidated by the transient response of the infrared (IR)-observable species as well as gaseous reactants and products. Result of our in situ infrared study coupled with the O$_2$ pulse revealed that Ag is able to (i) keep Pd in the reduced state and to (ii) promote NO oxidation and reduce CO oxidation, but is unable to mitigate the negative impact of O$_2$ on the NO-CO reaction.

A.3.2 Experimental Section

The experimental section describes the preparation and characterization of Pd/Al$_2$O$_3$ and Ag-Pd/Al$_2$O$_3$, and the reactor setup used during this study.
A.3.2.1 Catalyst Preparation and Characterization

The 5 wt% Pd/Al₂O₃ catalyst was prepared by incipient wetness impregnation of Pd(NO₃)₂·2·H₂O (Aldrich) solution onto α-Al₂O₃ (Aldrich, 2.95 m²/g). The 5 wt% Ag-Pd/Al₂O₃ catalyst was prepared by insipient wetness co-impregnation of Pd(NO₃)₂·2·H₂O (Aldrich) and Ag(NO₃) (Aldrich) solution onto α-Al₂O₃ support. The catalysts were filtered, rinsed with deionized water, dried over night at room temperature, calcined in air at 773 K (10 K/min) for 2 h, and reduced at 773 K in 5 vol% H₂ in He for 1 h.

A.3.2.2 In Situ IR/MS Reaction studies

The experimental apparatus consists of (i) a gas sampling system with 4-port and 6-port valve, (ii) a Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS, Harrick Scientific) reactor placed inside a Fourier Transform Infrared Spectrometer (FTIR, Varian Inc. FTS-4000), and (iii) a mass spectrometer (MS, Pfeiffer Omnistar™). The FTIR monitored the changes in the concentration of IR-observable adsorbates; MS measures the gaseous concentration of the DRIFTS reactor effluent. The 4-port valve was used to switch the inlet flow from 100% He to He/CO/NO (65/17.5/17.5 vol %) while maintaining the total flow rate at 45 cm³/min over 150 mg Pd/Al₂O₃ and Ag-Pd/Al₂O₃ catalysts. The 6-port valve allowed injection of 1 cm³ O₂ into the NO-CO flow. The background infrared spectrum was collected by co-adding 32 scans at a resolution of 4 cm⁻¹ during heating the catalyst from 298 to 573 K in He flow. The IR absorbance spectrum of the adsorbed and gaseous species during the reaction was obtained by taking a logarithmic ratio of the single beam spectrum of the catalyst with flowing reactants to the background spectrum of the catalyst free of the reactants. The difference spectra
were arithmetic subtraction of two different absorbance spectra. The infrared intensity curves were obtained by measuring the height of the adsorption band peak during the O$_2$ pulse into NO-CO. The effluent gases of the DRIFTS reactor were monitored by a Pfeiffer MS which followed the gaseous responses for m/z ratios corresponding to O$_2$ (m/z = 32), NO (m/z = 30), CO$_2$ (m/z = 22), CO$_2$/N$_2$O (m/z = 44) and NO$_2$ (m/z = 46). CO$_2$ (m/z = 22) is a result of ionization of the CO$_2^+$ of which intensity is 1.4% of CO$_2^+$ (m/z=44). In spite of its low intensity, CO$_2$ (m/z = 22) allows the separation of the contribution of N$_2$O (m/z=44) to the overall m/z=44.

A.3.3 Results and discussion

The NO-CO reaction using the pulse injection method is studied over Pd/Al$_2$O$_3$ and Ag-Pd/Al$_2$O$_3$ catalysts in the 323 to 723 K temperature region.

A.3.3.1 CO and NO adsorption on Pd/Al$_2$O$_3$ and Ag-Pd/Al$_2$O$_3$ catalysts

Figure A.15 shows the infrared spectra of gaseous reactants/products and adsorbed species during the switch from the He flow to the NO/CO/He flow over Pd/Al$_2$O$_3$ and Ag-Pd/Al$_2$O$_3$ at 298 K. Exposure of Pd/Al$_2$O$_3$ catalyst to the NO/CO/He flow led to an immediate formation of gaseous CO$_2$ at 2350 cm$^{-1}$, N$_2$O at 2234 cm$^{-1}$, Pd-NCO at 2170 cm$^{-1}$ [8, 95], bridge NO at 1627 cm$^{-1}$[96], Pd-NO$^-$ at 1590 and 1555 cm$^{-1}$ [97] followed by the formation of monodentate nitrate at 1534 and 1303 cm$^{-1}$ and monodentate nitrite species at 1393 cm$^{-1}$ after 0.56 min [98-99]. Switch back to the He flow resulted in the removal of the gaseous products and decreased IR intensity of Pd-NCO, Pd-NO$^-$, and nitrate species.
Figure A.15  IR spectra step switch to He/CO/NO on Pd/Al₂O₃ and Ag-Pd/Al₂O₃ catalyst at 298 K.
Exposure of Ag-Pd/Al₂O₃ catalyst to the steady state NO/CO/He flow produced N₂O at 2234 cm⁻¹, adsorbed NCO at 2170 cm⁻¹, Pd⁺-NO at 1792 cm⁻¹, Pd⁰-NO at 1758 cm⁻¹ [7], and gaseous NO₂ at 1627 cm⁻¹. It is interesting to observe that adsorbed NCO on Pd/Al₂O₃ and Ag-Pd/Al₂O₃ exhibit the same wavenumber at 2170 cm⁻¹. The intensity of adsorbed NCO is significantly higher on Ag-Pd/Al₂O₃ than on Pd/Al₂O₃. The observed intense NCO band on Ag-Pd/Al₂O₃ may be attributed to adsorbed NCO on Ag sites (i.e., Ag-NCO) since the intense NCO band has also been found on Ag/SiO₂ at temperatures up to 573 K [100]. The observation of Pd⁺-NO and Pd⁰-NO indicated the presence of both Pd⁺ and Pd⁰ sites on Ag-Pd/Al₂O₃. Switch back to the He flow caused the disappearance of Pd⁺-NO and removal of all gaseous species, leaving the adsorbed species: Ag-NCO, Pd⁰-NO, and nitrates. The NCO species has been found to form on Pd catalysts by the reaction of adsorbed CO and adsorbed nitrogen [101]. Adsorbed nitrogen is formed from NO dissociation. Thus, the formation of adsorbed NCO, can serve as evidence of NO dissociation on both Pd/Al₂O₃ and Ag-Pd/Al₂O₃ catalysts at 298 K.

A.3.3.2 Injection of O₂ pulse into the steady state NO-CO flow over Pd and Ag-Pd/Al₂O₃ catalysts

Figure A.16(a) shows the IR spectra obtained during the 1 cm³ O₂ pulse into NO/CO/He over Pd/Al₂O₃ catalyst at 373 K. Prior to the O₂ pulse, the IR-observable species were CO₂, N₂O, Pd-NCO, Pd⁰-NO, and nitrate species. Upon pulsing O₂, the major changes in IR intensity can be summarized as follows: (i) an increase in the intensity of CO₂ and Pd-NCO, and monodentate nitrate, (ii) a decrease in the Pd⁺-NO, and (iii) a formation of NO₂. The changes in IR intensity of adsorbed species and MS
intensity of gas products as a function of time were plotted in Figure A.16(b) and A.16(c), respectively.
Figure A.16 Pulse 1 cm$^3$ O$_2$ into the steady state He/CO/NO over Pd/Al$_2$O$_3$ catalyst at 373 K (a) IR spectra (b) IR intensity profiles of the species formed (c) the MS intensity curves for the gaseous species in the reactor effluent.
For careful comparison of the IR and MS data, the time scale for the MS intensity curves has been adjusted to match that of the IR intensity curves by aligning the peak maximum of IR and MS intensity curves for gaseous NO₂. The increase in the MS intensity of NO₂ was accompanied by a decrease in the IR intensity of Pd⁺-NO, which suggests the occurrence of the following reaction:

\[ Pd^+\text{-NO} + Pd\text{-O} \rightarrow Pd + Pd^+ + NO_2 \]  

This reaction caused 10 - 18 % increases in NO conversion relative to the steady state conversion, shown in Table A.7. The slight increase in the IR intensity profile of Pd-NCO in Figure A.16(b) indicates that adsorbed oxygen did not block the Pd sites required for NO dissociation. Preadsorbed oxygen atoms has recently been found to stabilize the adsorbed NCO on Pd(100) surface [95]. Following the O₂ pulse, the gaseous and adsorbed species returned to their steady state concentrations.

Figure A.17(a) shows the IR spectra during the 1 cm³ O₂ pulse over Ag-Pd/Al₂O₃ catalyst at 373 K. Prior to the oxygen pulse, steady state NO/CO/He over Ag-Pd/Al₂O₃ produced gaseous CO₂ and N₂O as well as adsorbed monodentate nitrite at 1412 and 1312 cm⁻¹. Adsorbed oxygen during the pulse caused an increase in the IR intensity of CO₂ and NO₂, an emergence of Pd⁰-NO at 1749 cm⁻¹. The assignment of this 1749 cm⁻¹ band to N₂O₄ [57] can be ruled out since its third intense 1520 cm⁻¹ band was not observed and this species can only be formed at low temperatures [58]. The absence of Pd⁰-NO during initial exposure of Ag-Pd/Al₂O₃ to NO-CO flow at 298 and 373 K and the emergence of this band after prolonged NO-CO exposure and the O₂ pulse suggest that (i) the formation of Pd⁰-NO was a result of disruption of the Ag overlayer on the Pd surface and (ii) Ag species was able to keep Pd in the reduced state in an oxidizing environment.
Table A.7  Steady state conversion and O₂ pulse conversion data.

Conversion (%)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Steady State</th>
<th>Pulse O₂ into NO-CO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X₉₀, Pd</td>
<td>X₉₀, Ag-Pd</td>
</tr>
<tr>
<td>373</td>
<td>4.8</td>
<td>6.1</td>
</tr>
<tr>
<td>473</td>
<td>16.7</td>
<td>18.2</td>
</tr>
<tr>
<td>573</td>
<td>21.6</td>
<td>30.3</td>
</tr>
</tbody>
</table>

Note: Maximum NO conversion occurred during Pulse O₂ into steady state NO-CO.
Figure A.17  Pulse 1 cm$^3$ O$_2$ into the steady state He/CO/NO over Ag-Pd/Al$_2$O$_3$ catalyst at 373 K (a) IR spectra (b) IR intensity profiles of the species formed (c) the MS intensity curves for the gaseous species in the reactor effluent.
Ag cluster on Al₂O₃ has been shown to disperse in oxidizing atmosphere and re-agglomerate in a reducing environment [18]; Ag and Pd has been shown to segregate on Al₂O₃ supported Ag-Pd particles in an oxidizing environment [102], supporting the possibility of the disruption of the reduced Ag overlayer on the Pd surface during the O₂ pulse. In contrast to Ag-Pd/Al₂O₃, the dominant adsorbed NO on the Pd surface of Pd/Al₂O₃ is Pd⁺-NO, further suggesting the presence of Ag kept Pd in the reduced state during the O₂ pulse at 373 K.

Comparison of MS intensity curves in Figure A.16(c) and A.17(c) revealed that Ag on Ag-Pd/Al₂O₃ caused the NO₂ curve to shift forward with respect to NO₂ curve on Pd/Al₂O₃. The leading edge of the NO₂ curve aligned with that of O₂ on Ag-Pd/Al₂O₃, shown in Figure A.17(c), indicating that Ag accelerated the rate of NO oxidation to NO₂. Ag metallic sites have been recognized as one of the most active catalyst for NO oxidation [103]. Comparison of CO₂ IR and MS intensity curves in Figure A.16(b)/(c) and 3(b)/(c) show that Ag delayed the CO₂ formation as evidenced by a trailing CO₂ IR and MS intensity curves on Ag-Pd/Al₂O₃. The lead-lag relationship suggests that Ag sites on Pd/Al₂O₃ produced adsorbed oxygen with different reactivities: (i) a more reactive one oxidizing NO to NO₂, giving a sharp NO₂ curve and (ii) a less reactive one, with respect to NO, oxidizing CO to CO₂, giving a trailing CO₂ curve. Difference in the reactivity of adsorbed oxygen can be related to its binding energy on Ag and Pd surface. The oxygen TPD study showed that oxygen desorbs at higher temperature over Pd films [104] than on Ag films [105], demonstrating that oxygen on Pd(111) has a higher binding energy than oxygen on Ag(111). O₂ has also been found to cause Ag enrichment on Ag-Pd films [106-107] with prolonged O₂ exposure causing dealloying of the Ag-Pd film.
Such Ag enrichment effect may allow Ag to stand alone for exhibiting its exceptionally high activity for NO oxidation.

The behavior of adsorbed NO during the O\textsubscript{2} pulse was further examined at 473 and 573 K. The lead-lag relationship between adsorbed species and gaseous product became less distinct at higher temperature. During the O\textsubscript{2} pulse, Figure A.18(a) shows more NO\textsubscript{2} and less CO\textsubscript{2} is produced over Ag-Pd/Al\textsubscript{2}O\textsubscript{3} than that of Pd/Al\textsubscript{2}O\textsubscript{3} at 437 and 573. These results are consistent with those observed at 373 K. The most important IR observations during the O\textsubscript{2} pulse were the changes in the IR intensity of Pd\textsuperscript{0}-NO and Pd\textsuperscript{+}-NO. These changes can be highlighted by the difference spectra in Figure A.18(b) obtained by subtracting the IR spectrum before the oxygen pulse from the spectrum taken at the maximum NO\textsubscript{2} concentration during the oxygen pulse. The negative peak in the difference spectra indicates a decrease in the concentration of the species while the positive peak reflects its increase in the concentration. These variations at different temperatures demonstrate the strong dependence of the reactivity of these adsorbed NO on temperature. The O\textsubscript{2} pulse decreased the intensity of Pd-NO\textsuperscript{+} at 1779 cm\textsuperscript{-1} over Pd/Al\textsubscript{2}O\textsubscript{3} at 373 K and increased at 473 and 573 K. The increase of Pd-NO\textsuperscript{+} at higher temperature is due to oxidation of Pd\textsuperscript{0} to Pd\textsuperscript{+} on Pd/Al\textsubscript{2}O\textsubscript{3} catalyst. The absence of Pd-NO\textsuperscript{+} on Ag-Pd/Al\textsubscript{2}O\textsubscript{3} at 373, 473, and 573 K could be attributed to the ability of Ag to keep the Pd surface in the reduced state.
Figure A.18  Infrared absorbance and difference spectra during O₂ pulse into steady state He/CO/NO over Pd/Al₂O₃ and Ag-Pd/Al₂O₃ catalysts at 373, 473, and 573 K. The IR spectra during NO/CO/O₂ which gave the highest NO₂ intensity were selected for display.
A.3.3 Conclusion

The NO-CO reaction on Pd/Al₂O₃ and Ag-Pd/Al₂O₃ were investigated using in situ IR spectroscopy coupled with an O₂ pulse technique in 373 – 573 K temperature range. Adsorbed NO was used as a surface probe to scrutinize the fundamental surface phenomena that take place during the NO-CO reaction on Pd/Al₂O₃ and the effect of the addition of Ag. In situ IR shows pulsing O₂ into NO-CO flow over Pd/Al₂O₃ caused the oxidation of Pd⁰ to Pd⁺ by the formation of Pd⁺-NO. The addition of Ag caused the formation of Pd⁰-NO, suggesting (i) O₂ disrupts the Ag overlayers over the Pd surface allowing exposure to NO and (ii) Ag species can maintain Pd in the reduced state in the presence of O₂ at 373 K. Increasing the temperature to 473 and 573 K produced Pd⁺-NO on Pd/Al₂O₃ catalyst but did not result in forming Pd⁺-NO on Ag-Pd/Al₂O₃, further confirming the ability of Ag in maintaining Pd in the reduce state. The trailing response for CO₂ and leading behavior of NO₂ product during the O₂ pulse over Ag-Pd/Al₂O₃ indicate adsorbed oxygen on Ag-Pd/Al₂O₃ is highly reactive towards NO oxidation and less reactive for CO oxidation. This observation revealed that adsorbed oxygen on Ag-Pd/Al₂O₃ exhibits wot distinctly different reactivities: one active for NO oxidation and the other for CO oxidation. Although Ag is able to maintain Pd in the reduced state, it was unable to eliminate the inhibition effect of O₂ on the NO-CO reaction.

A.4 Pulse Transient Responses of NO Decomposition and Reduction with H₂ on Ag-Pd/Al₂O₃

Catalytic decomposition of nitric oxide (NO) over Pd/Al₂O₃ and Ag-Pd/Al₂O₃ has been studied using the pulse transient response technique coupled with in situ infrared
(IR) and mass spectrometry (MS) at 723-823 K. In the absence of H$_2$, pulsing NO over the Pd/Al$_2$O$_3$ catalyst produces adsorbed NO species (i.e., Pd$^+$-NO, Pd$^0$-NO, Pd-NO$^-$) as well as gaseous N$_2$, O$_2$, and N$_2$O products. Transient responses of the N$_2$ and O$_2$ profiles show that the addition of Ag onto Pd/Al$_2$O$_3$ catalyst shifts the O$_2$ profile forward, increases oxygen formation and the oxidation resistance of Pd, but did not decrease the amount of retained oxygen (O$_{ret}$) and did not improve the catalytic cycle for NO decomposition. O$_{ret}$ on the Pd surface is not able to desorb in the temperature range of this study; however, O$_{ret}$ on Ag-Pd/Al$_2$O$_3$ can be desorbed at higher temperatures than its formation and adsorption temperature. The presence of H$_2$ during the NO pulse allowed NO reduction to occur, producing N$_2$, N$_2$O, O$_2$, NH$_3$, and H$_2$O. Pd/Al$_2$O$_3$ is a more active catalyst for the formation of NH$_3$ and H$_2$O than Ag-Pd/Al$_2$O$_3$. Comparison of the transient gaseous product responses over Pd/Al$_2$O$_3$ and Ag-Pd/Al$_2$O$_3$ catalysts show that Ag (i) promotes the formation of N$_2$, shifting its profile forward and (ii) suppresses the formation of NH$_3$ and H$_2$O, delaying their formation. The lack of the initial activity of Ag-Pd/Al$_2$O$_3$ for NH$_3$/H$_2$O formation can be attributed to the alloy state of Ag-Pd on Al$_2$O$_3$. As the NO reaction proceeds in the presence of H$_2$, adsorbed oxygen may cause the dealloying of Ag-Pd, producing Pd sites which are more selective for N$_2$ formation than that of NH$_3$ and H$_2$O.

A.4.1. Introduction

Effective removal of NO$_x$ from lean-burn and diesel engines has been considered to be the most challenging task to the automotive industry. Research has been focused on developing catalysts capable of removing NO$_x$ from O$_2$-rich exhaust either by the direct
decomposition of NOx to N2 and O2 (i.e. \[2NO \leftrightarrow N_2 + O_2\]) [9, 108-109] or by the selective catalytic reduction (SCR) with a reductant [110-112]. The direct NOx decomposition approach is an appealing approach for the removal of NOx from an exhaust mixture. The direct NO decomposition has been proposed to proceed via the following steps [113]:

\[
\begin{align*}
NO(g) & \rightarrow NO_{ads} & (1) \\
NO_{ads} & \rightarrow N_{ads} + O_{ads} & (2) \\
N_{ads} + N_{ads} & \rightarrow N_2(g) & (3) \\
O_{ads} + O_{ads} & \rightarrow O_2(g) & (4) \\
NO_{ads} + N_{ads} & \rightarrow N_2O(g) & (5) \\
NO_{ads} + O_{ads} & \rightarrow NO_2(g) & (6)
\end{align*}
\]

NO adsorbs on the catalyst surface (step 1) followed by the dissociation of adsorbed NO (NO_{ads}) to form adsorbed nitrogen (N_{ads}) and oxygen (O_{ads}) (step 2). Adsorbed nitrogen and oxygen can combine to form gaseous nitrogen (step 3) and oxygen (step 4), respectively. Adsorbed NO can also react with adsorbed nitrogen to form gaseous N2O (step 5) or with adsorbed oxygen to form gaseous NO2 (step 6). Studies on these proposed steps over single crystals and supported catalysts [9, 55, 113-114] have revealed that adsorbed oxygen from dissociation of NO_{ads} is strongly bounded on the metal catalyst surface, poisoning NO dissociation sites. The removal of O_{ads} should increase the concentration of active NO adsorbates and increase NO conversion.
Silver (Ag), known for its resistance to oxidation[48], has been shown to decrease the reduction temperature of metal oxides such as Co/Al₂O₃[115]. These results suggest that Ag may assist in desorption of O_ads on the catalyst surface. We have therefore postulated that Ag may promote desorption of adsorbed oxygen from the NO dissociation site and create free sites needed for further NO dissociation (step 2), allowing the completion of the catalytic NO decomposition cycle.

An alternative and common approach for the removal of O_ads is the addition of reducing agents such as H₂[110, 116-117], CO[45], hydrocarbons[111, 118], and NH₃[34]. Both H₂ and NH₃, reducing agents, have been shown to exhibit high reactivity toward the O_ads especially under lean-burn conditions[117]. Adsorbed hydrogen (H_ads) on the Pd surface can react not only with O_ads but also with N_ads. The reaction of H_ads with N_ads, a hydrogenation reaction step, produces NH₃ which can either (i) serve as a reducing agent to further remove O_ads or (ii) result in an undesirable slip from the reactor. Ag is also known for its low activity for catalysing hydrogen-related reactions such as suppressing the hydrogenation of ethylene in the acetylene hydrogenation reaction[102]. The addition of Ag may limit the formation of NH₃ during NO reduction.

This paper is aimed at determining the effect of Ag on Pd/Al₂O₃ during the NO decomposition and reduction with H₂ by in situ IR spectroscopy coupled with the NO pulse technique. The effect of Ag on Pd/Al₂O₃ on NO decomposition/reduction and the nature of the surface sites is elucidated by the transient response (i.e., changes in IR and MS intensity) of adsorbates and gaseous species. A fundamental understanding of the reaction pathway could help in guiding the preparation of the desired catalyst structure for enhancing NO decomposition activity and the H₂ selectivity in NO reduction.
A.4.2. Experimental Section

The experimental section describes the preparation and characterization of Pd/Al₂O₃ and Ag-Pd/Al₂O₃, and reactor setup used during this study.

A.4.2.1 Catalyst Preparation and Characterization

The 5% Pd/Al₂O₃ catalyst was prepared by incipient wetness impregnation of Pd(NO₃)₂·H₂O (Aldrich) aqueous solution onto α-Al₂O₃ (Aldrich) and dried at 298 K. The 5% Ag-5% Pd/Al₂O₃ catalyst was prepared by incipient wetness co-impregnation of Pd(NO₃)₂·H₂O (Aldrich) and Ag(NO₃) (Aldrich) aqueous solution onto α-Al₂O₃ (Aldrich) and dried at 298 K. The catalysts were calcined at 773 K in air for 2 h and reduced at 773 K in H₂ for 1 h. The Pd particle size was determined to be 6 nm for Pd/Al₂O₃ by X-ray Diffraction (XRD) using the Scherer equation from line broadening[53, 119]. XRD analysis shows the presence of a very broad Ag-Pd peak on Ag-Pd/Al₂O₃ indicating the existence of an Ag-Pd alloy phase and an Ag-Pd particle size less than 3 nm[119].

A.4.2.2 In Situ IR/MS Reaction Studies

The experimental apparatus, shown in Figure A.19, consist of (i) a reactant metering system (Brooks Instrument 5850 mass flow controllers), (ii) a gas sampling system with 4-port and 6-port valves, (iii) a Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS, Harrick Scientific) reactor containing 150 mg catalyst and placed inside a Fourier Transform Infrared Spectrometer (FTIR, Varian Inc. FTS-4000), and (iv) a mass spectrometer (MS, Pfeiffer Omnistar™) for determining changes in the DRIFTS reactor effluent concentrations.
Figure A.19. Experimental Apparatus.

The 4-port valve allows switching the inlet flow from 100% He to He/H₂ (90/10 vol %) while maintaining a total flow rate of 34 cm³/min over the Pd/Al₂O₃ or Ag-Pd/Al₂O₃ catalyst. The 6-port valve is used to pulse 1 cm³ NO into He or He/H₂ flow at 723, 773, and 823 K.

The changes in the concentration of IR-observable adsorbates are monitored by FTIR. The IR spectra collected by DRIFTS are reported in absorbance units which are more applicable for low adsorbate surface concentrations than that of Kubelka-Munk units[120]. The IR absorbance spectrum of adsorbed and gaseous species is obtained by
\[ A = -\log \left( \frac{I_o}{I} \right) \] [121], where \( I_o \) is the background IR single beam spectrum (32 co-added scans and resolution 4 cm\(^{-1}\)) of the catalyst under He or He/H\(_2\) flow and \( I \) is the IR single beam spectrum during the NO pulse reaction. The MS responses corresponding to \( \text{N}_2 \) (m/e = 28), NO (m/e = 30), O\(_2\) (m/e = 32), and N\(_2\)O (m/e = 44) are monitored.

A.4.3. Results

The NO-CO adsorption and NO decomposition reaction are studied over Pd/Al\(_2\)O\(_3\) and Ag-Pd/Al\(_2\)O\(_3\) catalysts using the transient pulse injection technique.

A.4.3.1 CO and NO adsorption on Pd/Al\(_2\)O\(_3\) and Ag-Pd/Al\(_2\)O\(_3\)

Figure A.20 shows the IR absorbance spectra of gaseous CO and NO as well as their adsorbed species on Pd/Al\(_2\)O\(_3\) and Ag-Pd/Al\(_2\)O\(_3\) catalysts at 298 K. CO adsorbed on Pd/Al\(_2\)O\(_3\) as linear CO at 2099 cm\(^{-1}\) and bridged CO at 1949 and 1994 cm\(^{-1}\) [102, 122]; CO adsorbed on Ag-Pd/Al\(_2\)O\(_3\) as a intense linear CO band at 2081 cm\(^{-1}\) and a weak bridged CO band at 1957 cm\(^{-1}\) [122]. The low IR intensity of bridged CO on Ag-Pd/Al\(_2\)O\(_3\) as compared to that on Pd/Al\(_2\)O\(_3\) indicates that Ag disrupts some of the Pd\(^0\)-Pd\(^0\) sites for CO adsorption[48, 123].

Exposure of the Pd/Al\(_2\)O\(_3\) catalyst to NO flow led to an immediate formation of Pd\(^0\)-NO at 1754 cm\(^{-1}\) [124]. Increasing NO exposure time produced N\(_2\)O at 2223 cm\(^{-1}\), NO\(_2\) at 1628 cm\(^{-1}\), and chelating bidentate nitrate at 1527 and 1307 cm\(^{-1}\) [36].

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Figure A.20. Infrared spectra of gaseous and adsorbed species (a) CO adsorption on Pd and Ag-Pd/Al₂O₃ (b) NO adsorption on Pd and Ag-Pd/Al₂O₃ at 298 K.
Flowing NO over Ag-Pd/Al₂O₃ produced gaseous N₂O at 2223 cm⁻¹ and Pd-NO⁺ at 1545 cm⁻¹. The formation of NO₂ at 1628 cm⁻¹ was accompanied by that of chelating bidentate nitrate species at 1527 and 1415 cm⁻¹. Pd⁰-NO has been identified as an active adsorbate species for NO dissociation, which is the required step for the formation of N₂O and NO₂[124]. The absence of Pd⁰-NO during NO exposure over Ag-Pd/Al₂O₃, did not prevent formation of the N₂O and nitrate species.

A.4.3.2 NO pulse reaction in He flow over Pd/Al₂O₃

Figure A.21(a) and A.21(b) shows the IR absorbance spectra and MS intensity profiles during the first and second NO pulses into He flow over Pd/Al₂O₃ catalyst at 773 K. The first NO pulse produced gaseous N₂O at 2223 cm⁻¹, Pd⁰-NO at 1735 cm⁻¹, bent NO (Pd-NO⁻) at 1641 cm⁻¹, and chelating bidentate nitrate species at 1573 cm⁻¹ [55, 88]. The intensities of the Pd⁰-NO followed closely that of gaseous NO. These adsorbed NO species showed a higher rate of disappearance than that of the nitrate at 1573 cm⁻¹, revealing the high reactivity of Pd⁰-NO, a precursor for N-O dissociation, step (2). The second NO pulse produced a lower IR intensity of Pd⁰-NO and a higher intensity of Pd⁺-NO at 1769 cm⁻¹ than the first NO pulse. Figure A.21(b) shows the second NO pulse also produced lower MS intensity profiles for N₂ and N₂O than the first NO pulse. The low MS intensity corresponds to the small amount of the products produced. The amount of the products formed from each pulse is calculated by integrating the area under the MS profile and summarized in Table A.8. The results show that the second pulse decreased the amount of N₂ produced by a factor of 2.6 and O₂ by a factor of 1.2 at 773 K.
Figure A.21. NO pulses over Pd/Al₂O₃ catalyst at 773 K (a) Infrared spectra (b) MS intensity spectra.
These factors increased markedly with increasing temperature, showing the occurrence of rapid catalyst deactivation at higher temperatures.

The decrease in the intensity of the Pd$^{0}$-NO, the amount of N$_2$, N$_2$O, and O$_2$ formed, and the increase in the Pd$^{+}$-NO intensity provide the direct evidence to confirm that Pd$^{0}$-NO is an active precursor for the dissociation of N-O, step (2)[7]. The O$_{ads}$ produced can further oxidize Pd$^{0}$ to Pd$^{+}$. The effect of lowering the number of Pd$^{0}$ sites and increasing the number of Pd$^{+}$ sites on the dynamic behavior of the product formation can be unravelled by examining the lead/lag of the N$_2$ and O$_2$ responses in the first and second pulses in Figure A.21(b) and subsequent pulses (not shown here). The second NO pulse, which occurred on the catalyst with more Pd$^{+}$ and less Pd$^{0}$ sites, caused the N$_2$ formation to lag behind those of O$_2$ and N$_2$O. In SSITKA (Steady-State Isotopic-Transient Kinetic Analysis), the delay time in the gaseous isotopically labelled product response corresponds to the residence time (i.e. the reciprocal of the intrinsic rate constant) of intermediates leading to the formation of the specific gaseous product[125-126]. This residence time concept can be extended to the single reactant reaction, i.e., NO decomposition, without complication of the second isotopically labeled reactant. Thus, the lagging N$_2$ response can be explained by an increase in the residence time of the intermediates leading to N$_2$, reflecting a decrease in the intrinsic rate constant of the combination of N$_{ads}$ and N$_{ads}$, step (3).

Figure A.22(a) illustrates the effect of reaction temperature on the IR intensity of adsorbates obtained after 0.25 min of the second NO pulse. Raising the reaction temperature from 723 to 823 K decreased the IR intensity of all the adsorbed species.
including partially positive charged Pd\(^+\)-NO at 1769 cm\(^{-1}\), Pd\(^0\)-NO at 1735 cm\(^{-1}\), and Pd-NO\(^-\) at 1641 and 1573 cm\(^{-1}\).

Figure A.22. NO pulses over Pd/Al\(_2\)O\(_3\) catalyst at 723, 773, and 823 K (a) Infrared spectra (b) MS intensity spectra for gaseous N\(_2\) and O\(_2\) species.
The adsorbate IR intensity variations result from changes in the number of Pd\(^0\)/Pd\(^+\) sites, the adsorption equilibrium, and rate constants. Given a quasi-equilibrium state of these adsorbed species, the intensity ratio of Pd\(^+\)-NO/Pd\(^0\)-NO would reflect the molar ratio of Pd\(^+\) to Pd\(^0\) sites.

Table A.8 show that the amount of O\(_2\) produced is significantly less than that of N\(_2\) at higher reaction temperatures. An equal (i.e. stoichiometric amount) amount of N\(_2\) and O\(_2\) formed would be the completion of the catalytic NO decomposition cycle (\(2NO \rightarrow N_2 + O_2\)). The amount of the retained oxygen (i.e. O\(_{\text{ret}}\)) would correspond to the number of the incomplete NO decomposition cycle (\(2NO \rightarrow N_2 + 2Pd-O_{\text{ret}}\)). The amount of O\(_{\text{ret}}\) on the catalyst during each pulse, shown in Table A.8, can be estimated by taking the difference between the amounts of N\(_2\) and O\(_2\) produced, and the amount of oxygen remaining after the N\(_2\)O formation (\(N_2O = N_2 - O_2\)). The ratio of oxygen retained to gaseous oxygen formed increased from 2.46 (first pulse) to 3.60 (second pulse) at 723 K, shown in Table A.8. These retained oxygen species could further convert Pd\(^0\) site to Pd\(^+\) sites, as evidenced by the increasing IR intensity ratio of Pd\(^+\)-NO/Pd\(^0\)-NO with temperature.

Figure A.22(b) shows increasing temperature slowed down the response of O\(_2\), shifting the O\(_2\) maxima of the O\(_2\) response from 0.28 min at 723 K to 0.48 min at 823 K. This shift corresponds to an increase in the intensity ratio of Pd\(^+\)-NO/Pd\(^0\)-NO, further suggesting that the formation of Pd\(^+\) sites could be the key factor slowing down the O\(_2\) response, decreasing the reactivity of oxygen intermediates.
Table A.8  

First and second NO pulse into flowing He, conversion, selectivity, and product species formation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp. (K)</th>
<th>Quantity of gas species (μmol)</th>
<th>Conversion and Selectivity (%)</th>
<th>Ea (kJ/mol)</th>
</tr>
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<tr>
<td></td>
<td></td>
<td>N₂</td>
<td>O₂</td>
<td>N₂O</td>
</tr>
<tr>
<td>1st NO pulse</td>
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</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>723</td>
<td>0.32</td>
<td>0.29</td>
<td>0.65</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
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<td>0.97</td>
<td>0.41</td>
<td>0.85</td>
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<td>3.98</td>
<td>0.6</td>
<td>0.92</td>
</tr>
<tr>
<td>Ag-Pd/Al₂O₃</td>
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<td>4.05</td>
<td>0.86</td>
<td>1.59</td>
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<tr>
<td>Ag-Pd/Al₂O₃</td>
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<td>5.37</td>
<td>0.98</td>
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</tr>
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<td>Ag-Pd/Al₂O₃</td>
<td>823</td>
<td>7.15</td>
<td>1.03</td>
<td>1.02</td>
</tr>
<tr>
<td>2nd NO pulse</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
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<td>0.61</td>
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<td>Ag-Pd/Al₂O₃</td>
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<td>1.21</td>
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<td>Ag-Pd/Al₂O₃</td>
<td>823</td>
<td>3.1</td>
<td>0.92</td>
<td>0.98</td>
</tr>
</tbody>
</table>
A.4.3.3 NO pulse reaction in He flow over Ag-Pd/Al₂O₃

The NO pulse on Ag-Pd/Al₂O₃ at 773 K produced gaseous N₂O at 2223 cm⁻¹, shown in Figure A.23(a), as well as the formation of N₂ and O₂ in Figure A.23(b). The absence of adsorbed NO species indicates that the rate of desorption and conversion of these adsorbed species is higher than those of their formation. Table A.8 show that the amount of N₂ produced was increased 5.5 times during the first pulse, and 7.4 times during the second pulse; the amount of O₂ produced was increased 2.2 times during both the first and second pulse when Ag is added onto Pd/Al₂O₃ in the 723-823 K temperature region. In summary, the presence of Ag increased the amount of N₂ and O₂ formed as well as the ratio of O₂/O₂. The N₂ selectivity and NOₓ conversion during the first NO pulse over Pd/Al₂O₃ and Ag-Pd/Al₂O₃ at 723, 773, and 832 K obtained from this study generally fall in the same range as those in the literature[40, 127-135], shown in Table A.9.

MS profiles in Figure A.23(b) shows that the initial O₂ profile led those of N₂O and N₂ on Ag-Pd/Al₂O₃, in contrast to the O₂ lagging behind the N₂ on Pd/Al₂O₃ in Figure A.17(b). These results reveal that the increase in O₂ formation is closely related to the promotion effects of Ag on O₂ desorption. This promotion effect is consistent with the observed increase in N₂ formation as well as decreases in Eₘ (activation energy) for oxygen formation on Ag-Pd/Al₂O₃. The Eₘ for O₂ was decreased from 18.46 kJ/mol on Pd/Al₂O₃ to 4.46 kJ/mol on Ag-Pd/Al₂O₃ during the first NO pulse and from 20.9 kJ/mol to 6.74 kJ/mol during the second pulse. The enhancement of oxygen desorption by Ag is also consistent with the reported Ag effect on the removal of oxygen from Ag bimetallic catalysts in which Ag facilitate the reduction of Co supported on Al₂O₃[115].

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Figure A.23. NO pulses over Ag-Pd/Al₂O₃ catalyst at 773 K (a) Infrared spectra (b) MS intensity spectra.
Table A.9: Literature values for NOx conversion and selectivity data during NO decomposition study on Pd based catalysts.

<table>
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<tr>
<th>Catalyst</th>
<th>NOx</th>
<th>H2</th>
<th>CxHy</th>
<th>Temp. (K)</th>
<th>NOx Conv. (%)</th>
<th>SN2 (%)</th>
<th>SN2O (%)</th>
<th>SV (hr^-1)</th>
<th>Ref.</th>
</tr>
</thead>
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<td>Tb-Pt/Al2O3</td>
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<td>0</td>
<td>723</td>
<td>16.05</td>
<td>1.18</td>
<td>52.36</td>
<td>-</td>
<td>[9]</td>
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<td></td>
<td></td>
<td>773</td>
<td>16.99</td>
<td>3.15</td>
<td>53.57</td>
<td>-</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>873</td>
<td>18.60</td>
<td>5.93</td>
<td>55.52</td>
<td>-</td>
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</tr>
<tr>
<td>Cu-ZSM-5</td>
<td>1^a</td>
<td>0</td>
<td>0</td>
<td>673</td>
<td>7.2</td>
<td>0</td>
<td>46.78</td>
<td>-</td>
<td>[40,130]</td>
</tr>
<tr>
<td></td>
<td>2.5^b</td>
<td>1^a</td>
<td></td>
<td>673</td>
<td>8.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Pd-Mo/Al2O3</td>
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<td>0</td>
<td>0</td>
<td>673</td>
<td>25</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>0.1^b</td>
<td></td>
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<td>473</td>
<td>80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[133]</td>
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<td>Pd/Al2O3</td>
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<td>1^b</td>
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<td>94.2</td>
<td>-</td>
<td>6500</td>
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<td>973</td>
<td>97^c</td>
<td>17</td>
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<tr>
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<td>81.8</td>
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<td>87.5</td>
<td>12.5</td>
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</table>

Note:  
^a Pulse data  
^b Steady state data  
^c Deactivation after time exposed to reactants.
Figure A.24(a) and A.24(b) shows the IR absorbance spectra and MS intensity profiles during the second NO pulse over Ag-Pd/Al₂O₃ at 723, 773, and 823 K. Although Ag-Pd/Al₂O₃ was more active than Pd/Al₂O₃ for the NO decomposition, Ag-Pd/Al₂O₃ was not able to give an appreciable IR intensity for adsorbed NO in the entire temperature range of the reaction study. The effect of Ag on the reaction must be elucidated mainly by the MS profile results. The N₂ response profile show a significant trailing, revealing N₂ formation is slowed down by the presence of Ag on Pd. The O₂ MS profile show less variation with respect to temperature on Ag-Pd/Al₂O₃ than on Pd/Al₂O₃, further confirming low Eₐ for oxygen formation on Ag-Pd/Al₂O₃. However, this Eₐ value is lower than those commonly observed for a catalytic reaction. Furthermore, the amount of O₂ is less than that of N₂, showing the majority of the catalytic NO decomposition cycle was not completed and a large fraction of adsorbed oxygen was retained on the catalyst.

To understand the nature of the O₂ formation, we further examined the O₂ MS intensity profiles (i.e., response) while increasing the reaction temperature from 773 to 823 K in Figure A.25(a) and A.25(b). Heating the Ag-Pd/Al₂O₃ catalyst from 773 to 823 K, shown in Figure A.25(b), caused an increase in the O₂ MS intensity profile (i.e., oxygen desorption) compared to the absence of variation over Pd/Al₂O₃ in Figure A.25(a). The different dependence of oxygen desorption on temperature on Pd and Ag-Pd/Al₂O₃ indicates that the presence of Ag on Pd/Al₂O₃ shift the O₂ desorption equilibrium at each specific temperature, lowering the capacity of retained oxygen (i.e. O₉ₑᵣₑᵗ) on Pd/Al₂O₃.
Figure A.24  NO pulses over Ag-Pd/Al₂O₃ catalyst at 723, 773, and 823 K (a) Infrared spectra (b) MS intensity spectra gaseous N₂ and O₂ species.
A.4.3.4 NO pulse reaction in He/H₂ flow over Pd/Al₂O₃

Figure A.26(a) shows that the first NO pulse at 773 K produced gaseous NH₃ IR bands at 3336 and 1624 cm⁻¹, and a broad band at 1847 cm⁻¹. This broad band which is overlapped with gaseous NO band may be related to either a H₂O-NO complex [136] or a di-nitrosyl species [97]. The gaseous NH₃ IR band at 1624 cm⁻¹ overlapped with that of adsorbed H₂O at 1641 cm⁻¹. The amount of N₂ produced is about 4 to 8 times more in the presence of H₂ than in the absence of H₂, by comparing Tables A.8 and A.10. In the absence of H₂, N₂ can be produced by (i) dissociation of adsorbed NO (step 2) over Pd⁰ followed by (ii) the combination of adsorbed nitrogen and desorption of N₂ (step 3). In the presence of H₂, N₂ can also be produced via the reaction of Pd⁰-NO with adsorbed NH₃ which is formed by the reaction of N_ads with H_ads. The transient response of the NO pulse in Figure A.26(b) showed that the formation of NH₃ lagged that of N₂. This lag time between the initial N₂ and NH₃ formation represents the difference in the intrinsic activity for N₂ and NH₃ formation. This delay is shortened during the second NO pulse, Figure A.26(b), because the build up of adsorbed NH₃ after the first NO pulse facilitate
NH₃ desorption. The NH₃ produced appears to participate in the NO reduction, causing the NO MS profile to decrease to the baseline within 0.5 min, in contrast to the NO profile dragging for more than 1.5 min during the NO pulse in He, shown in Figure A.21(b).

The effect of temperature on the IR intensity of adsorbed species is shown in Figure A.27(a). Changing the reaction temperature did not shift the wavenumber of the IR observable species, but caused a variation in IR intensities as a result of greater or lesser amounts of products formed (i.e. NH₃ and H₂O) in this temperature region. Figure A.27(b) shows that the major effect of raising the reaction temperature is to shift the NH₃, O₂ and H₂O profiles forward.
Figure A.26  NO pulses into H$_2$ over Pd/Al$_2$O$_3$ catalyst at 773 K (a) Infrared spectra (b) MS intensity spectra.
Figure A.27  NO pulses into H$_2$ over Pd/Al$_2$O$_3$ catalyst at 723, 773, and 823 K (a) Infrared spectra (b) MS and intensity spectra gaseous NO, N$_2$, O$_2$, NH$_3$, and H$_2$O species.
The most dramatic shift is observed for NH₃ profiles when increasing temperature from 723 to 773 K. Further increasing temperature to 823 K does not advance the NH₃ profile closer to the initial N₂ elution time.

A.4.3.5 NO pulse reaction in He/H₂ flow over Ag-Pd/Al₂O₃

Figure A.28(a) shows that the first NO pulse produced low IR intensities of NH₃ at 3336 and 1624 cm⁻¹ on Ag-Pd/Al₂O₃ as compared to those over Pd/Al₂O₃, shown in Figure A.26(a). The NH₃ IR band emerged at 0.36 sec; the NH₃ MS profile increased at 0.4 sec in Figure A.26(b). The significant delay in NH₃ over Ag-Pd/Al₂O₃ compared with Pd/Al₂O₃ indicates that the N-H bond formation is inhibited by the presence of Ag. Figure A.28(b) shows that the O₂, NO, and N₂O responses appear prior to the emerging of the NH₃ and H₂O responses. The profiles for the O₂ and N₂ responses here resemble those produced from the NO pulse in Figure A.23(b).

Figure A.29(a) shows that raising the temperature increases the IR intensity of both gaseous NH₃ and H₂O bands. Figure A.29(b) shows increasing the temperature did not alter the contours and the maxima of NO, N₂, and O₂, but shifted the NH₃ response forward. The major shift occurred when the temperature increased from 723 K where NH₃ was not formed to 773 K where NH₃ emerged.
Figure A.28  NO pulses into H₂ over Ag-Pd/Al₂O₃ catalyst at 773 K (a) Infrared spectra  
(b) MS intensity spectra.
Figure A.29  NO pulses into H$_2$ over Ag-Pd/Al$_2$O$_3$ catalyst at 723, 773, and 823 K (a) Infrared spectra (b) MS intensity spectra gaseous NO, N$_2$, O$_2$, NH$_3$, and H$_2$O species.
A.4.4. Discussion

Vibrational spectroscopy has provided evidence for the adsorption of NO over single crystals and supported catalysts \[7, 56, 97, 137-140\]. NO adsorbs on the Pd(111) single crystal in the 1735-1755 cm\(^{-1}\) region as Pd\(^{0}\)-NO from 150 to 350 K \[56, 97, 139\]. Pd\(^{0}\)-NO adsorbs on supported Pd catalysts at 1741-1754 cm\(^{-1}\) between 303 and 673 K during NO-CO reaction \[7, 140\]. Pd\(^{0}\)-NO were observed on Pd/Al\(_{2}\)O\(_{3}\) at 1735 cm\(^{-1}\) in the temperature range of 723 - 823 K during NO decomposition, shown in Figure A.21 and A.22. The presence of this species under such a high temperature, indicates that (i) the rate of its conversion (i.e., desorption and decomposition) is not sufficiently high for its depletion and (ii) Pd\(^{0}\) sites remain on the Pd surface. It can also be further inferred that Pd(111) is the dominant surface structure \[56, 70\] of Pd/Al\(_{2}\)O\(_{3}\) used in this study which has a Pd particle size of about 6 nm. The wavenumbers of bridged/multiple bonded NO (i.e., NO on three fold hollow sites) and bent NO fall in the range of the nitrate species. The overlapping of these bands makes it difficult to identify the dynamic behaviour of these species on supported Pd catalysts which give the prominent nitrate IR bands during NO-CO reaction \[124\] and NO decomposition, shown in Figure A.21(a).

The decrease in the IR intensity for Pd\(^{0}\)-NO at 1735 cm\(^{-1}\) as well as the formation of N\(_{2}\), in Figure A.21 and A.22, confirm that reduced Pd\(^{0}\) is needed for the conversion of NO to N\(_{2}\). The subsequent formation of Pd\(^{+}\)-NO at 1769 cm\(^{-1}\) along with the amount of O\(_{\text{ret}}\) (listed in Table A.8) reveals that O\(_{\text{ads}}\), which do not desorb as oxygen molecules, are retained at Pd\(^{0}\) sites oxidizing Pd\(^{0}\) to Pd\(^{+}\). The lagging O\(_{2}\) and leading N\(_{2}\) profiles in Figure A.21(b) further reveal that the O-O formation, step (4), is slower than the N-N formation, step (3). The leading N\(_{2}\) and lagging O\(_{2}\) profiles in Figure A.21 suggest that
the N-N formation step (3) is faster than the O-O formation step (4). The weak dependence of O₂ formation on temperature over both Pd/Al₂O₃ and Ag-Pd/Al₂O₃ indicates that the O₂ formation may not be a catalytic process in nature.

Ag was added on Pd/Al₂O₃ with the intention of increasing catalytic NO decomposition activity by (i) enhancing the oxidation resistance of Pd⁰ sites, (ii) decreasing O_{ret}, and (iii) increasing the rate of O₂ desorption. It is indeed surprising to observe that the addition of Ag shifted the O₂ response forward and increased the amount of N₂ and O₂ formation, but did not decrease the ratio of O_{ret}/O₂. The ratio corresponds to that of the number of incomplete catalyst NO decomposition cycle to the complete NO decomposition cycle. The leading response of O₂ on Ag-Pd/Al₂O₃ indicates the high reactivity of these O_{ads} for desorption.

Small Pd particle has also shown a higher tendency to be oxidized than large Pd particle. A similar trend has been observed for NO decomposition study over Pt/Al₂O₃ which shows decreasing the Pt particle size results in higher activity for NO dissociation and higher temperature for oxygen desorption, indicating the higher tendency to be oxidized[141]. Small Pd particles allow oxygen to move to subsurface sites[142], exhibiting higher oxygen uptake and desorbing oxygen at higher temperature than large Pd particles. Our XRD results show the Ag-Pd particles on Al₂O₃ are smaller than 3 nm which is less than half of the Pd particle size on Pd/Al₂O₃. The smaller Ag-Pd particles show a higher oxygen uptake capacity and thus give a higher ratio of O_{ret}/O₂. However, these O_{ret} on the Ag-Pd surface are significantly different from those on Pd, exhibiting a unique property for its desorption. The O_{ret} on the Pd particle oxidizes Pd⁰ to Pd⁺ and are not able to desorb from the Pd surface in the 723-823 K region; the O_{ret} produced on Ag-
Pd particles can be desorbed at higher temperatures (i.e. O_{ret} produced at 723 K can be desorbed at 773 K and those produced at 773 K can be desorbed at 823 K) as shown in Figure A.25(b). Furthermore, these O_{ret} species are not able to oxidize Pd\(^0\) on Ag-Pd/Al\(_2\)O\(_3\), as evidenced by the absence of Pd\(^+\)-NO. Thus, it can be concluded that increasing oxidation resistance of Pd by Ag through the removal of O_{ret} is an unnecessary requirement for the enhancement of catalytic NO decomposition. Further studies are needed to look into the nature of oxygen desorption sites and the approaches for inhibiting conversion of adsorbed oxygen from dissociated NO to O_{ret}, the type which oxidize Pd\(^0\) to Pd\(^+\).

The effectiveness of H\(_2\) in the reduction of NO can be inferred from the formation of N\(_2\), N\(_2\)O, O\(_2\), NH\(_3\), and H\(_2\)O. Adsorbed hydrogen not only accelerates the NO conversion and N\(_2\) formation but also reacts with adsorbed nitrogen and oxygen to produce NH\(_3\) and H\(_2\)O, respectively. During the in situ formation of NH\(_3\) and H\(_2\)O, the IR spectra in Figure A.26(a) show a broad band at 1845 cm\(^{-1}\) that has been assigned to the di-nitrosyl species having a symmetric vibration at 1779 cm\(^{-1}\) and an antisymmetric band at 1855 cm\(^{-1}\) [57]. The di-nitrosyl species is known to exhibit IR adsorption bands at 1855 and 1826 cm\(^{-1}\) at relatively high temperature on the Pd(111) single crystal[97]. Interestingly, this species is absent on the Ag-Pd/Al\(_2\)O\(_3\) catalyst. It has been proposed that the di-nitrosyl species is an active species for N\(_2\)O formation[143]. The absence of di-nitrosyl species as well as the high rate of N\(_2\)O formation on Ag-Pd/Al\(_2\)O\(_3\) (see table A.10) suggests that Ag may promote the rapid conversion of the di-nitrosyl species to N\(_2\)O.
Figure A.26(b) and A.28(b) shows gaseous NH$_3$ emerged prior to H$_2$O, revealing that adsorbed hydrogen is more reactive toward $N_{ads}$ than $O_{ads}$ on both Pd/Al$_2$O$_3$ and Ag-Pd/Al$_2$O$_3$ catalysts. The major effect of Ag is to delay the formation of NH$_3$ and H$_2$O. The MS profile in Figure A.28(b) shows that the initial NH$_3$ formation occurred 0.3 min after that of N$_2$, O$_2$, and N$_2$O on Ag-Pd/Al$_2$O$_3$. These observations suggest that the presence of Ag on Pd/Al$_2$O$_3$ suppresses initial hydrogenation of adsorbed nitrogen and adsorbed oxygen, allowing these species to recombine to form molecular N$_2$ and O$_2$, respectively.
Table A.10  First and second NO pulse into flowing He/H₂, conversion, selectivity, and product species formation.

<table>
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<tr>
<th>Catalyst</th>
<th>Temp. (K)</th>
<th>N₂ (μmol)</th>
<th>O₂ (μmol)</th>
<th>N₂O (μmol)</th>
<th>NH₃ (μmol)</th>
<th>X_{NO} (%)</th>
<th>S_{N₂} (%)</th>
<th>S_{N₂O} (%)</th>
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<td>1st NO pulse Pd/Al₂O₃</td>
<td>723</td>
<td>2.81</td>
<td>0.13</td>
<td>0.42</td>
<td>5.54</td>
<td>29.3</td>
<td>87</td>
<td>13</td>
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<td>773</td>
<td>3.99</td>
<td>0.12</td>
<td>0.3</td>
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<td>92.9</td>
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<td>54.2</td>
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<td>5.1</td>
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<td>80.5</td>
<td>19.5</td>
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<td>8.8</td>
<td>0.44</td>
<td>1.22</td>
<td>4.23</td>
<td>59.3</td>
<td>87.8</td>
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<td>67.4</td>
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<tr>
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<td>57.4</td>
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<tr>
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<td>0.37</td>
<td>7.37</td>
<td>65.3</td>
<td>96.2</td>
<td>3.8</td>
</tr>
</tbody>
</table>

\[
X_{NO} (%) = \frac{mol \text{ NO}_m - mol \text{ NO}_o}{mol \text{ NO}_m} \times 100
\]

\[
b S_{N₂} (%) = \frac{mol \text{ N}_2}{mol \text{ N}_2 + mol \text{ NO} + mol \text{ NO}_2} \times 100
\]

\[
c S_{N₂O} (%) = \frac{mol \text{ NO}_2}{mol \text{ N}_2 + mol \text{ N}_2O + mol \text{ NO}_2} \times 100
\]
Ag has long been known to exhibit very low activity for hydrogen chemisorption due to a high activation barrier for H\textsubscript{2} dissociation\cite{144}. H\textsubscript{2} temperature-programmed desorption (TPD) studies show that the addition of Ag on Pd/Al\textsubscript{2}O\textsubscript{3} significantly suppresses hydrogen adsorption on the Pd catalyst surface\cite{145}. Acetylene hydrogenation study has also shown that addition of Ag on Pd inhibits the formation of Pd hydride\cite{146}. Low activity of Ag for hydrogen chemisorption is suggested as a key factor in suppressing hydrogenation of ethylene and enhancing the selectivity of acetylene hydrogenation to ethylene\cite{102}.

Ag-Pd has been shown to form an alloy in a hydrogen reducing environment and to de-alloy in an oxygen environment\cite{147}. The de-alloying process by oxygen causes the enrichment of Ag on the Ag-Pd surface\cite{107,147}. This enrichment process has been shown to be driven by the high adsorption energy of oxygen on a specific metal\cite{148}, such as Ag. The surface enrichment of an alloying species and re-alloy process has also been reported for Au-Pt\cite{149} and Ni-Cu\cite{150} alloys. This surface behavior may explain why NO was first converted to N\textsubscript{2}, O\textsubscript{2}, and N\textsubscript{2}O in the NO decomposition pathway during the first 0.25 min and then converted to NH\textsubscript{3} and H\textsubscript{2}O, shown in Figure A.28(b). The initial NO decomposition can be attributed to the presence of Ag-Pd alloy on Ag-Pd/Al\textsubscript{2}O\textsubscript{3} due to its exposure to steady state H\textsubscript{2} flow. The presence of this Ag-Pd alloy is supported by the absence of bridged CO on Ag-Pd/Al\textsubscript{2}O\textsubscript{3} in Figure A.20(a). The Ag-Pd could facilitate desorption of N\textsubscript{2} and O\textsubscript{2}, providing sites for NO dissociation. The remaining oxygen (O\textsubscript{ret}) on Ag-Pd exhibit a peculiar behavior which (i) give a low E\textsubscript{a} for O\textsubscript{2} formation during NO decomposition and (ii) show a significant O\textsubscript{2} desorption profile upon increasing temperature. These O\textsubscript{ret} on the catalyst surface may cause enrichment of
Ag on Pd through de-alloying, allowing the formation of Pd metal sites for the adsorption of Pd$^0$-NO\[^{151}\] which react with hydrogen to form NH$_3$ and H$_2$O. The de-alloying process is a solid state atomic diffusion process which possesses high E$_a$\[^{152}\]. Thus, de-alloying could only occur at 773 and 823 K at a very limited extent and do not occur at 723 K. Furthermore, the presence of hydrogen would remove the retained oxygen, produced from NO dissociation, allowing the catalyst surface to return to the alloying state.

The lack of NH$_3$ and H$_2$O formation on Ag-Pd/Al$_2$O$_3$ at 723 K suggests that the de-alloying process did not occur at this temperature. Ag-Pd/Al$_2$O$_3$ is more selective for the formation of N$_2$ from dissociated NO than that of NH$_3$ compared to Pd/Al$_2$O$_3$ which is not selective between N$_2$ and NH$_3$ formation at 723 K. Thus, it should be feasible to increase the activity and selectivity of Ag-Pd/Al$_2$O$_3$ for catalyzing the NO decomposition pathway by controlling the reaction temperature and the amount of hydrogen exposure.

A.4.5. Conclusion

The pulse transient responses show that NO decomposes over Pd/Al$_2$O$_3$ to form products in the following sequence: N$_2$, N$_2$O, and then O$_2$. During the NO pulse, the intensity of adsorbed Pd$^0$-NO at 1735 cm$^{-1}$ decreased while the intensity for Pd$^+$-NO at 1769 cm$^{-1}$ and the amount of gaseous N$_2$ product increased. Subsequent NO pulses increased the intensity of Pd$^+$-NO and slowed down the N$_2$ product response, confirming that the reaction occurs on the Pd$^0$ sites and oxygen retained on the catalyst oxidizes Pd$^0$ to Pd$^+$ sites. The addition of Ag to Pd/Al$_2$O$_3$ shifted the O$_2$ response forward. This leading behaviour for oxygen desorption from Ag-Pd/Al$_2$O$_3$ appears to be related to its
low $E_a$ for $O_2$ formation. $O_{\text{ret}}$ on Ag-Pd exhibits a unique activity where those $O_{\text{ret}}$ produced from dissociated NO at 723 K can be desorbed at 773 K and those produced at 773 K can be desorbed at 823 K. These $O_{\text{ret}}$ species are not able to oxidize $Pd^0$ on Ag-Pd/Al$_2$O$_3$ to $Pd^+$ in contrast to those on Pd. Improving oxidation resistance of Pd did not result in increasing the catalytic cycle for NO decomposition.

NO pulse into H$_2$ (i.e., NO reduction) over Pd/Al$_2$O$_3$ produced N$_2$, N$_2$O, O$_2$, NH$_3$, and H$_2$O. The addition of Ag allowed the formation of N$_2$, O$_2$, and N$_2$O in the absence of NH$_3$ and H$_2$O responses at 723 K indicating Ag delayed and suppressed NH$_3$/H$_2$O formation. This observation indicates that adsorbed hydrogen on Ag-Pd/Al$_2$O$_3$ is effective in maintaining Pd in the reduced state for NO decomposition; adsorbed hydrogen species is not able to react with adsorbed nitrogen and oxygen for NH$_3$ and H$_2$O formation at 723 K. Increasing the temperature above 723 K decreased the extent of Ag suppression for NH$_3$ and H$_2$O formation.

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APPENDIX B

CALIBRATION OF FTIR, MS, AND GC

B.1 Step Calibration

In the NO/CO reaction a large variety of products besides N\textsubscript{2} are formed all of which have close molecular weights and overlapping mass spectrometric (MS) fragmentation patterns. Unfortunately electron impact mass spectrometry cannot directly be used to access the concentrations of the various species present in the DRIFTS reactor effluent because of mass fragment overlap. Therefore in order to deconvolute the MS signals and to arrive at the measurement that directly is attributed to each species a matrix inversion technique is used to directly derive the MS intensities which correspond to known concentrations from calibration experiments of the mass spectrometer.

Table B.1 lists the mass fragmentation patterns for gaseous CO, CO\textsubscript{2}, H\textsubscript{2}, N\textsubscript{2}, N\textsubscript{2}O, NO, NO\textsubscript{2}, and O\textsubscript{2}. The mass spectrometer measures the total intensity derived from the contributions of all the respective compounds. The total intensity (I\textsubscript{\text{total}}\text{)} is a linear combination of the contributions from the different overlapping fragments found in the gas mixture plus the background as shown in Eqn. (B1):\n
\[
I_n^{\text{total}} = \sum_{i=1}^{n} \alpha_{n}^{\text{species}} \cdot I_n^{\text{species}} + I_n^{\text{background}} \quad \text{(B1)}
\]
The background can be obtained by performing a blank experiment using CaF\(_2\) in the DRIFTS reactor. The total intensity, for each m/e, may be written out explicitly as shown in Eqn. (B2) through (B7). Using the linear combination of fragmentation patterns, it is possible to deconvolute the overlapping intensities using a matrix inversion technique.

\[
I_{14}^{\text{total}} = 0 \cdot I_{28}^{CO} + 0 \cdot I_{44}^{CO_2} + \alpha_{14}^{N_2} \cdot I_{28}^{N_2} + \alpha_{14}^{N_2O} \cdot I_{44}^{N_2O} + \alpha_{14}^{NO} \cdot I_{30}^{NO} + \alpha_{14}^{NO_2} \cdot I_{44}^{NO_2}
\] (B2)

\[
I_{16}^{\text{total}} = \alpha_{16}^{CO} \cdot I_{28}^{CO} + \alpha_{16}^{CO_2} \cdot I_{44}^{CO_2} + 0 \cdot I_{28}^{N_2} + \alpha_{16}^{N_2O} \cdot I_{44}^{N_2O} + \alpha_{16}^{NO} \cdot I_{30}^{NO} + \alpha_{16}^{NO_2} \cdot I_{44}^{NO_2}
\] (B3)

\[
I_{28}^{\text{total}} = \alpha_{28}^{CO} \cdot I_{28}^{CO} + \alpha_{28}^{CO_2} \cdot I_{44}^{CO_2} + \alpha_{28}^{N_2} \cdot I_{28}^{N_2} + \alpha_{28}^{N_2O} \cdot I_{44}^{N_2O} + 0 \cdot I_{30}^{NO} + 0 \cdot I_{44}^{NO_2}
\] (B4)

\[
I_{30}^{\text{total}} = 0 \cdot I_{28}^{CO} + 0 \cdot I_{44}^{CO_2} + 0 \cdot I_{28}^{N_2} + \alpha_{30}^{N_2O} \cdot I_{44}^{N_2O} + \alpha_{30}^{NO} \cdot I_{30}^{NO} + \alpha_{30}^{NO_2} \cdot I_{44}^{NO_2}
\] (B5)

\[
I_{44}^{\text{total}} = 0 \cdot I_{28}^{CO} + \alpha_{44}^{CO_2} \cdot I_{44}^{CO_2} + 0 \cdot I_{28}^{N_2} + \alpha_{44}^{N_2O} \cdot I_{44}^{N_2O} + 0 \cdot I_{30}^{NO} + 0 \cdot I_{44}^{NO_2}
\] (B6)

\[
I_{46}^{\text{total}} = 0 \cdot I_{28}^{CO} + \alpha_{46}^{CO_2} \cdot I_{44}^{CO_2} + 0 \cdot I_{28}^{N_2} + 0 \cdot I_{44}^{N_2O} + 0 \cdot I_{30}^{NO} + \alpha_{46}^{NO_2} \cdot I_{44}^{NO_2}
\] (B7)

Writing out all of the total MS intensities there are 6 unknown variables and 6 equations. The \(\alpha_{nm}^{\text{species}}\) are the ratios of the abundances of the fragments of a given species which are determined during the MS calibration experiments. The \(\alpha_{nm}^{\text{species}}\) are assumed to be constant for a given experiment and is defined by Eqn. (B8).
\[ \alpha_{\text{species}}^{\text{am}} = \frac{I_{n}^{\text{species}}}{I_{m}^{\text{species}}} \]  

(B8)

Where \( I_{n} \) and \( I_{m} \) are abundances at mass numbers \( n \) and \( m \) respectively. The \( \alpha_{\text{species}}^{\text{am}} \) values for all the species expected to be present are determined and listed in Tables B.2, B.3, B.4, and B.5.

Table B.1  Mass number assignments for the species of interest.

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Table B.2  Calibration Intensity data, Peak heights for three concentration profiles, CO, CO2, NO species.

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</tr>
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</tr>
<tr>
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<td>1.30E-10 1.12E-12 3.71E-12 2.64E-12 6.12E-11 -2.02E-12 2.49E-11 6.42E-12 -2.70E-12 -3.57E-14</td>
</tr>
<tr>
<td>Conc. (3)</td>
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</tr>
<tr>
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</tr>
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<td>Height (C1)</td>
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295
### Table B.3  Calibration Intensity data, Peak heights for three concentration profiles, N\textsubscript{2} species.

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### Table B.4  Calibration Intensity data, Peak heights for three concentration profiles, N\textsubscript{2}O species.

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### Table B.5  Calibration Intensity data, Peak heights for three concentration profiles, NO\textsubscript{2} species.

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</tbody>
</table>
Having 6 equations and 6 unknown variables (Eqn. B2 – B7) it is possible to solve for 6 unknown MS intensities of each contributing species using a matrix inversion mathematical technique. This may be accomplished by setting up a 6 X 6 matrix (see Eqn. B9) using Microsoft Excel built in matrix operators.

\[
\begin{bmatrix}
0 & 0 & \alpha_{14}^{N_2} & \alpha_{14}^{N_2O} & \alpha_{14}^{NO} & \alpha_{14}^{NO_2} \\
\alpha_{16}^{CO} & \alpha_{16}^{CO_2} & 0 & \alpha_{16}^{N_2O} & \alpha_{16}^{NO} & \alpha_{16}^{NO_2} \\
\alpha_{28}^{CO} & \alpha_{28}^{CO_2} & \alpha_{28}^{N_2O} & 0 & \alpha_{28}^{NO} & \alpha_{28}^{NO_2} \\
0 & 0 & 0 & \alpha_{30}^{N_2O} & \alpha_{30}^{NO} & \alpha_{30}^{NO_2} \\
0 & \alpha_{44}^{CO_2} & 0 & \alpha_{44}^{N_2O} & 0 & 0 \\
0 & \alpha_{46}^{CO_2} & 0 & 0 & 0 & \alpha_{46}^{NO_2}
\end{bmatrix}
\begin{bmatrix}
I_{14}^{CO} \\
I_{16}^{CO_2} \\
I_{28}^{CO} \\
I_{28}^{CO_2} \\
I_{44}^{N_2O} \\
I_{46}^{NO_2}
\end{bmatrix}
= 
\begin{bmatrix}
I_{14} \\
I_{16} \\
I_{28} \\
I_{30} \\
I_{44} \\
I_{46}
\end{bmatrix}
\]

(B9)

The functions “mmult” and “minverse” matrix multiplication and matrix inverse functions respectively are used to find a solution to the six linear equations according to the following method shown in Eqn. (B10) and (B11):

\[
Ax = b
\]

(B10)

where “A” is the matrix of the non-homogeneous equations, “x” is a vector of the unknown variables, and “b” is the vector solution to each linear equation. The unknown variables can be solved by taking the matrix inverse to obtain the following equation:
\[ x = A^{-1}b \]  \hspace{1cm} (B11)

where \( A^{-1} \) is the inverse of matrix \( A \).

The mass spectroscopic data is taken as a function of time and excel enables the solution of the linear equations simultaneously on the entire data set obtained during the experimental run. Having the MS intensities for each unknown species, a correlation can be made linking the unknown MS intensities obtained during the experiment with those of the known MS intensities from the calibration experiment.

The presence of nitrogen dioxide (NO\(_2\)) poses an additional experimental difficulty; the reaction of NO with O\(_2\) at room temperature is thermodynamically favorable for forming NO\(_2\) therefore the accuracy on data analysis in the FTIR, MS, and GC and the presence of NO\(_2\) need to be considered. The calibration experiments need to be carefully designed to back calculate the amount of NO\(_2\) in order to obtain the correct ratio of abundances (\( \alpha_{m}^{\text{species}} \)) for nitrogen dioxide as well as account for any gas phase reactions that may occur within the lines leading to the MS and GC. In order to back calculate the amount of NO\(_2\) formed at room temperature, two different concentration profiles needed to be performed. The two concentrations of NO and O\(_2\) lead to different peak intensities, and peak areas on the FTIR, shown in Figures B.2 and B.3, and GC spectroscopic data, shown in Figures B.6 through B.11, as well as different MS intensities on the mass spectrometer, shown in Figure B.1. To solve the room temperature NO\(_2\) problem a mass balance is developed based on the room temperature reaction of NO with O\(_2\). Using the mass balance, along with two different NO/O\(_2\) concentration profiles, it was possible to (i) separate gas phase reaction data taking place
within the lines and (ii) obtain the ratio of abundance for NO$_2$ (i.e. the FTIR data was correlated with the adjusted MS intensity data to achieve the corrected $\alpha_{\text{NO}_2}$).

Plotting the integrated areas for gas phase NO and CO obtained from the FTIR measurement are shown in Figure B.4. The integrated areas exhibit non-linearity and demonstrate the importance for choosing the correct concentration region while using the FTIR for quantifying the temperature programmed reaction data at high temperatures.
Figure B.1  Mass spectroscopic calibration intensity data for determination of MS intensities for each species.
Figure B.2  Infrared spectroscopic data of the first concentration profile; Infrared was used to calibrate the MS intensity data of CO, NO, and NO₂.
Figure B.3  Infrared spectroscopic data of the second concentration profile; Infrared was used to calibrate the MS intensity data of CO, NO, and NO2.
Figure B.4  Linear relationship of the FTIR peak heights and area for gas phase CO and NO.
Figure B.5  GC Calibration data to find the retention times of H₂, O₂, CO, and NO.
Figure B.6  Gas Chromatographic data, retention times, peak height and areas for CO, NO, O₂, N₂, and H₂.
Figure B.7  Gas Chromatographic data, retention times, peak height and areas for CO, NO, O₂, N₂, and H₂.
Figure B.8  Gas Chromatographic data, retention times, peak height and areas for CO, NO, O₂, N₂, and H₂.
Figure B.9  Gas Chromatographic data, retention times, peak height and areas for CO, NO, O₂, N₂, and H₂.
Figure B.10  Gas Chromatographic data, retention times, peak height and areas for CO, NO, O₂, N₂, and H₂.
Figure B.11  Gas Chromatographic data, retention times, peak height and areas for CO, NO, O₂, N₂, and H₂.
B.2 Pulse Calibration

The pulse technique makes it possible to determine the consumption and formation of reactants and products respectively in time for chemically reacting systems. In order to quantify the amounts of reactants and products resulting from a catalytic reaction, it is necessary to calibrate the MS by pulsing known reactants and products. In order to quantify unknown amounts of products formed it is necessary to calculate the amount/volume of species formed relative to a known concentration of another species. The unknown volume can be determined from Eqn. (B12).

\[
Volume_A = \frac{Area_A}{Area_B} \cdot \frac{Volume_B}{C_{A/B}} \tag{B12}
\]

The corresponding relationship between the known and unknown species is by what is called a calibration factor \(C_{A/B}\). The calibration factor relates the volume of moles of a known species relative to the volume of moles of another known species. For the experiment it is assumed the calibration factors are constant. In order to determine the calibration factors, a pulse of a known volume of pure gas into an inert carrier gas at room temperature is sent to the MS as shown in Figure B.12. The resulting pulse areas are integrated the respective mass fragments which correspond to the given species. With the integrated areas, the calibration factor can be calculated using Eqn. (B13).

\[
C_{A/B} = \left( \frac{Area_A}{Volume_A} \right) \frac{Volume_B}{Area_B} \tag{B13}
\]
Figure B.12  MS pulse data obtained for the NO/CO reaction calibration. (Pulse size = 0.53 ml)
In the case of the calibration experiment, the pulse volume remained the same therefore the calibration factors are simply the ratio of the integrated areas.

The calibration factors obtained for the NO/CO reaction were obtained pulsing 0.53 ml of pure gas into He as a carrier gas. Table B.6 shows the integrated areas of the MS responses for each species. The average integrated area is taken over three pulses in the calculation of the calibration factor. Table B.7 shows the values of the calibration factors for H₂, CO, CO₂, N₂, NO, N₂O, and O₂.
### Table B.6 Integrated areas of the calibration species obtained from the Pfeiffer Mass Spectrometer.

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### Table B.7 Listing of calibration factors for the Pfeiffer Mass Spectrometer. (m/e values shown in parenthesis with each species)

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APPENDIX C

ERROR ANALYSIS AND EVALUATION OF ANALYTICAL DATA

The evaluation of analytical data is essential when using laboratory equipment to collect and determine the quantitative amounts of CO₂, H₂S, or SO₂ desorbing from a sorbent. The reproducibility of results is an absolute necessity for gaining confidence in the measured results. Estimation of the accuracy of results is also an important part of experimental analysis because data of unknown reliability is essentially useless. This appendix is organized by first looking at precision, accuracy, and detection limit of the analytical instrumentation in the laboratory. It is important to understand the difference in what is meant by the use of precision, accuracy, and detection limits and how it is related to the reliability of our data. Then we will look at a few sources of variance that are inherently a part of the experimental laboratory.

C.1 Precision and Accuracy

Precision describes the reproducibility of results. The precision of a measurement refers to the agreement between numerical values for two or more replicate measurements. These measurements may be the result of experiments performed on the same or different days. The precision of an analytical method is easily obtained by simply repeating the measurement. From the repeated experiments, the precision may
then be described by (i) the standard deviation, (ii) the variance, and (iii) the coefficient of variation. These are standard statistical terms which may be found in most books on the design and analysis of experiments.

Accuracy describes the correctness of an experimental result that is defined by the closeness of the measured value to the true or accepted value. The accuracy of a measurement can be a relative term with respect to a given instrument. For example, one FTIR may be more accurate or inaccurate depending upon the age (weaker source) or improper alignment of the instrument. Using only one instrument along with frequent use of an internal standard for calibration can eliminate most accuracy issues. Accuracy is expressed in terms of either “absolute error” or “relative error.” The absolute error “E” of the mean or average (\( \bar{x} \)) of a small set of replicated measurements is given by the relationship in equation C1.

\[
E = \bar{x} - x_i \quad \text{(C1)}
\]

\(x_i\) is the true or accepted value of the amount being measured. Most often the error is expressed as relative error according to equation C2.

\[
E_r = \frac{\bar{x} - x_i}{x_i} (100) \quad \text{(C2)}
\]

The relative error is a percentage. The accuracy is related to error in two ways (i) random errors and (ii) systematic errors. Random error may be eliminated by replicating the
experiment 20 or more times. This becomes quite impractical when considering amine based sorbents that may show a deactivation after 5 or more adsorption/desorption cycles. Systematic errors can lead to bias in the measurement results. Bias causes the quantitative values determined from the analytical results to diverge from the true quantity. There are three types of systematic errors (i) instrumental, (ii) personal (human), and (iii) the experimental method. The instrumental error results from instruments that are non-ideal due to age, faulty calibrations, or the instrument is used under inappropriate conditions. Human error will be discussed in section C-5.

C.3 The Detection Limit

The detection limit is the lower limit of detection (LOD) of an analytical instrument. The LOD is the lowest possible quantity of a substance that can be distinguished from the absence of that substance that may be stated within a specific confidence limit (i.e. 1%). The LOD for most instruments may be obtained from the manufacturer in most cases. In the case when the LOD cannot be obtained from the manufacturer, the LOD may be estimated from the mean, standard deviation, and confidence factor of a blank run. There is no manufacturer specified LOD for CO₂ but it is noted the FTIR has an LOD much lower than atmospheric CO₂ (300 ppm).

- The FT-IR instrument in our laboratory manufactured by Varian Inc., LOD % v/v ethanol/H₂O is 0.08, peak height at 1045 cm⁻¹, 4.6 x 10⁻⁴ abs, the peak-to-peak noise at 1220-1120 cm⁻¹ is 1.4 x10⁻⁴ abs.
- The Pfeiffer MS detection limit lies between $1.0 \times 10^{-16}$ and $1.0 \times 10^{-14}$ A depending on the hold time constant between 2 sec to 100 ms. The typical hold time constant is set to 50 ms during the MS measurements.

- The SRI Instruments GC Thermal Conductivity Detector (TCD), can detect fixed gases $\text{O}_2$, $\text{N}_2$, CO, CO$_2$, H$_2$S, NO, and NO$_2$ down to around 100 ppm. The Flame Ionization Detector (FID) detector can provide 1 ppm detection for hydrocarbon species. The Helium Ionization Detector (HID) is used for volatile inorganics (i.e. NO$_x$, CO, CO$_2$, O$_2$, N$_2$, and H$_2$) and makes possible detection down to 10 ppm.

C.4 Error and Sources of Variance

Analytical techniques are utilized to collect the data as one performs a test or series of tests by varying input variables of a process or system. There are certain physical limitations inherent within these analytical techniques thus it is only possible to obtain a representative sampling of the population of interest. The action of measuring the sample results in inherent imperfections which give raise to variance leading to errors in the measured data. The resulting measurement therefore is an approximation to the true population of interest requiring a statement of the uncertainty of the approximation. The confidence of the measurement to its real value relates to the accuracy of the analytical technique and the reproducibility of the measurement as noted earlier. Sources of error which affect measurement include:
1. Human error

2. Sampling error introduced from the analytical technique.

3. Poor material quality, a chemical such as peroxide (H₂O₂) has a shelf life which can introduce error if the chemical has reached its expiration.

Once a representative sample (the data) has been collected it is important to interpret the data in pictorial form by plotting the data and utilizing tabular methods in descriptive statistics to gain understanding of the precision of measurement. Many visual techniques that can be utilized include frequency tables, histograms, pie charts, scatter diagrams, etc. Visual summaries of data are excellent tools for obtaining preliminary impressions and insights.

Reproducibility of a measurement gauges the quality of the measured data. The center of data is an important and useful measure called the mean or arithmetic average of the set shown in equation C3.

\[
\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}
\]  

(C3)

Where “\(x_i\)” represents an individual measurement from a set of “n” measurements. The primary measure of variability involves measuring the deviations from the mean (i.e. \(x_i - \bar{x}\)). This variability or sample variance is called the standard deviation and can be calculated using equation C4.
The sample variance will improve (decrease) by increasing the set of “n” measurements. Finally, the measured quantity can be expressed as $\bar{x} \pm \sigma$ a simple measure of uncertainty.

The relationship between $\bar{x}$ and $\sigma$ for a large number of measurements where the data is Gaussian or mound shaped the “Empirical Rule” applies where 68% of the data are within one standard deviation of the mean value ($\bar{x} - \sigma \leq \text{values} \leq \bar{x} + \sigma$), 95% of the data are within two standard deviations of the mean ($\bar{x} - 2\sigma \leq \text{values} \leq \bar{x} + 2\sigma$), and virtually all of the data is within three standard deviations of the mean ($\bar{x} - 3\sigma \leq \text{values} \leq \bar{x} + 3\sigma$).

C.5 Human Error

Human error is also a factor in experimental analysis due to the latency time of oligosynaptic muscle response to stimuli obtained via the visual cortex (human eye). This application occurs while setting flow rates for the process gases; the process gases are measured visually using a bubble meter and a stop watch. The error occurs when trying to establish the flow rate of the process gases via the stop watch because a physical response is required from the experimenter thus causing variations in flow rates between experiments.

Research that has been conducted analyzing short latency reflex (Hoffman reflex) and the long latency reflex pathways for various muscle groups in the human body.
Thus, average response times for the human hand muscle corresponding to various stimuli have been well documented in the literature. \[119-125\] The mean short latency and mean long latency response times are approximately 31.5ms and 56.5ms respectively for a healthy adult. \[125\]

C.6 Infrared Spectrometer Error

The Infrared (IR) spectrometer was utilized to obtain information about the surface of the catalyst in a qualitative manner and not quantitative. Therefore error associated with absorbance spectra is not important. However, the error associated with IR is expressed in signal-to-noise ratio (SNR). Noise is the most unavoidable type of problem in a spectrum using Fourier transform spectrometer resulting from the detector and results in spectra looking blurry and lacking definition (i.e. fuzzy). Therefore it is important to increase the set of “n” measurements. Typically 32 spectra are averaged to reduce the SNR.

C.7 Mass Spectrometer Error

The mass spectrometer is used for both qualitative and quantitative measurements. Quantitative measurements for, conversion and selectivity measurements, require replication (reproducibility) as the primary source for determining error during calibration of the mass spectrometer. Calibration involves making a step change in concentration or pulsing gas species to the mass spectrometer. The resultant data are analyzed by integrating the individual peaks and averaging to obtain an accurate value for
the area. The deviations in area obtained from a series of three pulses are less than 1%.

MS calibration is discussed in Appendix B.
D.1 Electron Paramagnetic Resonance Literature Summary

Electron paramagnetic resonance (EPR) is a spectroscopic technique used for identifying paramagnetic substances and for investigating the nature of bonding within molecules by identifying the unpaired electrons and their interaction with nearby atoms. Unpaired electrons behave as paramagnetic species therefore, EPR has been used to study adsorbed oxygen on metal oxide surfaces and including charge transfer between such paramagnetic species. Colloidal TiO$_2$ particles have been used as models for studying charge-transfer processes at the liquid-semiconductor interface [1]. Electrons produced during band-gap UV-irradiation are trapped as surface Ti$^{3+}$ sites in the presence of suitable hole scavengers. In the absence of hole scavengers, trapping occurs only at interior sites. Acid/base studies have shown that in acidic solution all of the trapped electrons are accounted for as Ti$^{3+}$ and in basic solutions only 10% of the electrons are detected as EPR-visible Ti$^{3+}$. The photochemical event occurring in such systems on UV-irradiation is the production of electrons and holes, but the subsequent reactions which take place are not well understood including recombination of electrons and holes, trapping, charge transfer across the semiconductor gas/liquid interface, and reaction with adsorbed molecules. The extinction coefficient for electron adsorption and wavelength
varies with pH of TiO$_2$ in solution, suggesting that the electron trap sites are located at the surface of the colloidal particles. This is also supported by the observation that the appearance of EPRR spectrum can differ between different colloid preparations.

Adsorption of oxygen on the surface of various oxides under UV irradiation has been extensively investigated [1-8]. EPR spectroscopy has shown that typically O$_2^-$ species are formed, where the unpaired electron is stabilized in an anti-bonding pi-orbital. Oxygen adsorbed upon TiO$_2$ and irradiated with UV light causes three different paramagnetic species, O$_2^-$, O$_3^-$, O$_3^{2-}$. The reactivity of the oxygen species with CO at low temperature has also been studied and it has been shown that CO readily reacts with the O$_3^{2-}$ species at 77 K [9].

The effect of pre-treatment by temperature and H$_2$O$_{ad}$ on the UV photo-adsorption of O$_2$ on TiO$_2$ has also been studied [3]. It was found that the level of hydroxylation determines the oxygen species and photo-adsorption mechanisms. A quantitative relation has been found between the number of hydroxyl groups on the TiO$_2$ surfaces and their photo-activity, while a change of mechanism from first order to a diffusion controlled process was observed when the OH groups were progressively removed from the surface. The best known of the oxy-radicals is O$_2^-$ whose stability against redox exchange with Ti$^{3+}$ ions has been recently supported on the basis of quantum-mechanical arguments, while the peroxide ion O$_2^{2-}$ seems unlikely on the basis of the most recent results in aqueous solutions [3]. It is well known that several other oxy-radicals are created on the UV-irradiated TiO$_2$ surfaces such as the existence of O$_3^-$ and O$_3^{2-}$ species, in addition to O$_2^-$ and Ti$^{3+}$, when the TiO$_2$ surfaces, pre-treated at 500 °C, are UV-irradiated at low
temperatures (77 K). The aim of the study was to use EPR to investigate the evolution of radicals at the TiO₂ anatase surface as a function of its hydroxylation state, in order to see whether a correlation could be established between the kinetic results and the types of radicals on the surface.

Other studies have investigated ZnO [2] and MgO [4] to identify the effect of surface –OH groups on the paramagnetic species. ZnO is doped with Cu forming a complex of impurity centers with distinct EPR properties. Surface hydroxyl groups lower the coordination symmetry for Cu²⁺ ions at the cation lattice sites. The low temperature EPR spectrum of Cu²⁺ shows a strong influence of motional effects on the shape of the Cu²⁺ hyperfine structure lines. MgO was investigated in order to confirm the existence of an O⁻ species on the Mg surface [4]. EPR spectroscopy confirmed the existence of the oxygen ion. It was determined that the ion may be stabilized by trapping in a solid matrix (i.e. alkali halide) such as KCl and KBr crystals. The O⁻ species could be produced on MgO by adsorption of N₂O on the MgO surface in the presence of trapped electrons. The interaction of oxygen with UV-irradiated ZnO and MgO indicate that adsorption of oxygen at room temperature results in the rapid formation of the radical species [10]. Though the nature of room temperature oxygen adsorption on metal oxides has been the subject of numerous investigations, it is not clear however whether the chemisorbed species is O₃⁻, O⁻, a peroxy group that is covalently bonded to the surfaces as S-O-O or some combination of these. Thermodynamic considerations also rule out the possibility of certain species not mentioned. It has been shown that a charge-transfer step is involved when O₂ is adsorbed on an n-type semiconductor such as ZnO. Oxygen adsorption has also been studied on nickel oxide, magnesium oxide, and silica gel.
Vacuum studies along with EPR analysis during UV-irradiation of hydrated anatase suggest Ti$^{3+}$ sites within the bulk and holes trapped at the lattice oxide ions below the surface [1]. In the presence of O$_2$, the trapped electrons are removed and the trapped holes are stable to 77 K and warming the TiO$_2$ to room temp results in the loss of trapped holes and formation of O$_2^-$ at the surface.

EPR spectroscopy has been widely used to examine paramagnetic species on TiO$_2$ surfaces in order to identify radicals formed during UV irradiation which may be important in photocatalytic processes. The majority of such EPR studies to date have however employed anhydrous TiO$_2$ out gassed at high temperatures, a pre-treatment which leaves the surface free of adsorbed H$_2$O and containing isolated hydroxyl groups. In the important area of photocatalytic decomposition of water over TiO$_2$-based catalyst, the surface chemistry of the catalysts is dominated by –OH groups and adsorbed water, yet there is little information available about radical species formed on such hydrated surfaces. Radicals formed during the photo-oxidation of phenol on TiO$_2$ shows that in the absence of phenol the presence of H$_2$O$_2^-$ radicals are detected on UV-irradiated anatase, their relative contributions to the spectra depend on the hydration state of the surface [11]. A number of studies about the mechanism of TiO$_2$ photo-reactivity have lead to the proposal of several different mechanisms on the initial steps during the initiating reaction. It is proposed that two species have been considered as the active species for the initial oxidation step: valence band holes are transferred directly to the organic substrate, and $OH^-$ radicals formed by hole oxidation of OH- groups or H$_2$O molecules on the TiO$_2$ particle surface. Taking the $OH^-$ radical as the oxidant, two
situations have been proposed, distinguished by whether oxidation occurs by $OH^-$ species at the particle surface or by a free $OH^-$ radical which desorbs.

The Ti$^{3+}$ species are also responsible for the blue color which develops during UV-irradiation of colloidal TiO$_2$ in the presence of hole scavengers. An understanding of the reaction pathways available to holes and electrons produced by band-gap irradiation of TiO$_2$ and related materials is essential if improved water dissociation catalysts are to be developed. This study takes hydroxylated TiO$_2$ with the objective of identifying the species produced by initial trapping of holes and electrons and their subsequent reaction products.

TiO$_2$ has the ability to oxidize a number of hazardous materials to nontoxic products and it has become the benchmark semiconductor in photo-detoxification of contaminated water [5]. Band-gap UV-irradiation of TiO$_2$ leads to the generation of electron-hole pairs and irradiation of small TiO$_2$ particles in the presence of H$_2$O leads to the formation of OH radicals formed by trapping of photo-generated holes by the surface OH groups [6]. For example, UV irradiation of the sample containing adsorbed H$_2$O at 77 K gives rise to an EPR signal at $g_1 = 2.014$ and $g_2 = 2.003$, showing an increasing intensity with the UV-irradiation time at 77 K, shown in Table D-1. The formation of this signal is accompanied the formation of a much smaller amount of Ti$^{3+}$ ions characterized by $g = 1.988$ [7].

EPR results of paramagnetic traps produced on hydrothermally prepared TiO$_2$ particles during water photolysis at room temperature under band-gap irradiation [8] indicate that the trapped holes correspond to O$^-$ species adjacent to cation vacancies that are formed to compensate for the hydroxyl ions in the subsurface layers. The trapped
electrons are accounted for as Ti$^{3+}$ in the conduction band. The mechanism of light-induced charge transfer processes at TiO$_2$ particles are of interest to those working on hydrogen energy systems through water photolysis. It is essential to understand the reaction paths for photogenerated holes and electrons. Now oxygen adsorbed on slightly reduced TiO$_2$ has been investigated using oxygen enriched with isotopic $^{17}$O$_2$ [12]. On anatase TiO$_2$, oxygen adsors as $O_2^-$ producing a hyperfine splitting of the EPR signal. On rutile TiO$_2$, oxygen adsorbs as $O_2^-$ on two sites having different thermal stability located at (i $g_1=2.0030$, $g_2=2.008$, $g_3=2.004$, and (ii) $g_1=2.020$, $g_2=2.009$, $g_3=2.003$. Evidence suggests $O_2^-$ exists in an ionic form on the TiO$_2$ and other oxides. Adsorption of oxygen on the surface of oxides, investigated using EPR spectroscopy, suggest electron transfer occurs during the adsorption process to produce the oxygen species $O_2^-$, $O_2^+$, and O$^-$ on the TiO$_2$ surface [13].
Table D.1  g-values of oxygen, and other EPR observable species.

<table>
<thead>
<tr>
<th>Radicals</th>
<th>g&lt;sub&gt;1&lt;/sub&gt;</th>
<th>g&lt;sub&gt;2&lt;/sub&gt;</th>
<th>g&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>O&lt;sup&gt;-&lt;/sup&gt; (rutile+Ga)</td>
<td>2.007</td>
<td>2.023</td>
<td>2.030</td>
<td>[2]</td>
</tr>
<tr>
<td>O&lt;sup&gt;-&lt;/sup&gt; (rutile+Al)</td>
<td>2.003</td>
<td>2.019</td>
<td>2.026</td>
<td>[2]</td>
</tr>
<tr>
<td>O&lt;sup&gt;-&lt;/sup&gt; (V center, TiO&lt;sub&gt;2&lt;/sub&gt; surface)</td>
<td>2.004</td>
<td>2.016</td>
<td>2.028</td>
<td>[3]</td>
</tr>
<tr>
<td></td>
<td>2.002</td>
<td>2.042</td>
<td>2.042</td>
<td>[4]</td>
</tr>
<tr>
<td></td>
<td>2.0026</td>
<td>2.021</td>
<td>2.016</td>
<td>[14]</td>
</tr>
<tr>
<td>Ti&lt;sup&gt;+&lt;/sup&gt; (hydrated anatase)</td>
<td>1.960</td>
<td>1.990</td>
<td>1.990</td>
<td>[1]</td>
</tr>
<tr>
<td>Ti&lt;sup&gt;3+&lt;/sup&gt;O&lt;sup&gt;-&lt;/sup&gt;Ti&lt;sup&gt;4+&lt;/sup&gt;O&lt;sup&gt;-&lt;/sup&gt;</td>
<td>2.0073</td>
<td>2.0188</td>
<td>2.0273</td>
<td>[5]</td>
</tr>
<tr>
<td>·OH (in H&lt;sub&gt;2&lt;/sub&gt;O ice)</td>
<td>2.0027</td>
<td>2.009</td>
<td>2.059</td>
<td>[15]</td>
</tr>
<tr>
<td>·OH (on TiO&lt;sub&gt;2&lt;/sub&gt; surface)</td>
<td>2.0032</td>
<td>2.0146</td>
<td>2.0146</td>
<td>[6]</td>
</tr>
<tr>
<td>Ti&lt;sup&gt;3+&lt;/sup&gt; (interstitial, colloidal TiO&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>1.957</td>
<td>1.988</td>
<td>1.988</td>
<td>[16]</td>
</tr>
<tr>
<td>Ti&lt;sup&gt;3+&lt;/sup&gt; (surface, colloidal TiO&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>1.885</td>
<td>1.925</td>
<td>1.925</td>
<td>[16]</td>
</tr>
<tr>
<td>Ti&lt;sup&gt;3+&lt;/sup&gt; (surface, colloidal TiO&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>1.885</td>
<td>1.930</td>
<td>1.930</td>
<td>[16]</td>
</tr>
<tr>
<td>Ti&lt;sup&gt;3+&lt;/sup&gt; (surface, colloidal TiO&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>1.880</td>
<td>1.945</td>
<td>1.945</td>
<td>[16]</td>
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<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;H&lt;sup&gt;-&lt;/sup&gt;</td>
<td>2.002</td>
<td>2.008</td>
<td>2.034</td>
<td>[11]</td>
</tr>
<tr>
<td>Ti(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>1.988</td>
<td>1.892</td>
<td>1.892</td>
<td>[7]</td>
</tr>
<tr>
<td>Ti&lt;sup&gt;3+&lt;/sup&gt;VoTi&lt;sup&gt;4+&lt;/sup&gt;</td>
<td>1.965</td>
<td></td>
<td></td>
<td>[8]</td>
</tr>
<tr>
<td>TiO&lt;sup&gt;-&lt;/sup&gt;Ti&lt;sup&gt;4+&lt;/sup&gt;OH&lt;sup&gt;-&lt;/sup&gt;</td>
<td>2.030</td>
<td>2.030</td>
<td>2.030</td>
<td>[8]</td>
</tr>
<tr>
<td>Ti&lt;sup&gt;3+&lt;/sup&gt; (anatase+Nb)</td>
<td>1.962</td>
<td>1.992</td>
<td>1.992</td>
<td>[17]</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt; (on TiO&lt;sub&gt;2&lt;/sub&gt;, adsorbed oxygen)</td>
<td>2.003</td>
<td>2.009</td>
<td>2.025</td>
<td>[12]</td>
</tr>
<tr>
<td>O&lt;sub&gt;2-&lt;/sub&gt; (on TiO&lt;sub&gt;2&lt;/sub&gt;, adsorbed oxygen)</td>
<td>2.001</td>
<td>2.009</td>
<td>2.021</td>
<td>[9]</td>
</tr>
<tr>
<td>O&lt;sub&gt;2-&lt;/sub&gt; (on ZnO, absorbed oxygen)</td>
<td>2.002</td>
<td>2.008</td>
<td>2.051</td>
<td>[10]</td>
</tr>
<tr>
<td>O&lt;sub&gt;2-&lt;/sub&gt; (on zeolites, adsorbed oxygen)</td>
<td>2.004</td>
<td>2.009</td>
<td>2.057</td>
<td>[13]</td>
</tr>
</tbody>
</table>
Figure D.1 EPR spectra of TiO$_2$ at 115 K without UV-irradiation in the absence of ethanol.
Figure D.2  EPR spectra of TiO$_2$ at 115 K without UV-irradiation in the presence of ethanol.
Figure D.3  EPR spectra of TiO$_2$ at 115 K during UV-irradiation in the absence of ethanol.
Figure D.4  EPR spectra of TiO$_2$ at 115 K during UV-irradiation in the presence of ethanol.
Figure D.5 EPR spectra of TiO$_2$ at 115 K after 30 min UV-irradiation in the presence of ethanol.
Figure D.6  EPR spectra of TiO$_2$ during the first 20 min on UV-irradiation in the absence of ethanol.
Figure D.7 EPR spectra of TiO$_2$ during the first 20 min following UV-irradiation (turn off UV) in the absence of ethanol.
Figure D.8 EPR spectra of TiO$_2$ during the first 10 min on UV-irradiation in the presence of ethanol.
Figure D.9  EPR spectra of TiO$_2$ during 60 min following UV-irradiation (turn off UV) in the presence of ethanol.
Figure D.10 EPR spectra of TiO$_2$ during 15 min on UV-irradiation at 298 K in the absence of ethanol.
Figure D.11  EPR spectra of TiO$_2$ during 15 min following UV-irradiation (turn off UV) at 298 K in the absence of ethanol.
Figure D.12 EPR spectra of TiO$_2$ during 15 min on UV-irradiation at 298 K in the presence of ethanol.
Figure D.13  EPR spectra of Au/TiO$_2$ during 20 min on UV-irradiation at 115 K in the absence of ethanol.
Figure D.14  EPR spectra of Au/TiO$_2$ during 20 min following UV-irradiation (turn off UV) at 115 K in the absence of ethanol.
Figure D.15  EPR spectra of Au/TiO$_2$ during 20 min on UV-irradiation at 115 K in the presence of ethanol.
Figure D.16  EPR spectra of Au/TiO$_2$ during 20 min following UV-irradiation (turn off UV) at 115 K in the presence of ethanol.
D.2 Bibliography


APPENDIX E

IN SITU IR STUDY OF ADSORBED SPECIES AND PHOTOGENERATED ELECTRONS DURING THE OXIDATION OF ETHANOL OVER AU/TIO₂, PD/TIO₂, AND TIO₂ CATALYSTS

E.1 Catalyst Preparation

The 1 wt% Pd/TiO₂ catalysts were prepared by the incipient wetness impregnation of \( Pd (NO_3)_2 \cdot H_2O \) (Aldrich) onto TiO₂ (Degussa P25) and dried at 298 K. The catalyst was calcined in air at 673 K for 30 min. The gold reference catalyst (1.49 wt% Au/TiO₂) was obtained from the World Gold Council. The Pd/TiO₂ and Au/TiO₂ catalysts were studied without pretreatment. The catalysts were characterized by X-ray Diffraction (XRD) Philips Analytical X-Ray PW1710 diffractometer using Cu k\( \alpha \) radiation operating at 49 kV and 35 mA.

E.2 In Situ IR Reaction Studies

The experimental apparatus, shown in Figure E.1, consist of (i) a reactant metering system (Brooks Instrument 5850 mass flow controllers), (ii) a gas sampling system with 4-port valve, (iii) a Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS, Harrick Scientific) reactor containing 89.6 mg catalyst and placed inside a Fourier Transform Infrared Spectrometer (FTIR, Varian Inc. FTS-4000),
and (iv) a 350 W mercury lamp (Oriel 6286) with light condenser (Oriel 77800) used for
irradiating the catalyst surface. The 4-port valve allows switching the inlet flow from
100% Ar to 100% O₂ or Ar/H₂ (95/5 vol %) while maintaining a total flow rate of 35
cm³/min over the Au/TiO₂ or Pd/Al₂O₃ catalysts.

The changes in the concentration of IR-observable adsorbates are monitored by
FTIR. The IR absorbance spectrum of adsorbed and gaseous species is obtained by
\[ A = -\log \left( \frac{P_o}{P} \right) \] [1], where \( P_o \) is the background IR single beam spectrum (32 co-added
scans and resolution 4 cm⁻¹) of the catalyst under 100% Ar flow and P is the IR single
beam spectrum during the reaction study.

E.3 XRD Characterization

Figure E.2 shows the XRD patterns for the Au/TiO₂ catalyst before and after the
photocatalytic study. The XRD peaks for the anatase phase of TiO₂ occur at 25.4°, 37.9°,
48.0°, 54.0°, and 55.0°, the rutile phase of TiO₂ occur at 27.5°, 36.0°, 39.8°, 41.3°, and
56.6° [2]. The peaks for Au at 38.0°, and 43.8° were observed on the Au/TiO₂ catalyst
[3]. The peaks for PdO at 33.9° [4], Pd(111) at 40.4°, and Pd(200) at 46.4° were observed
on the Pd/TiO₂ catalyst [5]. XRD analysis shows that the photocatalytic reaction did not
result in any serious structural modifications. The Au particle size was determined to be
3.6 nm for Au/TiO₂ measured by TEM. The Pd particle size was determined to be 5.8
nm for Pd/TiO₂ by X-ray Diffraction (XRD) using the Scherer equation from line
broadening [6].
E.4 Key Observations

The key observations during the ethanol photocatalytic decomposition are summarized in the following sections for Au/TiO₂ and Pd/TiO₂ catalysts.

E.4.1 Au/TiO₂ Catalyst

1. Reducing the catalyst in 5% H₂/Ar at 400 °C for 30 min produced free electrons on the catalyst surface by an increase/decrease in IR absorbance/single beam spectra.

2. Adsorbing 2-propanol on the pre-reduced Au/TiO₂ catalyst did not affect the surface free electrons.

3. Adsorbing ethanol on the pre-reduced Au/TiO₂ catalyst did not affect the surface free electrons. The IR adsorption spectra indicate there are differences in the adsorbing species before and after reduction.

4. Sending oxygen into the reactor after 2-propanol was adsorbed upon the surface did not cause a background shift. Acetone (C=O) formation occurs immediately but this does not occur without prior reduction of the catalyst.

5. Sending oxygen into the reactor after ethanol was adsorbed upon the surface did not cause a background shift. There was no total oxidation to CO₂.

6. Irradiating the catalyst (2-propanol) results in further formation of acetone (C=O) species. There is a background shift that occurs during irradiation.

7. Irradiating the catalyst (ethanol) causes slight CO₂ formation. (i) There is significant C-H cleavage occurs (decrease in IR intensity), (ii) a significant
amount of water produced as compared to the 2-propanol. The presence of Au appears to promote H$_2$O formation rather than CO$_2$.

E.4.1 Pd/TiO$_2$ Catalyst

1. Total oxidation to CO$_2$ occurs.
2. There is an interesting H$_2$O desorption IR spectrum during 2-propanol and ethanol adsorption study (1698 and 1628 cm$^{-1}$).
3. Pd/Al$_2$O$_3$ catalyst is unreactive as a photo-catalyst for both 2-propanol and ethanol.
4. Reducing the catalyst in 5% H$_2$/Ar at 400 °C for 30 min produces free electrons on the catalyst surface which are observed in the infrared during reduction and during the adsorption of the 2-propanol and ethanol species.
5. Adsorbing 2-propanol on the pre-reduced Pd/TiO$_2$ did not affect the surface free electrons
6. Adsorbing ethanol onto the pre-reduced Pd/TiO$_2$, (i) adsorbing ethanol consumed a portion of the free electrons evidenced by a decreasing broadband adsorption, (ii) ethanol dehydrated the catalyst surface the background shift returns resulting from further freeing of electrons, (iii) the free electrons were not effective in oxidizing the ethanol to CO$_2$
7. Sending oxygen into the reactor after 2-propanol was adsorbed upon the surface resulted in the oxygen species consuming the free electrons on the surface (negative broadband adsorption) and immediate formation of ketone (C=O) species. NO CO$_2$ was formed.
8. Sending oxygen into the reactor after ethanol was adsorbed upon the surface resulted in the oxygen species consuming the free electrons on the surface (negative broadband adsorption) and the formation of CO\textsubscript{2}.

9. Irradiating the catalyst (ethanol) results in oxidation to CO\textsubscript{2}.
Figure E.1  Experimental Apparatus.
Figure E.2  XRD analysis of Au/TiO$_2$ catalyst before and after photo-catalytic reaction.
Figure E.3  IR absorbance spectra adsorption of ethanol on (a) Au/TiO$_2$, (b) Pd/TiO$_2$, and (c) TiO$_2$ catalysts at 30°C.
Figure E.4 IR difference spectra during UV irradiation adsorbed ethanol on (a) Au/TiO$_2$, (b) Pd/TiO$_2$, and (c) TiO$_2$ catalysts at 30 °C.
Figure E.5  IR single beam spectra during H₂ reduction of Au/TiO₂ catalyst 30 – to – 673 K.
Figure E.6  IR absorbance spectra during post reduction ethanol adsorption on (a) Au/TiO$_2$, (b) Pd/TiO$_2$, and (c) TiO$_2$ catalysts at 30 °C.
Figure E.7  IR absorbance spectra during post reduction introduction of O$_2$ over adsorbed ethanol on (a) Au/TiO$_2$ and (b) Pd/TiO$_2$ catalyst at 30 °C.
Figure E.8  IR difference spectra during UV irradiation of adsorbed ethanol on (a) Au/TiO₂, (b) Pd/TiO₂, and (c) TiO₂ catalysts at 30 °C.
E.5 Bibliography


APPENDIX F
MESOPOROUS MATERIALS IN DRUG DELIVERY
AND HYDROGEN STORAGE.

F.1 Ph.D. Candidacy Exam Questions

Micro/mesoporous materials with well defined pore sizes, high surface area, controlled morphology, and specific functionality provide new opportunities in applications such as drug delivery and hydrogen storage.

I. Examine the literature in the use of mesoporous materials for the controlled release of pharmaceutical species (i.e., drug).
   a. Summarize the results of recent studies.
   b. Discuss the advantages and disadvantages of the related approaches.
   c. Propose a method to study the mechanism of drug release.

II. Examine the literature in the use of micro/mesoporous materials for hydrogen storage.
    a. Summarize the results of recent studies.
    b. Discuss the advantages and disadvantages of the related approaches.
    c. Propose a method to study the mechanism of hydrogen storage.
F.2 Background

Prior to describing a summary of the literature, brief background information on mesoporous materials MCM-41 and SBA-15, what they are and how they are made will be described. Then, addressing the candidacy exam questions (i) a review of the literature on mesoporous materials and their usage in drug delivery and hydrogen storage, (ii) a summary of the advantages and disadvantages on the use of mesoporous materials in drug delivery, as well as, a summary of the advantages and disadvantages on the use of mesoporous materials in hydrogen storage will be described, and (iii) an innovative method will be proposed for studying the mechanism of drug delivery and hydrogen storage.

F.3 Mesoporous Materials

A variety of mesoporous materials have been investigated across the literature including MCM-41, MCM-48, SBA-15, H form Y type zeolites, mesoporous silica nanospheres, poly(D,L-lactide-co-glycolide) (PLGA)/mesoporous silica hybrid structures, and organic/inorganic mesoporous silica to name a few. A review of the literature however demonstrates MCM-41, MCM-48, and SBA-15 are among the most popular of the mesoporous materials being investigated in the last 10-15 years. Therefore, MCM-41 and SBA-15 shall be the focus of the materials described in this brief background on ordered mesoporous materials.

MCM-41 type materials were developed in the early 1990’s by Beck et al [1] when working with a silica type material. MCM-41 stands for Mobil Composition of Matter No. 41 after Mobil Oil Corporation. Considerable progress in developing new
mesoporous materials based upon the original MCM-41 synthesis has been performed in the literature. According to the IUPAC (International Union of Pure and Applied Chemistry) definition, porous materials are divided into three classes; microporous (pore size < 2nm), mesoporous (2–50nm), and macroporous (>50nm) materials. The term nanoporous has also been used increasingly in the literature to describe ordered mesoporous materials.

There are slight structural differences between MCM-41, MCM-48, and SBA-15. These structural differences result from the preparation of each material. In the preparation of MCM-41, the ionic surfactant and inorganic species interact such that the mesopores form a hexagonal mesostructure. MCM-48, the ionic surfactant and inorganic species interact such that the mesopores form a cubic mesostructure. SBA-15, exhibits a hexagonal mesostructure similar to MCM-41 however there are micropores within the mesowalls connecting the neighboring mesopores as a result of the block co-polymer template used in its preparation.

In MCM type materials, the mesopore sizes are primarily controlled by the length of the alkyl chain of the ionic surfactant used. Also, addition of what is called auxiliary organic molecules such as aromatics, n-alkanes, or fatty acids can lead to an expansion of the mesopore size. For example, mixing two alkyl ammonium surfactants with different alkyl chain lengths can be used to adjust the pore size between the short chain and long chain surfactants. [2] This method is the cooperative pathway and demonstrates interaction between the surfactant and the inorganic species where an organic/inorganic mesostructure composite is formed. It is also possible to use a preformed surfactant liquid crystalline phase where the precursor is preloaded and ready for the inorganic
material. The liquid crystalline precursor is called the true liquid crystal templating method.

MCM-41 type materials which are typically synthesized according to published synthesis routes [3-6] fall into three categories, (1) cooperative pathway method, (2) true liquid templating method, (3) nanocasting method. A possible mechanistic pathway for the formation of MCM-41 is shown in Figure 1.

MCM-41 preparation methods

1. Cooperative pathways method [7-9]
2. True liquid crystal templating method [10]
3. Nanocasting method utilizing preformed ordered mesoporous materials as hard templates [11, 12]

SBA-15 is prepared by a different synthesis route as compared to the MCM type materials. The synthesis route involves a co-polymer templating route; clearly this is different than the ionic surfactant route used for MCM type materials. The mesopore diameter of SBA-15 depends upon the experimental conditions, for example, increasing the gel aging temperature leads to a larger pore diameter. [13, 14] An additional property of SBA-15 is the interconnected mesopores; there is microporosity in the mesopore wall in SBA-15 which is a function of the block co-polymer templating connecting each neighboring mesopore. [14]
MCM-41 synthesis [15] begins with an ionic template chemical used to form the mesopores. The template material is hexadecyltrimethylammonium chloride (CTACl). Next a surfactant is added; in this case 9.64 g Ludox S.A.-40 is mixed in a beaker with 9.72 g tetraethylammonium hydroxide (TEAOH) obtained from Aldrich, 20 wt% in H2O, 10.00 g H2O and 8.08 g cetyltrimethylammonium chloride (25 wt% in H2O). The mixture is stirred for 15 min. at room temperature. Then an additional 16.17 g cetyltrimethylammonium chloride and 10.00 g H2O are added while stirring. The molar ratio of the solution is SiO2 : 0.2 TEAOH : 0.3 CTACl : 44.8 H2O. The solution is then added to a steel autoclave and heated to 110 °C for 24 h. The solution is then washed in H2O and ethanol heated to 40 °C. The templated material is then calcined at 540 °C at a heating rate of 1 °C/min. The mesoporous structure of MCM-41 is formed upon calcination.

SBA-15 synthesis [16, 17] begins with a polymer which is used as a template to form the mesopores. The template is a tri-block co-polymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) which is commercially available as Pluronics (P123, PEO20PPO70PEO20) obtained from BASF. Typically, 3 g of P123 is dissolved in 60 ml (1.5M) HCl. Next surfactants are added, cetyltrimethyl ammonium bromide (CTAB) 0.6 g in 25 ml DI H2O, and trimethylbenzene (TMB) in 25 ml DI H2O, which are then mixed together as 20 ml ethanol is added. The specific ratioed amount of TMB (between 0 – 0.5) added depends upon the pore size desired. Then, 10 ml tetraethyl orthosilicate (TEOS) is added dropwise to the surfactant solution as the solution is stirred continuously for 35 min. at 35 °C. The solution is then transferred to a PTFE (polytetrafluoroethylene) bottle and stored under static conditions at 75 °C for 10 h and
then aged at 80-125 °C depending upon the pore size desired. The mesoporous structure of SBA-15 is formed upon calcination at 550°C for 6 h at a heating rate of 1 °C/min.

F.4 Summary of Recent Studies

A summary of the recent literature for drug delivery, drug loading, drug release, and hydrogen storage catalysis are reported in the following sections.

F.4.1 Drug Delivery

Drug discovery is costly and time consuming taking an estimated 10-15 years which is a risky business for pharmaceutical companies. Drug delivery systems however can be developed at 20% of the cost and in half the time it takes to manufacture the drug. In the past decades polymer based delivery systems were developed for controlling and distributing site-specific drugs. Typically, cross-linked polymeric matrices such as hydrogels and supramolecular polymer aggregates as well as microencapsulation vehicles were investigated. There are various factors which contribute to having a good drug delivery system. The drug delivery system needs to maintain drug levels for long periods of time and prevent toxic peaks in drug concentration within the patient. Control via polymeric matrices offered improved efficiency and reduced toxicity [18] as well as sol-gel derived SiO₂ based materials can also be used as bioactive bone regenerative implants or bone filling material that offers controlled release properties along with bone regeneration properties. One drawback however is relatively low drug loading of the initial sol-gel derived materials preventing long term drug release. Secondly, protection
against chemical enzymatic degradations is also a problem. Polymer delivery systems do not offer such protection very well.

In contrast to the polymer based systems mesoporous materials are finding application as drug delivery systems. A review of the literature, Table 1, demonstrates MCM-41, MCM-48, and SBA-15 are among the most popular of the mesoporous materials being investigated in the last 10-15 years. Mesoporous materials offer high adsorption capacity for high drug loading, where loading is a function of the surface area and pore size which are both customizable properties. Uniform and consistent cylindrical structures and pore sizes offering reproducibility is ideal for mesoporous materials as well as offering protection against chemical enzymatic degradations, encapsulation, and long term drug release by custom functionalization of the mesopore walls.

F.4.2 Drug Loading

In Table 1, micro porous materials showed the lowest initial drug adsorption capacity and mesoporous material (MCM-41) shows a maximum initial drug adsorption capacity of up to 59 wt% when ibuprofen was used as the drug studied. [19-30] SBA-15 exhibited lower initial storage capacity as compared to MCM-41. [31-34] MCM-48 exhibited similar initial drug adsorption as the SBA-15 [35-37]. Other mesoporous silica materials were evaluated and exhibit similar initial drug adsorption as the MCM-41 and SBA-15 materials averaging around 25 wt% loading [38, 39].

The drug loading kinetics is affected by the interactions between the drug, the solvent, and the support matrix which the drug is loading upon. For fast and high loading to occur, the mesopore-substrate and substrate-substrate interactions must be more
favorable than the substrate-solvent interaction. For example, if the drug is dissolved in a hydrophilic solvent, the solvent will compete with the hydrophilic sites on the mesoporous materials resulting in lower drug loading. This is the source of the divergence in loading between different MCM-41 using ibuprofen as the drug. [19-21, 25, 26, 40] Furthermore, hydrocarbon solvents such as hexane is unlikely to form hydrogen bonds with the drug molecule being adsorbed which is why drug loading with hexane produces higher drug loading than with ethanol and DI water as the drug solvent [19-21, 24, 25, 27, 29, 31, 40].

F.4.3 Drug Release

In Table 1, the various mesoporous silica and SBA-15 exhibited slower drug release rate than the MCM-41 and MCM-48. The various mesoporous silica material investigated demonstrated similar initial drug adsorption as the SBA-15 and MCM-41 however, the reported drug release is slower, and thus drug loading does not affect the kinetics for drug release. SBA-15 also exhibited slower drug release than that of MCM-41. SBA-15 has a larger pore diameter and lower surface area as compared to the MCM-41 and MCM-48 materials. However, the slower release rate may be the result of the interconnected mesopores. The interconnected mesopores may alter the diffusion of the drugs leading to slower diffusion rates.

Likewise for drug release, the drug release kinetics is affected by the interactions between the drug, the solution, and the support matrix. For efficient drug release to occur, the mesopore-substrate and substrate-substrate interactions must be less favorable than the substrate-solvent interaction. [31] The solution most researchers used is a
simulated body fluid (SBF). SBF solution has an ionic composition similar to that of human body plasma, [41, 42] having a molar composition of 142.0/5.0/2.5/1.5/147.8/4.2/1.0/0.5 for Na+/K+/Ca2+/Mg2+/Cl-/HCO3-/HPO42-/ SO42-, and a pH of 7.4.

F.4.4 Hydrogen Storage

Hydrogen storage has received a lot of media attention as a source of energy to replace fossil fuels as well as in the use of fuel-cell based cars and portable electronics. Energy and environmental concerns have lead to the proposal of the hydrogen economy. Having an efficient hydrogen economy in turn requires safe and efficient storage, production, and transportation of hydrogen. The U.S. Department of Energy (DOE) has established a multistage target for hydrogen storage capacity. The design targets for an onboard hydrogen storage system are 4.5 wt% by 2007, 6 wt% by 2010, and 9 wt% by 2015 at moderate temperature and pressure. [27, 43]

Various materials have been studied for hydrogen storage, (i) single walled nanotubes (SWNTs), [44] (ii) multiwalled nanotubes (MWNTs), [44] (iii) pure metals (i.e. Li, K, Mg, Mg-Ni), (iv) doped graphite or graphite nanofibers (GNFs), [45] (v) activated carbon, [46-48] (vi) nanostructured metallic alloy (i.e. Mg-Ni), [49] (vii) metal oxides (i.e. ZnO), [50] (viii) inorganic nanotubes (i.e. BN, TiS2, MoS2), (ix) nanocrystalline metal, (x) complex hydrides (i.e. LiH, MgH2, LiBH4, NaAlH4, Mg(AlH4)2), [51] and (xi) microporous metal organic frameworks (MOFs). [27, 52-57] The primary challenge in this field is to discover materials with reversible high hydrogen sorption capacity which meets the DOE benchmarks. Among the many materials
available and those materials being studied, none is capable of meeting the DOE benchmarks for personal transportation vehicles. Recently however a new MOF catalyst was capable of reaching 4.0 wt% at 25 °C and 98 atm. [27, 57]

A survey of the literature Table 2 and patent literature Table 3 demonstrate previously the highest storage capabilities result from using mesoporous materials as a template to manufacture nanoporous activated carbons with a surface area around 3000 m²/g. [46] Templating utilizing mesoporous silica can be a way to manufacture various types of metal or carbon mesoporous materials. The technique of templating is called nanocasting. A schematic description of nanocasting is shown in Figure 3.

Typically the nanocasting technique starts with mesoporous silica such as SBA-15 or MCM-48. The mesoporous silica is used as a template for carbon material such as sucrose or furfuryl alcohol which is subsequently converted to carbon by high temperature. The silica template is removed with HF acid or NaOH. The subsequent removal of the silica material leaves a negative of the original mold which can then be used as a template by incorporating a polymer or metal oxide. New mesoporous materials can be manufactured using this synthesis route.

Design of a safe and compact H₂ storage device is crucial for the development of mobile applications. Unfortunately mesoporous activated carbon does not meet the DOE hydrogen storage requirements due to the low temperature requirements for storage. New surface chemistries need to be introduced in order to increase the storage capability of these new materials. Simply increasing the surface area isn’t going to be enough to allow for adsorption at higher temperatures because thus far the primary storage is performed via physisorption.
The new class of ordered solids composed of metal ions and organic linkers known as metal-organic frameworks (MOFs) have emerged as a promising storage alternative to high-pressure and liquefied hydrogen tanks, metal hydrides, and carbon based adsorbents. MOFs demonstrate exceptional H\textsubscript{2} uptake [27, 57] by mass. Adjustment of the electronic structure of the metal ions and exposure to higher concentrations of coordination sites will help to increase the binding energy of the H\textsubscript{2} and thus raise the storage capacity closer to ambient temperatures. Dissociation/spillover of H\textsubscript{2} has demonstrated great progress toward high adsorption at room temperature. [57] The development of MOF catalysts (crystalline coordinated polymers) with ordered high surface areas will be instrumental in meeting the DOE requirements in hydrogen storage in the future.

Figure F.1  Templating using the nanocasting technique, schematic diagram provided by Taguchi et al. [2]
<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation</th>
<th>Drug</th>
<th>BET (m²/g)</th>
<th>Pore Dia. (nm)</th>
<th>Pore Vol. (cm³/g)</th>
<th>wt%</th>
<th>Time (h)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41</td>
<td>Weight of support: 0.10-0.35 g</td>
<td>Ibuprofen</td>
<td>41 wt%</td>
<td>1200</td>
<td>3.3</td>
<td>1.0</td>
<td>80</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>The drug was dissolved in hexane and the mesoporous support was soaked in soln. for 3 days at room temp.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature: 25 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCM-41</td>
<td>Weight of support: 0.60 g</td>
<td>Ibuprofen</td>
<td>6.4 wt%</td>
<td>1124</td>
<td>4.3</td>
<td>0.92</td>
<td>80</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>The drug was dissolved and the mesoporous support was soaked for 3 days where impregnation equilibrium occurred.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>200mg drug in 10ml methanol</td>
<td>Simulated intestinal fluid (Na₃PO₄ + NaOH + H₂O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature: 25 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCM-41</td>
<td>Weight of support: 0.5 g</td>
<td>Ibuprofen</td>
<td>59 wt% Hex</td>
<td>920</td>
<td>3.4</td>
<td>0.62</td>
<td>80</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>The drug was dissolved in hexane/ethanol (65mg/ml) and the mesoporous support was soaked in soln. for 24 h.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature: 25 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBA-15</td>
<td>Weight of support: 0.1 g</td>
<td>Ibuprofen</td>
<td>34 wt% Erythromycin</td>
<td>787</td>
<td>8.8</td>
<td>1.06</td>
<td>15</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>The drug was dissolved in toluene and acetonitrile (30 mg/ml), the mesoporous support was soaked for 3 days at room temp.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature: 25 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: a MCM-41 and SBA-15 materials were prepared by typical methods according to the literature. [2, 16, 58-60] The preparation listed in the table deals with how the drug was prepared w.r.t. the mesoporous support.
b BET theory a well known rule of the physical adsorption of gas molecules on a solid surface to determine surface area of a catalyst. See reference [61]
Table F.1  Summary of mesoporous materials for the controlled release of pharmaceutical drugs. (continued)

<table>
<thead>
<tr>
<th>Support / Sample</th>
<th>Preparation</th>
<th>Drug</th>
<th>Surface area</th>
<th>Pore Dia. (nm)</th>
<th>Pore Vol. (cm³/g)</th>
<th>Release wt%</th>
<th>Time (h)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15-C18ACE</td>
<td>Weight of support: 0.1 g</td>
<td>18 wt% Erythromycin</td>
<td>71</td>
<td>5.4</td>
<td>0.19</td>
<td>5</td>
<td>1</td>
<td>[31]</td>
</tr>
<tr>
<td>Pellet 13mm X 3mm</td>
<td>The drug was dissolved in toluene and acetonitrile (30 mg/ml), the mesoporous support was soaked for 3 days at room temp.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>The SBA-15 was functionalized by anchoring HC chains on the surface. (C₁₁H₂₆O₃Si, Fluka)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>23</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature: 25 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCM-41 Size N/A</td>
<td>Weight of support: 0.1 g</td>
<td>14.8 wt% Fluorescein</td>
<td>403</td>
<td>5.2</td>
<td>-</td>
<td>60</td>
<td>1</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>The drug was dissolved in water, ethanol, and acetone, then the mesoporous material was soaked the soln.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>70</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature: 25 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCM-41 type Mesoporous Si Nano-sphere</td>
<td>Weight of support: 0.1 g</td>
<td>- ATP</td>
<td>-</td>
<td>2.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td>The drug was dissolved in aqueous soln., mesoporous support was soaked for 24 h.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature: 25 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H form Y type zeolite Z100 Disks</td>
<td>Weight of support: 0.3 g</td>
<td>51 wt% Ibuprofen</td>
<td>413</td>
<td>2.5</td>
<td>0.22</td>
<td>10</td>
<td>1</td>
<td>[24]</td>
</tr>
<tr>
<td></td>
<td>The drug was dissolved in hexane (33 mg/ml), the support was soaked for 3 days.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature: 25 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>21</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>35</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>
Table F.1 Summary of mesoporous materials for the controlled release of pharmaceutical drugs. (continued)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation</th>
<th>Drug</th>
<th>Surface area</th>
<th>Pore Dia.</th>
<th>Pore Vol.</th>
<th>Release wt%</th>
<th>Release Time (h)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41 Disks</td>
<td>Weight of Support: 0.3 g - The drug was dissolved in hexane, the support was soaked for 3 days.</td>
<td>34 wt% Ibuprofen</td>
<td>1157</td>
<td>3.63</td>
<td>0.98</td>
<td>17</td>
<td>1</td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SBF</td>
<td></td>
<td></td>
<td></td>
<td>38</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>47</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>MCM-41 Disks</td>
<td>Weight of Support: 0.3 g - The drug was dissolved in hexane, the support was soaked for 3 days.</td>
<td>34 wt% Ibuprofen</td>
<td>1157</td>
<td>3.6</td>
<td>0.84</td>
<td>14.8</td>
<td>1</td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SBF</td>
<td></td>
<td></td>
<td></td>
<td>29.6</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>59.3</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>99</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>MCM-41 type meso Si nano-spheres (MSN)</td>
<td>Weight of Support: - The drug was dissolved in aqueous soln., mesoporous support was soaked for 24 h - 2-(propyldisulfanyl) ethylamine functionalized mesoporous silica nano-sphere</td>
<td>4.4 wt% (3.0 µmol) Vancomycin</td>
<td>941.0</td>
<td>2.3</td>
<td>-</td>
<td>0</td>
<td>1</td>
<td>[26]</td>
</tr>
<tr>
<td>Avg. size 200nm</td>
<td>- Temperature: 25 °C. - MW\text{\textsubscript{Vanc}}= 1450.2783 - MW\text{\textsubscript{ATP}}= 507.1838</td>
<td>7.8 wt% (15.5 µmol) ATP</td>
<td></td>
<td></td>
<td></td>
<td>55</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>PBS buffer soln. pH 7.4</td>
<td></td>
<td></td>
<td></td>
<td>83</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>98</td>
<td>75</td>
<td></td>
</tr>
</tbody>
</table>

Note: The Vancomycin release follows very closely to the ATP release profile.
Table F.1  Summary of mesoporous materials for the controlled release of pharmaceutical drugs. (continued)

<table>
<thead>
<tr>
<th>Support / Sample</th>
<th>Preparation</th>
<th>Drug</th>
<th>Surface area (BET $m^2/g$)</th>
<th>Pore Dia. (nm)</th>
<th>Pore Vol. (cm$^3/g$)</th>
<th>Release wt%</th>
<th>Time (h)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41 Size 25mm disk</td>
<td>Weight of Support: -</td>
<td>-</td>
<td>729</td>
<td>2.71</td>
<td>0.664</td>
<td>CFU/ml</td>
<td>8.5</td>
<td>0</td>
</tr>
<tr>
<td>MCM-41 Size 25mm disk</td>
<td>The drug was dissolved in toluene, the functionalized MCM-41 was refluxed in soln.</td>
<td>Ibuprofen</td>
<td>(0.54 mmol)</td>
<td>&amp;</td>
<td>&amp;</td>
<td>8.5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>MCM-41 Size 25mm disk</td>
<td>surfaces were functionalised using a silanisation reaction with 3-glycidoxypropyltrimethoxysilane.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.9</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>MCM-41 Size 25mm disk</td>
<td>The MCM-41 particles were adsorbed in 25mm cellulose disks</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.2</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>MCM-41 Size 25mm disk</td>
<td>Temperature: 25 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>MCM-41 Size 25mm disk</td>
<td>Weight of Support: 0.3 g</td>
<td>Ibuprofen</td>
<td>30 wt%</td>
<td>1157</td>
<td>2.5</td>
<td>0.2-0.35</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>MCM-41 Size 25mm disk</td>
<td>The drug was dissolved in hexane (33mg/ml), the mesoporous material was soaked in the soln for 24 h.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>MCM-41 Size 25mm disk</td>
<td>MCM-41 treated with two surfactants C16TAB &amp; C12TAB</td>
<td>SBF</td>
<td></td>
<td></td>
<td></td>
<td>35</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>MCM-41 Size 25mm disk</td>
<td>Temperature: 25 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>60</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>MCM-41 Size 25mm disk</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>65</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>PLGA mesoporous silica</td>
<td>Weight of Support: 0.1 g</td>
<td>Gentamicin</td>
<td>22.4 wt%</td>
<td>-</td>
<td>4.9</td>
<td>0.789</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>PLGA mesoporous silica</td>
<td>The drug was added dropwise (50 mg/ml) to the mesoporous silica till a gel-like mixture. The silica particles were soaked for 5 days at 4 °C followed by freeze-drying.</td>
<td>PBS buffer soln pH=7.4</td>
<td></td>
<td></td>
<td></td>
<td>40</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>PLGA mesoporous silica</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>78</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>Preparation</td>
<td>Surface area (BET $\text{m}^2/\text{g}$)</td>
<td>Pore Dia. (nm)</td>
<td>Pore Vol. ($\text{cm}^3/\text{g}$)</td>
<td>Release wt%</td>
<td>Time (h)</td>
<td>Ref.</td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
<td>------------------------------------------------------------------------------</td>
<td>------------------------------------------</td>
<td>----------------</td>
<td>-----------------------------------</td>
<td>-------------</td>
<td>----------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>SBA-15 silica</td>
<td>Weight of Support: 0.5 g</td>
<td>190</td>
<td>5.9</td>
<td>0.40</td>
<td>36</td>
<td>90</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>rods</td>
<td>The drug was dissolved in water (20 wt%), the mesoporous silica rods were soaked 4 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature: 25 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCM-41 Size N/A</td>
<td>Weight of Support: 0.5 g</td>
<td>1024</td>
<td>3.59</td>
<td>1.021</td>
<td>11</td>
<td>67</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>The drug was dissolved in ether (25mg/ml), the mesoporous material soaked in soln. for 24 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature: 25 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBA-15 Disks</td>
<td>Weight of Support: 0.25 g</td>
<td>244</td>
<td>5.5</td>
<td>0.405</td>
<td>26</td>
<td>20</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>The mesoporous material was soaked in saturated atenolol soln (6.67 mg/ml) for 4 days.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature: 25 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBA-15 Size 16mm dia. disk</td>
<td>Weight of Support: 0.2 g</td>
<td>590</td>
<td>8.6</td>
<td>0.95</td>
<td>25</td>
<td>90</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>The drug was dissolved in hexane (30 mg/ml), the mesoporous material was soaked for 3 days.</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>SBA-15 was functionalized with 3-aminopropyltrimethoxysilane (APTMS)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Temperature: 25 °C.</td>
<td></td>
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</tr>
</tbody>
</table>

Table F.1 Summary of mesoporous materials for the controlled release of pharmaceutical drugs. (continued)
Table F.1  Summary of mesoporous materials for the controlled release of pharmaceutical drugs. (continued)

<table>
<thead>
<tr>
<th>Support / Sample</th>
<th>Preparation</th>
<th>Drug</th>
<th>BET (m²/g)</th>
<th>Pore Dia. (nm)</th>
<th>Pore Vol. (cm³/g)</th>
<th>Release wt%</th>
<th>Time (h)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41 Spheres</td>
<td>Weight of Support: 0.15 g</td>
<td>Ibuprofen</td>
<td>46.5</td>
<td>2.0</td>
<td>0.97</td>
<td>50</td>
<td>1</td>
<td>[27]</td>
</tr>
<tr>
<td>Size 10 mm dia X 0.5 mm disk</td>
<td>The drug was dissolved in hexane (0.1M), the mesoporous material was soaked for 2 h.</td>
<td>Sim. Proximal intestine fluid</td>
<td></td>
<td></td>
<td></td>
<td>76</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>MCM-48 Size 13 mm X 3 mm disk</td>
<td>Weight of Support: 0.1 g</td>
<td>Ibuprofen</td>
<td>28.7</td>
<td>3.6</td>
<td>1.048</td>
<td>60</td>
<td>1</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td>The drug was dissolved in hexane (10 mg/ml), mesoporous material was soaked for 4 days.</td>
<td>SBF</td>
<td></td>
<td></td>
<td></td>
<td>80</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>MCM-48 Size 6 mm X 3 mm disk</td>
<td>Weight of Support: 0.1 g</td>
<td>Aspirin</td>
<td>23.6</td>
<td>2.5</td>
<td>0.781</td>
<td>17</td>
<td>1</td>
<td>[37]</td>
</tr>
<tr>
<td></td>
<td>The drug was dissolved in anhydrous ethanol (40 mg/ml), the mesoporous material was soaked for 24 h.</td>
<td>SBF</td>
<td></td>
<td></td>
<td></td>
<td>27</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Mesoporous silicon (PSi)</td>
<td>Weight of Support:</td>
<td>Ibuprofen</td>
<td>30.4</td>
<td>6-12</td>
<td>0.87</td>
<td>15</td>
<td>1</td>
<td>[38]</td>
</tr>
<tr>
<td>Size Particles &lt; 38 µm (400 mesh)</td>
<td>The drug was dissolved in ethanolic soln. (700 mg/ml), the mesoporous material was soaked for 1 h.</td>
<td>(pH=7.4) buffered (10 mM MES/HEPES) Hank's balanced salt solution (HBSS)</td>
<td>248</td>
<td></td>
<td></td>
<td>20</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature: 25 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>35</td>
<td>10</td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>50</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>
Table F.2 Summary of mesoporous materials for Hydrogen Storage.

<table>
<thead>
<tr>
<th>Support / Sample</th>
<th>Preparation</th>
<th>Surface area (BET m²/g)</th>
<th>Pore Dia. (nm)</th>
<th>Pore Vol. (cm³/g)</th>
<th>H₂ Adsorption wt%</th>
<th>Pressure (atm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic &amp; inorganic mesoporous silica</td>
<td>Weight of Support: N/A</td>
<td>Organic 34</td>
<td>3.5</td>
<td>0.66</td>
<td>0.2</td>
<td>5</td>
<td>[62-64]</td>
</tr>
<tr>
<td>Size</td>
<td>Organic</td>
<td>34</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N/A</td>
<td>Inorganic</td>
<td>142</td>
<td>3.1</td>
<td>1.4</td>
<td>0.4</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Organic N/A</td>
<td>Mesostructures Silica nanofibers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inorganic 50-300nm</td>
<td>Temperature of adsorption: 25 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoporous SiOOC ceramic</td>
<td>Weight of Support: 0.1 g</td>
<td>1762.89</td>
<td>3.25</td>
<td>0.99</td>
<td>0.60</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>TSA-2</td>
<td>No functionalization of the mesoporous material.</td>
<td></td>
<td></td>
<td></td>
<td>0.12</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Size</td>
<td>The electrostatic interaction between the positively charged quaternary ammonium salt (–N(CH₃)₃⁺) of TSA and negatively charged head group (–OSO₃⁻) of the anionic surfactant, SDS, is the key to the formation of the self-assembled structure.</td>
<td>0.60</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N/A</td>
<td>Soln. pH in the range of 8.8–10.5 in the preparation of the mesoporous SiOC ceramic material.</td>
<td>1.10</td>
<td>15</td>
<td>0.98</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>Temperature of adsorption: 25 °C.</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Table F.2 Summary of mesoporous materials for Hydrogen Storage. (continued)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area</th>
<th>Pore Dia.</th>
<th>Pore Vol.</th>
<th>H₂ Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoporous Carbon</td>
<td>886</td>
<td>6.0</td>
<td>1.01</td>
<td>0</td>
</tr>
<tr>
<td>Size ~200 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoporous carbon/silica nanocomposite</td>
<td>860</td>
<td>2.0-2.8</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>Mesoporous ordered carbon (MOCs)</td>
<td>1245</td>
<td>2-10</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>Size N/A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Weight of Support: N/A
- Ordered mesoporous carbon spheres.
- No functional groups were added to the mesoporous carbon materials.
- Temperature of adsorption: -196 °C.
- Si → Si/C → C mesoporous materials are compared, carbon mesoporous material exhibited highest H₂ capacity.
- Temperature of adsorption: -196 °C.
- Weight of Support: 0.925 g (SBA15) 0.848 b (MCM48)
- Order MOC-SBA15 and MOC-MCM48 were prepared and compared.
- The MOC-MCM48 material exhibited slightly higher adsorption capability.
- Temperature of adsorption: -196 °C.
- H₂ adsorption data for MOC-MCM48

Ref. 47 48 66
Table F.2  Summary of mesoporous materials for Hydrogen Storage. (continued)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation</th>
<th>Surface area</th>
<th>Pore Dia. (nm)</th>
<th>Pore Vol. (cm³/g)</th>
<th>wt% H₂ Adsorption</th>
<th>Pressure (Atm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanoporous carbon spheres</td>
<td>Weight of Support: N/A</td>
<td>CM5B-9</td>
<td>CM5B</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>(CM5B-9)</td>
<td>The nanoporous carbon spheres were prepared using MCM-48 as a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.15</td>
<td>[67]</td>
</tr>
<tr>
<td>(CM5A-8)</td>
<td>template and sucrose as a surfactant.</td>
<td>CM5B-8</td>
<td>CM5B</td>
<td>1646</td>
<td>2.6</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>Size</td>
<td>CM5B-9: the sample was heated abruptly to 1000 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>N/A</td>
<td>CM5B-8: the sample was heated at 10 °C/min to 1000 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature of adsorption: -196 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanoporous polymers</td>
<td>Weight of Support: N/A</td>
<td>CM5B-9</td>
<td>CM5B</td>
<td>1060</td>
<td>0.8</td>
<td>0.12</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td>Nanoporous polymers (commercial resins)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.18</td>
<td></td>
</tr>
<tr>
<td>Size</td>
<td>Amberlite XAD4</td>
<td></td>
<td></td>
<td></td>
<td>1.8</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>N/A</td>
<td>Wofatit Y77</td>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
<td>19.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lewatit VP °C 1064</td>
<td></td>
<td></td>
<td></td>
<td>2.1</td>
<td>29.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hypersol-Macronet MN200</td>
<td></td>
<td></td>
<td></td>
<td>2.15</td>
<td>39.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hypersol-Macronet MN200</td>
<td></td>
<td></td>
<td></td>
<td>2.16</td>
<td>49.3</td>
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</tr>
<tr>
<td></td>
<td>Hypersol-Macronet MN200</td>
<td></td>
<td></td>
<td></td>
<td>2.18</td>
<td>59.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature of adsorption: -196 °C.</td>
<td></td>
<td></td>
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<td></td>
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</tbody>
</table>
Table F.2  Summary of mesoporous materials for Hydrogen Storage. (continued)

<table>
<thead>
<tr>
<th>Support / Sample</th>
<th>Preparation</th>
<th>Surface area BET (m$^2$/g)</th>
<th>Pore Dia. (nm)</th>
<th>Pore Vol. (cm$^3$/g)</th>
<th>H$_2$ Adsorption wt%</th>
<th>Pressure (atm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF Cu$_3$(BTC)$_2$</td>
<td>- Weight of Support: N/A</td>
<td>1239</td>
<td>-</td>
<td>0.62</td>
<td>0</td>
<td>0</td>
<td>[56]</td>
</tr>
<tr>
<td>Cu$_3$(BTC)$_2$</td>
<td>- Metal-Organic Frameworks (MOFs)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>- are crystalline coordination polymers</td>
<td></td>
<td></td>
<td></td>
<td>0.43</td>
<td>0</td>
<td>19</td>
</tr>
<tr>
<td>Size</td>
<td>with specific surface areas exceeding</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N/A</td>
<td>that of traditional adsorbents such as</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>zeolites and active carbons</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Temperature of adsorption: -196 °C.</td>
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<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Nanoporous activated carbon</td>
<td>- Weight of Support: 1.5 g</td>
<td>3000</td>
<td>0.7-2.0</td>
<td>1.6</td>
<td>0</td>
<td>0</td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>- Commercial activated carbon PICACTIF SC from PICA, NORIT R0.8,</td>
<td></td>
<td></td>
<td></td>
<td>2.4</td>
<td>0.2</td>
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</tr>
<tr>
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<td></td>
<td></td>
<td>5.9</td>
<td>0.4</td>
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<tr>
<td>Size</td>
<td>- Temperature of adsorption: -196 °C.</td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.3</td>
<td>0.6</td>
<td></td>
</tr>
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<td></td>
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<td>12.4</td>
<td>0.8</td>
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<td></td>
<td></td>
<td></td>
<td>16.0</td>
<td>1</td>
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</tr>
<tr>
<td>nanoporous metal-benzenedicarboxylate M(OH)(O$_2$C–C$_6$H$_4$CO$_2$)</td>
<td>- Weight of Support: 0.5 g</td>
<td>MIL-53 (Al)</td>
<td>1020</td>
<td>53 (Al)</td>
<td>0</td>
<td>0</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>- MIL-53 (Al), M = Al$^{3+}$</td>
<td></td>
<td></td>
<td></td>
<td>0.6-1.2</td>
<td>N/A</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>- MIL-53 (Cr), M = Cr$^{3+}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>MIL-53(Cr)</td>
<td></td>
<td></td>
<td></td>
<td>3.5</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>Size</td>
<td>- Temperature of adsorption: -196 °C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N/A</td>
<td>- MIL-53 (Al) exhibited higher H$_2$ storage and is reported.</td>
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<tr>
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<td></td>
<td></td>
<td>1026</td>
<td>MIL-53(Cr)</td>
<td>3.75</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>53(Cr)</td>
<td>0.6-1.2</td>
</tr>
<tr>
<td>Sample</td>
<td>Preparation</td>
<td>Surface area (m²/g)</td>
<td>Pore Dia. (nm)</td>
<td>Pore Vol. (cm³/g)</td>
<td>H₂ Adsorption wt%</td>
<td>Pressure (atm)</td>
<td>Ref.</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>------------------------------------------</td>
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<td>-------------------</td>
<td>---------------------</td>
<td>----------------</td>
<td>------</td>
</tr>
<tr>
<td>AX-21, (Anderson Development Corp.) activated carbon</td>
<td></td>
<td>2790</td>
<td>1.5</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>[44]</td>
</tr>
<tr>
<td>OTCNT, open-tipped, multiwalled carbon nanotubes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.8</td>
<td>0.78</td>
<td>0.36</td>
<td>0</td>
<td>0.016</td>
<td>0.016</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>15.4</td>
<td>0.78</td>
<td>0.36</td>
<td>0</td>
<td>0.016</td>
<td>0.016</td>
<td>0</td>
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</tr>
<tr>
<td>0.78</td>
<td>0.2</td>
<td>0.094</td>
<td>0.2</td>
<td>0.094</td>
<td>0.094</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>1.87</td>
<td>0.4</td>
<td>0.28</td>
<td>0.6</td>
<td>0.28</td>
<td>0.28</td>
<td>0</td>
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</tr>
<tr>
<td>4.21</td>
<td>0.6</td>
<td>0.62</td>
<td>0.8</td>
<td>0.62</td>
<td>0.62</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>6.24</td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalytically grown graphite nanofibers</td>
<td></td>
<td>1000</td>
<td>~50</td>
<td>0.36</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Graphite nanofibers</td>
<td>- Weight of Support: 0.5 g</td>
<td></td>
<td>0</td>
<td>0.016</td>
<td>0.016</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>- Temperature of adsorption: -196 ⁰C.</td>
<td></td>
<td></td>
<td>0.016</td>
<td>0.016</td>
<td>0.016</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>- The presence of water vapor inhibits H₂ storage.</td>
<td></td>
<td></td>
<td>0.016</td>
<td>0.016</td>
<td>0.016</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>- Temperature of adsorption: -196 ⁰C.</td>
<td></td>
<td></td>
<td>0.016</td>
<td>0.016</td>
<td>0.016</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>0.28</td>
<td>0.6</td>
<td>0.62</td>
<td>0.8</td>
<td>0.62</td>
<td>0.62</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>8.59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weight of Support: 0.3 g</td>
<td>1 = [Mn(DMF)6]3p(Mn4Cl)3(BTT)8-(H₂O)12]2<em>42DMF</em>11H₂O*20CH₃O</td>
<td>1¹</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>[52]</td>
</tr>
<tr>
<td>MOF with exposed Mn²⁺</td>
<td>- Weight of Support: 0.3 g</td>
<td></td>
<td>0</td>
<td>0.016</td>
<td>0.016</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>- Temperature of adsorption: -196 ⁰C.</td>
<td></td>
<td></td>
<td>0.016</td>
<td>0.016</td>
<td>0.016</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>- Temperature of adsorption: -196 ⁰C.</td>
<td></td>
<td></td>
<td>0.016</td>
<td>0.016</td>
<td>0.016</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>39</td>
<td>6.2</td>
<td>59</td>
<td>6.2</td>
<td>59</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>78</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>Preparation</td>
<td>Surface area BET (m²/g)</td>
<td>Pore Dia. (nm)</td>
<td>Pore Vol. (cm³/g)</td>
<td>H₂ Adsorption wt%</td>
<td>Pressure (atm)</td>
<td>Ref.</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------------------------------------------------------------------------------------</td>
<td>-------------------------</td>
<td>----------------</td>
<td>------------------</td>
<td>-------------------</td>
<td>----------------</td>
<td>---------</td>
</tr>
<tr>
<td>MOF</td>
<td>Weight of Support: 5.5 g</td>
<td>700</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>54, 55</td>
</tr>
<tr>
<td>NaNi₃(OH)(SIP)₂</td>
<td>Na₂Ni₆O₃₄ clusters bridged by 5-sulfoisophthalate form a 3D network.</td>
<td>-</td>
<td>0.26</td>
<td>0.59</td>
<td>0.82</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>N/A</td>
<td>Temperature of adsorption: -196 °C.</td>
<td>-</td>
<td>1.08</td>
<td>1.30</td>
<td>1.70</td>
<td>0.52</td>
<td></td>
</tr>
</tbody>
</table>

| MOF          | Weight of Support:                                                                           | 839                     | 6.2            | 0.33             | IRMOF -1          | 3.5            | 27, 57, 68 |
| IRMOF-1      | Constructed by linking tetrahedral [Zn₄O]₆⁺ clusters with linear carboxylates.               | -                       | -              | -                | IRMOF -8          | 98             |         |
| IRMOF-8      |                                                                                              | -                       | -              | -                | IRMOF             | 98             |         |
| N/A          | The storage capacity for IRMOF-8 increased to 4% at 25 °C and 10 MPa.                       | -                       | -              | -                | 5 wt% Pt loading  | 4.0            |         |
| N/A          | Active carbon primary receptor for hydrogen                                                  | -                       | -              | -                | Temperature of adsorption: 25 °C. |         |         |

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Table F.3  Summary of patent literature for mesoporous materials and hydrogen storage.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation</th>
<th>Surface area</th>
<th>Pore Dia. (nm)</th>
<th>Pore Vol. (cm$^3$/g)</th>
<th>H$_2$ Adsorption wt%</th>
<th>Pressure (atm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoporous alumina molecular sieve &amp; nanotube</td>
<td>Weight of Support: N/A Mesoporous alumina molecular sieve and alumina nanotubes were claimed as H$_2$ storage devices.</td>
<td>429</td>
<td>4.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>[69]</td>
</tr>
<tr>
<td>Size 5-10 nm</td>
<td>Temperature of adsorption: 25 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoporous carbon film</td>
<td>Weight of Support: N/A Mesoporous carbon film is made from a mesoporous Si framework.</td>
<td>300-3,000</td>
<td>2.0-50</td>
<td>0.35-1.5</td>
<td>0</td>
<td>0</td>
<td>[70]</td>
</tr>
<tr>
<td>Size 20-200 nm</td>
<td>Temperature of adsorption: -193 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbide-derived nanoporous carbons</td>
<td>Weight of Support: The material used is a nanoporous carbon produced by halogen treatment of chlorination of metal carbide. The template material and metal are extracted leaving the nanoporous carbon material.</td>
<td>300-2000</td>
<td>0.5-10</td>
<td>1.2</td>
<td>0</td>
<td>0</td>
<td>[71]</td>
</tr>
<tr>
<td>Size</td>
<td>Temperature of adsorption: 25 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


F.5 Advantages and Disadvantages

The advantages and disadvantages of pharmaceutical control in drug delivery, and mesoporous materials in hydrogen storage are summarized in the following sections.

F.5.1 Advantages of Pharmaceutical Control in Drug Delivery

Commercial pharmaceutical drug delivery systems consist of a polymeric matrix in which the drug is released under appropriate conditions (i.e. site specific release). [72] A number of materials have been employed such as (i) mixtures of polymers and (ii) polymer based composites with bioactive glass or ceramics.[73-75] The drugs are deposited by (i) direct compression, (ii) wet granulation, or (iii) mechanical mixture of both drug and support material which is a very simplistic method of preparation.

F.5.2 Disadvantages of Pharmaceutical Control in Drug Delivery

In the polymer based delivery system, typically the polymer support material is synthesized in situ with the pharmaceutical drug. The purpose is to form some linkage between the drug and polymer system in order to enable release upon some biological trigger/stimulation to make delivery site specific. Some stimulants include temperature, pH, and a magnetic field. [23] The disadvantage to in situ synthesis results when the pharmaceutical drug needs to be preserved while the polymer support and linkage reactions are taking place. Furthermore, the delivery of the drug is also a function of the degradation kinetics of the polymer system resulting in inconsistent release.

Polymer based composite materials which are made by mixing; direct compression, wet granulation, and mechanical mixture also have disadvantages. One
such disadvantage is heterogeneity of samples. Due to the difficulty of ensuring homogeneous distribution of the drug through the matrix there is the possibility of having a heterogeneous mixture resulting in inconsistent drug delivery. In-homogeneity causes drug release problems, and that is a serious issue, especially in toxicology in drug release. Toxic anti-tumor drugs, hormones and neurotransmitters must have guaranteed release rates between samples to ensure the safety of the patient.

F.5.3 Advantages of Mesoporous Materials in Drug Delivery

In contrast to the polymer based delivery systems, mesoporous materials are finding application as drug delivery systems. The advantage of using mesoporous materials are the presence of ordered network of pores which are homogeneous in size, high pore volume, large specific surface area and stability of the structure resulting in consistent drug release kinetics. Mesoporous materials offer high adsorption capacity for high drug loading as compared to the conventional polymer based delivery systems. Drug loading is related to the surface area and pore size of the mesoporous materials which are both customizable properties. Uniform hexagonal arrangement of cylindrical pores leads to reproducibility in controlled releases. The highly porous material allows for incorporation of organics onto the structures allowing for customizable controlled release of designer drugs. In the polymer based systems, the polymer material is synthesized in the presence of the drug in order to form linkages; in situ synthesis causing difficulties related to drug reactivity and structural changes of the pharmaceutical drug. In contrast, drug loading in mesoporous materials is very simple; drug loading occurs by a simple soaking procedure where the drug loads by diffusional processes. The mesopore
walls provide silanol groups which can be reactive toward appropriate guest molecules such as drug molecules without modification of the pore walls. Functionalizing the mesopore wall is also possible as shown in Figure 4; ibuprofen molecule is loaded into a functionalized mesopore.

Mesoporous materials comprised of silica have the added benefit of biocompatibility due to the matrices affinity for water. The mesoporous material enhances the bioavailability of poorly adsorbed drugs resulting in lowering the therapeutic dosage needed. Mesoporous materials can also entrap slightly water-soluble drugs. The drugs within the mesopore channels remain in the molecular amorphous state and do not crystallize. The encapsulated drugs that remain in a molecular and amorphous state enable the rapid liberation of the drug during release. In the case of non-water soluble drugs, the mesoporous material can encapsulate the drug without having to alter the physical state of the drug molecule as occurs in conventional polymer delivery systems where the delivery system is synthesized in situ. [23]

F.5.4 Disadvantages of Mesoporous Materials in Drug Delivery

A review of the literature shows the drug release experiments performed by most researchers was in a simulated body fluid (SBF). Mesoporous materials studied for drug delivery consists of SiO₂ type materials; SiO₂ solubility and bioactivity has been found to be a problem in the SBF solution during experiments. There was a potential of forming calcium phosphates on the silica support restricting diffusional processes. Furthermore, SiO₂ also had a tendency to dissolve in the SBF fluid. The rate of silica dissolution in the SBF fluid is determined to be a function of the immersion time. However, drug release is
dominated by diffusion, the dissolution of silica into the SBF fluid was slower than the
diffusion rate therefore the drug release is not a function of SiO₂ dissolution. [19] After
drug release studies, there is a collapse of the porous structure due to erosion of the SiO₂
in the solution, this was determined by N₂ adsorption measurements of the surface area
after the particles were filtered of the buffer solution. [21]

Drug adsorption occurs as a function of the solvent properties during the soaking
phase. Toxic solvents such as hexane demonstrate higher drug loading however
deleterious effects in biological systems can be a problem upon release. Planar drug
molecules also have difficulty entering into the mesopores even though the mesopores are
larger than the dimensions of the planar drug. [22]

Other mesoporous materials such as PLGA/mesoporous silica hybrid [29] demonstrated short initial burst of drug release as well as PLGA not being very stable
encapsulation material due to its degradation product is acidic and could initiate
inflammation within a patient. [29]

Loading the drug and its preparation as an oral pellet can also have a disadvantage
depending upon the procedure of loading. In one case, the drug was loaded into MCM-41
initially before formation of the pellet. [29] The compression of the material caused the
drug matrix mixture to lead to a decrease of pore size and narrowing and/or closing of the
pore cavity. This introduced inconsistent release results reducing the diffusion rate to
slow or incomplete release of ibuprofen due to diffusion constraints. The mesoporous
material should be compacted into pellet form first and then loaded with the drug such
that the ibuprofen drug would follow the same pathway through the mesoporous network
as it was loaded for consistent results. Also, in pill technology, biodegradable binders are
used to hold the polymer/drug systems together which can also cause diffusional problems in mesoporous based delivery systems if binders are used in the pellet forming process.

F.5.5 Advantages of Mesoporous Materials in Hydrogen Storage

Hydrogen storage, at cryogenic temperatures, has been correlated with the surface accessible hydrogen on the storage media. [47] Thus, carbonaceous materials offer advantages of both low density material and high storage capacity. Templated activated carbons having a surface area 3000 m²/g have demonstrated the highest adsorption ability at cryogenic temperatures.

A high temperature stable mesoporous SiOC ceramic was also investigated as a potential candidate for hydrogen storage. [65] The SiOC mesoporous material demonstrated a very rugged design that can be used under harsh operating conditions. The SiOC material is stable with a high surface area (1762 m²/g) up to 800 °C in addition, the mesoporous product showed 1.1 wt% H₂ adsorption at 25 °C and 25 atm which is higher than the activated carbon material at room temperature.

A new class of ordered materials composed of metal ions and organic linkers known as MOFs have emerged which are promising for storage of hydrogen. The coordinatively unsaturated metal centers in MOFs can increase the affinity for H₂ adsorption by exhibiting stronger binding interactions needed as well as maintaining the ordered and high surface area which is required for H₂ sorption. Furthermore, MOFs have the advantage of taking up hydrogen via the H₂ spillover process. Dissociation/spillover of H₂ has demonstrated great progress toward high adsorption at
room temperature. [57] The development of MOF catalysts (crystalline coordinated polymers) with ordered high surface areas will be instrumental in meeting the DOE requirements in hydrogen storage in the future.

F.5.6 Disadvantages of Mesoporous Materials in Hydrogen Storage

The adsorption of $\text{H}_2$ on carbonaceous materials is primarily a physisorption process, therefore, in order to achieve high adsorption cryogenic temperatures are required to slow down the molecular motion of $\text{H}_2$ in order to maximize the physisorption process. Therefore, carbon nanostructure materials can not store the amount of $\text{H}_2$ required for automotive applications at room temperature. This includes all hydrogen storage catalysts whose primary adsorption mechanism is by a physisorption process. The reason relates to practical conditions for hydrogen storage, it is not practical to incorporate an onboard cryogenic storage system for automotive applications (i.e. Fuel cell based automobile).

Preparation of MOFs in scale-up applications also has limitations. Methods for the preparation of MOF single crystals yield significantly small amounts of products. Some MOF preparation procedures are highly sensitive towards variations in concentration, pressure, and solvent purity which are why the specific surface area of MOF-5 varies significantly across the literature. [56] Other MOFs are prepared with a metal azide which is very water sensitive and potentially explosive if handled incorrectly. It has also been reported the MOF framework becomes unstable and may collapse under subsequent guest molecule removals. [62]
F.6 Proposed Mechanism to Study Drug Delivery and Hydrogen Storage

The following sections describe the proposed mechanism and experimental hypothesis for studying drug delivery and hydrogen storage.

F.6.1 Hypothesis

Drug release kinetics requires the knowledge of bonding and interaction chemistry as it is applied to the drug being investigated as well as the support material used. A review of the literature demonstrates a clear weakness in understanding the rates of loading and release at standard operating conditions 36.6 °C and SBF (Simulated Body Fluid). The rate of loading and release is a function of the bonding interaction between the drug and substrate and any functional groups which may be grafted upon the mesopore walls of the support material. The hypothesis is by functionalizing the mesopore walls it is possible to modify the drug loading and release kinetics. A novel method for studying drug loading and release kinetics is necessary to modify the diffusional process more intuitively which can be achieved by studying the bonding and interaction chemistry between the functional groups, drug, and mesoporous materials.

Improving hydrogen storage to meet the DOE requirements will require a novel catalyst along with a novel method to study the mechanistic processes involved in improving storage capacity. The hypothesis is by improving hydrogen spillover it is possible to increase the storage capacity of MOF type catalysts. Improving spillover requires investigation of (i) active site for dissociation of hydrogen, (ii) the interface between active site and carbon material, and (iii) the primary and secondary spillover phenomena upon a novel Ni/C-MOF type catalyst. There are tremendous
physical/energy barriers for surface diffusion of hydrogen atoms from one material to the next thus in situ study can help to elucidate the mechanism as well as the rate limiting step in order to improve hydrogen storage capacity.

F.6.2 Drug Delivery Proposal

Drug release is an important aspect of drug delivery in its application to cutting edge technologies. However, a review of the literature indicates there is a lack of understanding behind the physical mechanisms of dissolution of the drug loading and release processes. This is partly due to the lack of analytical techniques capable of providing bonding and interaction chemistry on the microscopic scale. I propose in situ Fourier transform infrared (FTIR) spectroscopic imaging employing focal plane array (FPA) and the FAST-IR (single pass Attenuated Total Reflection (ATR)) accessory (Figure 5 (a)) to study drug loading and release upon mesoporous materials.

The Lancer™ Focal Plane Array (FPA) is an infrared array detector device for laboratory spectroscopy. This detector provides spectrochemical imaging where the data can be collected in rapid-scan, step-scan, and kinetics mode. Kinetics mode offers time resolved spatial and spectrochemical imaging designed for in situ studies. Data is collected along with the use of a Varian FTIR spectrometer where the FTIR spectrometer is the IR source.

Imaging generally refers to taking a visible picture of some object in which the visual picture is referred too as an image. In the case of the FPA, the acquisition of an infrared (IR) picture is also a form of imaging. Generally speaking, taking pictures in the past was performed by generating images on film, and more recently on digital
photography. The same can be done with the IR sensitive film in order to take an IR image of the object in question. There is a disadvantage to doing IR imaging in this way; the overall IR response of the sample from all wavelengths are hitting the IR sensitive film and can produce difficult to interpret results due to overlap. The ideal IR spectroscopic image is one in which specific wavelength images are obtained. In this way it is possible to look at the spatial distribution of the IR wavelengths across the sample. This is achieved by the use of the Varian FTIR spectrometer. The Lancer™ FPA can produce a two dimensional image at all wavelengths in a single measurement by combining both the FPA and the FTIR.

The Lancer™ FPA is a two dimensional array of infrared sensitive detectors and is capable of measuring an interferogram at every single point simultaneously. In this case the entire sample is imaged on the whole array and so each pixel of the IR detector provides fast IR data collection. The approximate spatial resolution for a 32 X 32 array detector is 5.5-11 microns. The analysis times are in the order of seconds to minutes which means fast data collection and more productivity. Present applications for the FPA are reported from analyzing leaf tissue [76] and imaging micro arrays of bacteria [77], to achieving higher throughput experimentation in catalysis research. [78]

One of the most important tasks in organic chemistry is the determination of organic structures. During drug delivery, it is important to understand the bonding whether ionic or covalent bonding is occurring, how the drug molecule is interacting with the functional groups of the mesoporous walls, etc are all necessary in order to determine if the compound we have created has the desired structure, or to determine whether the structure has been changed, or some undesired product has been produced as a result.
Utilizing the FPA, it is possible to examine the spatial and chemical distribution of each species within the field of view during the infrared acquisition based upon the characteristic vibrational modes of each species being investigated. The in situ IR technique can observe the vibrations of bonds and provide evidence of the functional groups present as well as their interaction with the drug molecule.

Some difficulties may result however utilizing the in situ IR technique. With simple compounds infrared spectra may contain many different IR adsorptions, not just one for each bond. These adsorptions result from bending, stretching, or even from the entire molecule as a whole. In the case of drug delivery one is dealing with a complex molecule such as ibuprofen, furthermore, the mesopores may be functionalized. These functional groups will also provide vibrational adsorption spectra which may result in some overlap of the wavenumbers depending upon whether we are observing the drug molecule, the functional group upon the mesopore wall, or the interaction of the functional group with the drug molecule itself. During the analysis of the spectroscopic data, it may become troublesome to separate these different wavenumbers. One tool that may be utilized in order to help separate and evaluate the vibrations involved in the drug loading and delivery process is to use quantum chemical calculations to determine structural and vibrational information via theoretical studies of the process. Quantum chemical structural studies can be performed upon ibuprofen, as well as, its interaction with any functional groups which may be placed upon the mesopore walls.

The experimental setup is shown in Figure 5. The FAST-IR apparatus, which is a single pass ATR, along with the use of the FPA is shown in Figure 5 (a). The FPA detector, can be operated in kinetics mode which takes sequential time resolved scans of
the sample loaded onto the FAST-IR Prism. SBF solution can be added dropwise in order to investigate the drug release phenomena. The drug loading and release phenomena occurs upon the hexagonal structure of MCM-41 as seen in Figure 5 (b)-(d). In order to modify the loading and release kinetics functional groups shown in Figure 5 (e) such as an amine group can be loaded upon the mesopore walls. Upon loading and release, the drug ibuprofen interacts with the functional groups which are attached to mesopore walls shown in Figure 5 (f). While performing in situ studies, there may be some overlapping of the adsorption spectra which is shown in Figure 5 (g). Quantum chemical calculations can be performed upon ibuprofen, see Figure 5 (h), and adsorbed ibuprofen in order to help separate overlapping IR adsorption bands resulting from complex organic structures on the mesoporous materials.

In conclusion, in situ IR study with the use of the FPA and the FAST-IR helps to verify the hypothesis by providing (i) spatial distribution, (ii) chemical distribution, and (iii) bonding/interaction information of the drug as it is loaded and released from mesoporous materials. Furthermore, quantum chemistry calculations can be utilized to help separate any overlap that may result from very complex organic species.
Figure F.2  Experimental setup using Varian Inc. FPA, and FAST-IR accessory to study in situ diffusion phenomena of drug delivery upon mesoporous materials.
F.6.3 Hydrogen Storage Proposal

It has been demonstrated within the literature hydrogen storage by spillover is a promising technique to achieve significant hydrogen uptake in MOF type catalysts. [27, 57] In the literature atomic hydrogen from Pt metal is supported upon carbonaceous materials which are then brought into intimate contact with the desired MOF catalyst resulting in dramatically increased Hydrogen storage up to 4 wt% at room temperature. I propose a novel and inexpensive hydrogen catalyst can be prepared by using Ni metal as a less expensive material loaded upon activated carbon which can provide the same functionality to dissociate hydrogen. The Ni/carbon catalyst will then be brought into intimate contact with a MOF type material.

Preparation of this novel catalyst proceeds as follows. Zn(NO$_3$)$_2$ 6H$_2$O (1.19 g) and 2,6-naphthalenedicarboxylic acid (0.43 g) are dissolved in 40 ml of DMF during vigorous stirring at room temperature. Three drops of H$_2$O$_2$ aqueous solution (30 wt%) is added to the solution. Triethylamine is slowly added dropwise to the solution under vigorous stirring for 1 h. The yield is approximately 70% based on zinc. The precipitate is then washed in DMF three times. The sample then is degassed at room temp for 6 h, then heated to 180 °C at a heating rate of 1 °C/min and held at this temp for 12 h under degassing in vacuum. The metal organic framework is thus formed and the sample is ready for gas adsorption.

The carbon supported Ni is prepared by insipient wetness impregnation of an aqueous Ni nitrate solution. The resulting carbon supported nickel is calcined under an inert environment up to 400 °C in order to form Ni/carbon. The next step is to build carbon bridges between the MOF catalyst and the Ni/Carbon catalyst. MOFs however
are unstable at 300 °C therefore sucrose shall be used as a precursor to build the bridge which shall allow for secondary hydrogen spillover between the Ni/Carbon and MOF materials.

A review of the literature in hydrogen storage reveals there are no in situ studies of the different types of adsorbed hydrogen involved on MOF type catalysts. Deuterium trace studies can reveal and distinguish the different hydrogen species M-\( \text{OH} \) and M-OD, M-\( \text{H} \) and M-D (\( M = \text{metal} \)) involved in hydrogen storage using in situ FTIR as seen in Figure 7 (f). [79] This provides an opportunity for fundamental study to help elucidate the mechanism and rates of hydrogen adsorption upon the MOF type catalysts. The mechanism, rate, and heat of adsorption are an engineering phenomenon which can provide information to determine the kinetics and calculating the rate of loading which is another DOE objective (i.e. 1.5Kg \( \text{H}_2/\text{min} \) by 2010). [43] Filling a cylinder loaded with the catalyst is a batch loading process. Within this batch process there is going to be some point of equilibrium in which maximum hydrogen storage will occur. Using this information, a mechanism can be proposed, see Eqn. (1)-(3), for the process of hydrogen storage upon the novel catalyst in order to help us to determine the rate limiting step (i.e. the rate limiting step would be the slowest point which requires optimization in order to increase hydrogen storage capacity).

Proposed mechanism for hydrogen storage with spillover

Adsorption: \[ H_2 + 2S_1 \overset{\text{\large$\rightleftharpoons$}}\rightarrow H - S_1 + H - S_1 \]  \hspace{1cm} (1)

Migration: \[ H - S_1 \overset{\text{\large$\rightleftharpoons$}}\rightarrow H - S_2 \]  \hspace{1cm} (2)
Desorption: \[ H - S_i + H - S_i \xleftrightarrow{\text{reaction}} 2S_i + H_2 \] (3)

The catalyst is assumed to be loaded as a powder and not packed into the batch reactor. Therefore, the rate limiting step will exclude the diffusional process. For the purpose of this proposal it will be assumed the rate limiting step is the adsorption process. In order to determine the rate of adsorption we start by writing the rate equations for attachment and detachment of hydrogen which is shown in Eqn. (4) and (5) respectively. Where \( K_a \) is the rate constant for the adsorption process, \( P_{H_2} \) is the partial pressure of hydrogen, \( C_v \) is the concentration of vacant sites for hydrogen adsorption and \( C_{H-S} \) is the number of sites where hydrogen has adsorbed. Since the rate limiting step is assumed to be the adsorption process Eqn. (1), the rate equation for reaction can be written as shown in Eqn. (6). Where \( K_E \) is equilibrium constant defined as \( K_E = \frac{K_a}{K_a} \). The goal is to find the theoretical uptake of adsorbed hydrogen \( C_{H-S} \). In order to do this the total number of sites for adsorption needs to be considered and is written in Eqn. (7).

Rate of attachment = \( K_a P_{H_2} C_v \) (4)

Rate of detachment = \( K_a C_{H-S} \) (5)

\[-r_{AD} = \left( K_a P_{H_2} C_v - K_{-a} C_{H-S} \right) = K_a \left( P_{H_2} C_v - \frac{C_{H-S}}{K_E} \right) \] (6)

Site Balance: \( C_t = C_v + C_{H-S} \Rightarrow C_v = C_t - C_{H-S} \) (7)
By substitution and rearranging the rate equation we obtain a theoretical concentration of adsorption sites as a function of the partial pressure of hydrogen. Equation (8) is the theoretical adsorption isotherm which is a well known equation called the Langmuir isotherm and is also shown graphically in Figure 6.

\[ C_{H-S} = \frac{K_E P_{H_2} C_t}{1 + K_E P_{H_2}} = \frac{K_E P_{H_2}}{1 + K_E P_{H_2}} \]  

(8)

Figure F.3  Theoretical Langmuir Isotherm and empty cylinder curves in hydrogen storage.
Comparing the theory to experiment will show whether the adsorption reaction is truly the rate limiting step. Using FTIR it is possible to compare the Langmuir isotherm with experiment. By looking at hydride adsorption and C-H stretching spectra it is possible to determine the hydrogen uptake upon the novel MOF type catalyst. (Note: some calibration experiments will be necessary to obtain accurate representative results)

There are numerous data in the literature concerning the study of dissociative H\textsubscript{2} adsorption on different metal surfaces using high-resolution electron energy lose spectroscopy. The frequencies of the stretching vibrational modes for hydrogen adsorbed upon various metal surfaces are listed in Table 4. The stretching mode frequency of Hydrogen adsorption is strongly dependent upon the nature of the adsorption site. Adsorption occurs through dissociation of the two hydrogen atoms forming a hydride and hydroxyl. The resulting hydride and hydroxyl species can be observed via FTIR. It is possible to compare the hydrogen adsorption using the metal hydride adsorption band for nickel at 1110-1145 cm\textsuperscript{-1} for bridged sites, 1120 cm\textsuperscript{-1} for the 3-fold hollow site, and 530-630 cm\textsuperscript{-1} for 4-fold hollow sites. Adsorption upon the carbonaceous species can be correlated with the C-H stretching shown in Figure 7 (c).

The hydrogen-spillover phenomena has been observed on many supported catalysts such as alumina, carbon, etc. [80-82] Hydrogen-spillover is defined as the dissociative chemisorption of hydrogen upon a metal active site and then the subsequent migration of atomic hydrogen from the metal onto the surface of the support. The support would be considered the primary receptor for hydrogen; a secondary receptor for hydrogen would refer to a secondary material in which atomic hydrogen continues to migrate onto. Secondary spillover however requires intimate contact with the primary
material or some kind of bridging material which allows for the surface diffusion between the primary and secondary materials.

I propose a novel method of study by the use of in situ FTIR spectroscopic imaging using the focal plane array (FPA) along with the in situ transmission cell reactor. The experimental setup is shown in Figure 7. The experimental setup shows a method to perform isotopic study of adsorbed hydrogen upon a novel MOF type catalyst seen in Figure 7 (a). During the study, the resulting adsorption spectra is collected upon a 32 X 32 FPA detector, see Figure 7 (b), the resulting spectra for hydrogen adsorption can be pulled from any spatial location within the field of view of the FPA as shown in Figure 7 (c). The novel catalyst involves increasing hydrogen spillover upon new or existing MOF type catalysts as shown by the SEM picture in Figure 7 (d). The cage structure of the MOF catalyst in Figure 7 (e) has a high surface area for adsorption of hydrogen. The regions of the novel MOF type catalyst for increased spillover include (I) hydrogen adsorption and dissociation, (II) the interface for spillover onto the carbon and MOF material, (III) adsorption upon the carbonaceous material which will depend upon the carbon surface structure, and (IV) hydrogen adsorption onto the MOF cage as shown in Figure 7 (f).

In conclusion, the use of in situ studies can help to answer the hypothesis by providing mechanistic information and helping to determine the rate limiting steps in spillover which are inhibiting hydrogen storage processes.
Table F.4  The symmetric stretching frequencies measured for hydrogen adsorbed on a variety of single-crystal metal surfaces in the 4- and 3- fold hollow and bridge states.

<table>
<thead>
<tr>
<th>Metal Surface</th>
<th>( \nu_s ) (cm(^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bridged Sites</strong></td>
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<td></td>
</tr>
<tr>
<td>Rh(100)</td>
<td>1330</td>
<td>[83]</td>
</tr>
<tr>
<td>Ni(510)</td>
<td>1110-1145</td>
<td>[84, 85]</td>
</tr>
<tr>
<td>Fe(110)</td>
<td>1060</td>
<td>[84, 85]</td>
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<tr>
<td>Cu(111)</td>
<td>1040</td>
<td>[86]</td>
</tr>
<tr>
<td>W(100)</td>
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<td>[87, 88]</td>
</tr>
<tr>
<td>W(100)</td>
<td>1260-1220</td>
<td>[89]</td>
</tr>
<tr>
<td>Mo(100)</td>
<td>1200-1220</td>
<td>[89]</td>
</tr>
<tr>
<td>Mo(100)</td>
<td>1030-1125</td>
<td>[90, 91]</td>
</tr>
<tr>
<td><strong>3-Fold Hollow site</strong></td>
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<td></td>
</tr>
<tr>
<td>Ni(111)</td>
<td>1120</td>
<td>[92, 93]</td>
</tr>
<tr>
<td>Ru(001)</td>
<td>1140</td>
<td>[87]</td>
</tr>
<tr>
<td></td>
<td>685, 1140</td>
<td>[94]</td>
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<tr>
<td>Rh(111)</td>
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<td>[95]</td>
</tr>
<tr>
<td>Ir(111)</td>
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<tr>
<td>Pd(111)</td>
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<td>[97]</td>
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<tr>
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</tr>
<tr>
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<td>[101]</td>
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<td><strong>4-Fold Hollow site</strong></td>
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<tr>
<td>Ni(110)</td>
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<td>[102]</td>
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<tr>
<td>Ni(510)</td>
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<td>[84, 85]</td>
</tr>
<tr>
<td>Rh(1000)</td>
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<td>[103]</td>
</tr>
<tr>
<td>Pd(100)</td>
<td>510</td>
<td>[104]</td>
</tr>
</tbody>
</table>
Figure F.4 Experimental setup to investigate in situ the hydrogen spillover phenomena upon MOF catalysts.
F.7 Bibliography


