IN SITU INFRARED STUDY OF ADSORBED SPECIES DURING CATALYTIC OXIDATION AND CARBON DIOXIDE ADSORPTION

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IN SITU INFRARED STUDY OF ADSORBED SPECIES DURING CATALYTIC
OXIDATION AND CARBON DIOXIDE ADSORPTION

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Dissertation

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ABSTRACT

Hydrogen is considered to be the fuel of the next century. Hydrogen can be produced by either water splitting using the solar or nuclear energy or by catalytic cracking and reforming of the fossil fuels. The water splitting process using solar energy and photovoltaics is a clean way to produce hydrogen, but it suffers from very low efficiency. A promising scheme to produce H$_2$ from natural gas involves following steps: (i) partial oxidation and reforming of natural gas to syngas, (ii) water-gas shift reaction to convert CO in the syngas to additional H$_2$, (iii) separation of the H$_2$ from CO$_2$, and (iv) CO$_2$ sequestration.

The requirements for the above scheme are (i) a highly active coke resistant catalyst for generation of syngas by direct partial oxidation, (ii) a highly active sulfur tolerant catalyst for the water-gas shift reaction, and (iii) a low cost sorbent with high CO$_2$ adsorption capacity for CO$_2$ sequestration. This dissertation will address the mechanisms of partial oxidation, CO$_2$ adsorption, and water-gas shift catalysis using in-situ IR spectroscopy coupled with mass spectrometry (MS). The results from these studies will lead to a better understanding of the reaction mechanism and design of both the catalyst and sorbent for production of hydrogen with zero emissions.

Partial oxidation of methane is studied over Rh/Al$_2$O$_3$ catalyst to elucidate the reaction mechanism for synthesis gas formation. The product lead-lag relationship observed with in situ IR and MS results revealed that syngas is produced via a two-step
reforming mechanism: the first step involving total oxidation of CH₄ to CO₂ and H₂O and the second step involving the reforming of unconverted methane with CO₂ and H₂O to form syngas. Furthermore, the Rh on the catalyst surface remains predominantly in the partially oxidized state (Rh⁺²⁺ and Rh⁰).

For the water-gas shift reaction, addition of Re to the Ni/CeO₂ catalyst enhanced the water gas shift activity by a factor of three. The activity of the Ni-Re/CeO₂ catalyst was reduced by only 20% in the presence of sulfur compared to a 50% reduction with the Ni/CeO₂ catalyst. These results show that Re not only promotes the water-gas shift reaction but also enhances the sulfur tolerance of the Ni/CeO₂ catalyst.

Novel amine based solid sorbents have been developed to capture CO₂ reversibly using temperature-swing adsorption process. The IR study shows that CO₂ adsorbs on amine grafted SBA-15 to form carbonates and bicarbonates. Comparison of monoamine and diamine-grafted SBA-15 showed that diamine grafted SBA-15 provides almost twice the active sites for CO₂ adsorption. The adsorption of SO₂ on the amine-grafted SBA-15 revealed that SO₂ adsorbs irreversibly and the sorbent cannot be regenerated under normal operating conditions.

Results of these studies can be used to enhance the overall conversion of CH₄ to H₂ thus lowering the cost of H₂ product.
ACKNOWLEDGEMENTS

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Finally, I would like to dedicate this research work to my wife, Swati, and my parents, Amratlal and Premilaben. Without their patience and support, it would have been difficult to accomplish this work.
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CHAPTER I
INTRODUCTION

1.1. Energy Crisis and Global Warming

A continuous increase in the energy needs for the developed and developing countries has led to an increase in the cost of non-renewable energy sources such as oil and gas.\(^1\),\(^2\) Over 75\% of our energy needs are fulfilled by fossil fuels (coal, oil and gas) which are expected to deplete in the coming years and lead to further increases in the cost of energy.\(^1\),\(^3\) Figure 1.1 shows the current energy scenario for the world.\(^1\),\(^4\) The figure shows that the production of coal will peak around 2050 while that of oil and gas will peak in the year 2020. Meanwhile the demand for energy would be increasing continuously which needs to be fulfilled by an alternative energy source like non-fossil fuels or renewable energy.

The continuous rise in energy needs has also lead to an increase in the atmospheric CO\(_2\) levels. The concentration of CO\(_2\) has increased from 280 ppm in the year 1800 to 370 ppm in the year 1999.\(^3\),\(^5\) Figure 1.2 shows the CO\(_2\) concentration in atmosphere since pre-industrial level from ice core samples and in Mauna Loa in last 50 years. The concentration of CO\(_2\) was fairly constant before pre-industrial era (year 1800) as estimated from ice core samples. The increase in CO\(_2\) levels is a result of industrialization and the increased use of coal, oil and natural gas. Table 1.1 shows the amount of CO\(_2\) emitted from various fuels per GJ of energy produced. If we consider the
Figure 1.1. Current energy scenario

Millions of barrels/day (oil eq.)

1860, 1900, 1940, 1980, 2020, 2060, 2100

Non-Fossil, Coal, Demand Scenario, Coal, Gas, Add'l O&G, Tar & Shale, Oil

Figure 1.1. Current energy scenario \(^4\)
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<th>lb CO$_2$/10$^6$ Btu</th>
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<td>Bituminous coal (CH$<em>{0.8}$O$</em>{0.1}$)</td>
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<tr>
<td>Crude oil (CH$_{1.8}$)</td>
<td>160-172</td>
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<td>Natural gas (CH$_4$)</td>
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amount of CO$_2$ emitted per unit of energy produced from fossil fuels, coal and oil emit 87% and 39% more CO$_2$ than natural gas. The increase in the atmospheric CO$_2$ levels has been linked to the global warming

The effects of global warming have been linked to increased height of sea levels at coastal areas, melting of glaciers, and climatic change in ecosystem. The concern over drastic effects projected from global warming and continuous rise in energy prices call for an alternate, more effective, and cleaner source of energy.

1.2. Hydrogen Economy

Hydrogen has been long considered to be a clean source of energy. The only by-product from hydrogen combustion is water or water vapor. The cleanest way to produce hydrogen is by water splitting using solar energy. Although there is an abundant amount of water and solar energy available, the efficiency of solar water splitting process is only about 1%. Currently hydrogen is industrially produced by steam reforming coupled with water-gas shift reactions. Natural gas or higher hydrocarbons are reformed with steam to synthesis gas (syngas, a mixture of CO and H$_2$) which may be further enriched with H$_2$ by catalytic water-gas shift reaction as shown below.

$$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \quad \text{(1.1)}$$

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \text{(1.2)}$$

The CO$_2$ is separated from H$_2$ by absorption in aqueous amine solvents or membrane process and the hydrogen is supplied to the process plants by gas lines. The hydrogen gas can also be stored in cylinders and supplied to end users.

Although H$_2$ is considered to be a clean fuel, there is a debate on the way H$_2$ is currently produced via natural gas which produces CO$_2$ as a by-product. This CO$_2$ must
be either sequestered or used for generation of value added products. For realization of the hydrogen economy, the hydrogen needs to be stored and transported safely to the end users.

1.3. CO$_2$ Separation

Carbon dioxide from coal and gas fired power plants contribute to over 33% of global CO$_2$ emissions.$^{3,7}$ CO$_2$ capture from these stationary power plants is considered to be one alternative to stabilize the CO$_2$ in the atmosphere. With available technologies for CO$_2$ separation and sequestration, the cost of energy produced by coal increases by more than 70%.$^3$ An improvement in CO$_2$ capture technology can drastically reduce the cost of separation and make CO$_2$ capture from power plants feasible.

Removal and recovery of CO$_2$ with solid adsorbents is an attractive approach compared to the conventional liquid absorption by amines. The liquid amine process involves expensive stripping process with large amount of aqueous solvent (30% amines in water) and suffers from equipment corrosion due to aqueous amines.$^{8-10}$ Amine treated solid sorbents with high surface area are considered to be potential sorbents for CO$_2$ capture.$^{11-18}$

1.4. Objectives and Scope

1.4.1. Partial Oxidation of Methane

Hydrogen can be produced from various hydrocarbons by partial oxidation or steam reforming. Methane is of particular importance as it is available naturally and has high H$_2$/C ratio compared to other hydrocarbons. Partial oxidation of methane being an exothermic reaction is preferred over steam reforming, which is highly endothermic, for
production of syngas. Moreover, partial oxidation of methane produces H$_2$/CO ratio of 2 which is suitable for production of methanol and Fischer-Tropsch synthesis.

The production of syngas using partial oxidation of methane is studied over Rh/Al$_2$O$_3$ due to the high activity of Rh catalyst for this reaction and its resistance to coke formation. The oxidation of methane also leads to CO$_2$ and H$_2$O, the combustion products. It would be interesting to study this reaction for combination of partial, total, and reforming reactions that can occur simultaneously, and to determine the active sites and mechanism for generation of syngas.

In situ IR spectroscopy coupled with mass spectrometry and transient techniques can be used to study the surface of the catalyst and the reaction products from partial oxidation of methane. The adsorbed intermediates leading to partial and total oxidation products can be determined using this method which could lead to better understanding of the partial oxidation mechanism on Rh/Al$_2$O$_3$. Infrared studies of adsorbed products and reactants on the Rh surface during the reaction can shed light on the oxidation state of Rh particles.

The objective of the methane partial oxidation reaction on Rh/Al$_2$O$_3$ is to determine the reaction mechanism leading to partial and total oxidation products. A literature survey suggests that the reaction conditions, kind of support, and the method of catalyst preparation play an important role on metal supported catalysts for partial oxidation of methane. For Rh supported on Al$_2$O$_3$ catalyst, partial as well as total oxidation can take place depending on the catalyst composition, amount of oxygen present on the surface (CH$_4$/O$_2$ ratio) which will control the oxidation state of Rh, and the reaction temperature.
For Rh/Al$_2$O$_3$ catalyst, it is postulated that the reaction proceeds with total oxidation as a primary reaction leading to a secondary reforming reaction to produce syngas. In situ IR spectroscopy coupled with mass spectrometry will be used to study the dynamics of product formation on 2 wt% Rh/Al$_2$O$_3$ between 450-600 °C.

1.4.2. Water-Gas Shift Reaction

The production of CO-free H$_2$ for the PEM fuel cells using an integrated reformer is an active research area in the PEM fuel cell industry. The catalyst in the reformer should be active for steam reforming and water-gas shift reactions with high sulfur resistance so a variety of fuels can be used. Ni supported on Al$_2$O$_3$ is used industrially for steam reforming which is deactivated by coking and presence of sulfur.$^{29-37}$ Cu-ZnO and Fe$_3$O$_4$-Cr$_2$O$_3$ are used for water-gas shift reactions which also suffer from sulfur poisoning. Moreover, Cu-ZnO needs specific reduction profiles during start-up and special handling during discharge due to pyrophoric nature of the catalyst.$^{38}$

Metal supported on CeO$_2$ catalyst has gained considerable interest as water–gas shift catalysts due to its high activity at low temperatures.$^{36, 39, 40}$ The water-gas shift catalysts, steam reforming-Ni/Al$_2$O$_3$ catalysts, and other metal supported catalysts are often deactivated by sulfur compounds. It would be of scientific and industrial interest to impart sulfur resistance to steam reforming and water-gas shift catalysts due to sulfur present in the natural gas. Pt-Re used for catalytic reforming of napthas has been reported to be coke resistant and sulfur resistant due to electronic and geometric effects of Re in the bimetallic catalyst.$^{41, 42}$ It is postulated that Re would promote the sulfur resistance and its coke resistance ability would enhance the activity of the supported Ni catalyst.
The objective of this study is to (i) determine the activity of Ni and Ni-Re supported on CeO$_2$ for the water-gas shift reaction with in situ IR spectroscopy coupled with mass spectrometry, (ii) determine the active and spectator adsorbates for the water-gas shift reaction on Ni and Ni-Re catalyst, and (iii) determine the effect of sulfur treatment on the Ni and Ni-Re for water-gas shift reactions.

The scope of this study will focus on determining the Re effect on the sulfur resistance property of CeO$_2$ supported Ni-Re catalyst for water-gas shift reaction. Isotopic transient techniques will be used to determine the active adsorbates for water-gas shift reaction. The effect of sulfur will be studied by reducing the catalyst in a mixture of H$_2$ and H$_2$S and the activity of the catalyst will be compared using pure H$_2$ as a reducing agent.

1.4.3. CO$_2$ Adsorption on Amine treated SBA-15

Recent interests in CO$_2$ capture with solid sorbents with high CO$_2$ adsorption capacity has led to an active research in this area.$^{11-13,15,18}$ Amines immobilized on high surface area materials can be used as high capacity CO$_2$ capture sorbents. We postulate that CO$_2$ adsorption capacity can be enhanced by increasing the number of amine functional groups on the surface using diamines (an amine molecule with two amino groups). Further more, this sorbent can be used to capture other acid gases like H$_2$S and SO$_2$.

The objective of this study is to determine (i) the mechanism of aminosilanes grafting on SiO$_2$ surface using IR spectroscopy, (ii) the CO$_2$ adsorption capacity of diamine-grafted SBA-15, and compare it with monoamine-grafted SBA-15, (iii) the
active adsorbates on these sorbents, and (iv) the thermal and chemical stability of amine-grafted sorbents.

Results from this research will provide fundamental understanding of amine grafting process and the interaction of grafted amine species with gaseous CO$_2$. This information can lead to the development of a more efficient CO$_2$ adsorption solid sorbents.

The overall objective of this research is the production of hydrogen with zero emissions. The results of this research would lead to an integrated process for production of CO$_2$-free hydrogen using partial oxidation, water-gas shift reaction, and CO$_2$ adsorption. The scheme has been described in the conclusions chapter of the dissertation.

1.5. Dissertation Outline

Chapter I of dissertation provides an introduction and basic knowledge of the reactions being studied along with the hypotheses and the objectives of these studies. Chapter II provides background and a comprehensive literature survey in the fields of catalytic partial oxidation of methane, water-gas shift catalysis, and CO$_2$ absorption/adsorption. Chapter III provides the general experimental techniques used for these studies, more details about an individual experimental setup is provided in the specific chapters later on. Chapter IV discusses the results of partial oxidation of methane on Rh/Al$_2$O$_3$ catalyst. Chapter V covers the results and discussion of water-gas shift reaction on Ni and Ni-Re on CeO$_2$ catalysts. Chapter VI and VII discuss the results of solid amine based sorbents used for CO$_2$ capture, its thermal and chemical stability., Finally, everything is summarized in the chapter VIII.
2.1. Partial Oxidation of Hydrocarbons and Water-Gas Shift Reaction

Partial oxidation of hydrocarbons is a key step to produce thousands of industrially important products. Thermodynamically, total oxidation route of hydrocarbons is prominent and kinetic control is required to obtain desirable partial oxidation products. The partial and total oxidation reactions take place in parallel and in series to yield desirable and undesirable products. Partial oxidation reactions suffer from low conversion and low selectivity. Supported metals, metal oxides, and promoters are used to enhance the conversion and selectivity for desirable products and inhibit or suppress the side reactions and total oxidation.

This section of the chapter will be focused mainly on partial oxidation of methane to generate the synthesis gas (CO+H$_2$) and water-gas shift reaction to extract an extra mole of H$_2$ from water using CO from the synthesis gas.

2.1.1. Partial Oxidation of Methane

Partial oxidation and reforming of methane are industrially important reactions to produce hydrogen and synthesis gas (syn-gas). The reactions taking place during partial oxidation and steam reforming are described by the following equations:

\[
\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2
\]
\[
\begin{align*}
\text{CH}_4 + 2\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad (2.2) \\
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2 \quad (2.3) \\
\text{CH}_4 + \text{CO}_2 & \rightarrow 2\text{CO} + 2\text{H}_2 \quad (2.4) \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \quad (2.5)
\end{align*}
\]

The total oxidation reaction (2.2) is the undesired reaction which produces \(\text{CO}_2\) and \(\text{H}_2\text{O}\). \(\text{CO}_2\) and \(\text{H}_2\text{O}\) can act as reactants for steam reforming reaction (2.3) or dry reforming reaction (2.4) to produce syn-gas. The syn-gas is used for Fischer-Tropsch synthesis to produce higher hydrocarbons and oxygenated products of industrial value. A \(\text{H}_2/\text{CO}\) ratio of 2 is desired for production of methanol which is attained in single step by partial oxidation of methane. Syn-gas produced by partial oxidation or reforming reactions can further undergo a high temperature and a low temperature shift by water-gas shift reaction (2.5) to produce \(\text{CO}_2\) and \(\text{H}_2\). \(\text{CO}_2\) is separated from hydrogen using membranes or aqueous amine process; \(\text{CO}_2\) separation by amine process will be described in second section of this chapter.

There is considerable interest in partial oxidation and steam reforming reactions using higher hydrocarbons like gasoline or diesel which are readily available with the present infrastructure. Research is under its way to develop catalysts which are sufficiently active for these reactions at practical conditions.\textsuperscript{2-5} Partial oxidation is an exothermic reaction while the steam reforming is a highly endothermic reaction. A proper understanding of the temperature profile in the reactor is required to avoid hot spots that could lead to explosions. The heat of reactions for partial oxidation and steam reforming are described below using natural gas, gasoline (C\textsubscript{7} compounds), and diesel...
(C_{12} compounds) as well as a generic reaction is provided for alkanes. The heat of formation data is taken from NIST website.

Partial Oxidation:

\[ C_nH_{2n+2} + \frac{n}{2}O_2 \rightarrow n\text{CO} + (n+1)\text{H}_2 \]

\( n=1, \quad \Delta H^\circ = -17.1 \text{ kcal/mol} \)

\( n=7, \quad \Delta H^\circ = -140 \text{ kcal/mol} \)

\( n=12, \quad \Delta H^\circ = -247.4 \text{ kcal/mol} \)

Steam Reforming:

\[ C_nH_{2n+2} + n\text{H}_2\text{O} \rightarrow n\text{CO} + (2n+1)\text{H}_2 \]

\( n=1, \quad \Delta H^\circ = 49.3 \text{ kcal/mol} \)

\( n=7, \quad \Delta H^\circ = 264.6 \text{ kcal/mol} \)

\( n=12, \quad \Delta H^\circ = 446.2 \text{ kcal/mol} \)

Water-Gas Shift:

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H^\circ = -9.8 \text{ kcal/mol} \]

2.1.1.1. Partial Oxidation of Methane over Supported Metal Catalysts

Supported metals and metal oxides have been used as catalysts for partial oxidation and reforming to generate \( \text{H}_2 \) and syn-gas. Several researchers have published their work on supported metal catalyst, effect of support, effect of another metal (bi-metallic catalysts), and the mechanism of the reactions on the supported metal catalyst.\(^6\)

Supported Ni catalyst has shown very high activity for partial oxidation to synthesis gas, but suffers from coking (carbon deposition).\(^{26, 29, 45, 46} \) Ni supported on \( \text{Al}_2\text{O}_3 \) was studied by Dissanayake et al. in the temperature range of 450-900 °C.\(^6\) They
were able to achieve CO selectivity as high as 95% and revealed that three different states of catalyst were present along the length of the reactor. The initial part was Ni-Al alloy which had low activity for total oxidation, middle portion with NiO+Al$_2$O$_3$ was responsible for total oxidation, and the latter part was reduced Ni on Al2O3 which reformed the CH$_4$ with total oxidation products to CO and H$_2$.

The effect of support was studied extensively by Choudhary and coworkers.$^{25, 26, 28, 45-48}$ They revealed that addition of Co reduced coking on NiO supported on ThO$_2$. Partial oxidation of methane was also studied over supported noble metals by Green and co workers.$^{29-32}$ Mixed metal oxide, La$_2$Ru$_2$O$_7$, was able to achieve methane conversions of 94% at 775 °C with 97% selectivity for CO.$^{32}$ Partial oxidation of CH$_4$ on supported metal and metal oxides literature is summarized in Table 2.1.

Rh/Al$_2$O$_3$ has attracted considerable interest for partial oxidation and reforming due to its high activity for both reactions and resistance to coking.$^{33-44}$ Although, Rh is an expensive element, the cost benefit comes from long life time and high activity of the catalyst for both the reactions without coking. Several papers have been published recently on partial oxidation of CH$_4$ and higher hydrocarbons using supported Rh catalysts.$^2, 4, 5, 15, 38-40, 43, 44, 49$ High conversion (99%) with high selectivity to syn-gas (97%) has been reported. A brief survey has been included in the Table 2.1 along with the other partial oxidation literature.

2.1.1.2. Mechanism

There are two reaction mechanisms proposed for methane partial oxidation, namely (i) combustion and reforming reactions mechanism (ii) direct partial oxidation mechanism.$^{10, 15, 20, 39, 50}$ Researchers have reported that there is a temperature variation in
Figure 2.1 Heat distribution in a partial oxidation catalyst bed [Source York et. al]
Table 2.1. Partial oxidation of CH$_4$ on supported metal catalysts-literature survey

<table>
<thead>
<tr>
<th>Catalyst / Reaction Conditions</th>
<th>Key Observations</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% Ni on Al$_2$O$_3$ prepared by 3 different methods</td>
<td></td>
<td>22</td>
</tr>
<tr>
<td>Ni, Co, Pt, Pd, Ru on 12CaO.7Al$_2$O$_3$</td>
<td>Unpromoted CaO.Al$_2$O$_3$ had very low methane conversion and reaction did not proceed until 773 K</td>
<td>23</td>
</tr>
<tr>
<td>1% Pt, Pd, Ru and upto 10% Ni and 5% Co loading</td>
<td>With promoted Ni, Pt, and Pd catalysts, the reaction proceeded at 773 K and attained thermodynamic equilibrium 1073 K with H$_2$:CO ration of 2</td>
<td></td>
</tr>
<tr>
<td>CH$_4$:O$_2$ = 2:1</td>
<td>The amount of coke formed on 5% Ni was only 25% compared to 5% Ni supported on non-oxygen ion containing supports. The active oxygen ions trapped in nano-cages makes these catalyst more active and coke resistant</td>
<td></td>
</tr>
<tr>
<td>Ni:Al=1:10, 2:10, 5:10, Ni:Al of 1:10 is equivalent to 7.2 wt% Ni on Al$_2$O$_3$</td>
<td>On Ru and Co catalysts, the total oxidation was dominant in temperature range of 773-1073 K and partial oxidation products were obtained above that temperature</td>
<td></td>
</tr>
<tr>
<td>CH$_4$:O$_2$ = 2:1</td>
<td>The activity of 10% Ni was comparable to 1% Pt</td>
<td></td>
</tr>
<tr>
<td>Reaction Temp: 873-1073K</td>
<td>The mechanism is total oxidation leads to CO$_2$ and H$_2$O which further lead to steam and dry reforming of CH$_4$ to form CO and H$_2$</td>
<td></td>
</tr>
<tr>
<td>1:10 Ni-Al$_2$O$_3$ had strong metal support interaction</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>Strong metal-support interaction lead to difficulty in reduction but enhanced the activity and coke resistance of catalyst, H$_2$/CO ratio of 2 was obtained at 1073 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smaller Ni particles led to low carbon deposition and showed stable activity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst deactivation was due to coking, not sintering</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst / Reaction Conditions</td>
<td>Key Observations</td>
<td>Ref</td>
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</table>
| MoC₂/Al₂O₃ catalyst with Ni, K, or Cu as second component | • MoC₂ was prepared by carburization of MoO₃  
• Addition of second component had positive and negative impacts on catalyst performance  
• Addition of Ni led to better activity and selectivity of catalyst compared to MoC₂ or Ni by themselves  
• Addition of Cu showed high activity for initial period which decreased rapidly thereafter  
• Addition of K decreased the activity of MoC₂ catalyst  
• Addition of Cu and Ni promotes the reduction of MoO₃ by CH₄ and then carburization while K is unfavorable for this process | 24   |
| 24% Co on MgO, CaO, SrO, BaO | • Reaction T: 1073 K  
• CH₄:O₂ = 2:1  
• Co on MgO showed high activity and stability for 120 h run, while on other supports after initial activity the conversion and selectivity decreased with deactivation  
• With MgO, the conversion and selectivity decreased with increase in calcinations temperatures  
• Deactivation was observed for catalyst calcined at 773 to 973 K, and above 973 K, the catalyst had stable activity  
• The amount of catalyst and Co loading had impact on conversion and selectivity of catalysts | 18   |
| 0.5% Ru on TiO₂ doped with Ca²⁺ and W⁶⁺ | • Reaction T: 873-1073 K  
• CH₄:O₂ = 2:1  
• Ru particle size of 2 nm, dispersion higher on doped TiO₂ compared to undoped  
• Ca doped catalyst have high activity and selectivity then W⁶⁺; for CH₄ conversion less than 35%, selectivity was constant and then increased with increased conversion  
• CO and H₂ are primary products, while CO₂ and H₂O are secondary products  
• CH₄ dissociates to CH₃ and finally C on site S1 and adsorbed oxygen on site S2 then oxidize C to CO; S1 and S2 are different sites.  
• With increase in temperature, the number of metallic Ru particles increase during reaction. | 10   |
| 5wt% Group VIII metals on TiO₂ | • Reaction T: 873 K  
• Pulsing 1cc and 3cc of CH₄:O₂ = 2:1 in Ar stream  
• The activity had the following trend: Rh = Ir > Ru = Pd > Pt > Ni; selectivities were highest with Rh, Ru and Ir  
• Complete oxidation occurred over Pt and Ni on TiO₂; Ni was present as oxide, not active for partial oxidation  
• Rh, Ni, Pd exhibited higher CH₄ decomposition activity compared to Pt, Ir, and Ru | 8    |
<table>
<thead>
<tr>
<th>Catalyst / Reaction Conditions</th>
<th>Key Observations</th>
<th>Ref</th>
</tr>
</thead>
</table>
| • 1wt% Rh on various reducible and non-reducible oxides  
• Pulse reaction; CH\textsubscript{4}:O\textsubscript{2} = 2:1  
• Reaction at 1023 K                                                                                               | • Pt, Ni, and Ir follow 2 steps mechanism for syn-gas; Rh and Pd follow direct oxidation one step process for syn-gas production. Ru can follow either route.  
• Effect of reducible (CeO\textsubscript{2}, Nb\textsubscript{2}O\textsubscript{5}, Ta\textsubscript{2}O\textsubscript{5}, etc) and non-reducible (Al\textsubscript{2}O\textsubscript{3}, La\textsubscript{2}O\textsubscript{3}, MgO) was studied and it was reported that activity and selectivity of non-reducible supports was higher.  
• Al\textsubscript{2}O\textsubscript{3}, MgO, and La\textsubscript{2}O\textsubscript{3} have stable activities with MgO as best support, while SiO\textsubscript{2} and Y\textsubscript{2}O\textsubscript{3} were deactivated over time  
• Among reducible oxides, Ta\textsubscript{2}O\textsubscript{5} provided high activity as well as selectivity which decayed over time  
• Pulse reactions suggested 100% CO\textsubscript{2} selectivity for almost all the supports with no metal component  
• XRD studies show formation of RhMgO adduct with Rh/MgO catalyst, this gives high stability to this catalyst and Rh\textsuperscript{0} is generated during reaction condition and are active sites for partial oxidation | 15   |
| • 1-4 wt% Rh and Ru over SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} supports  
• Pulse reactions; CH\textsubscript{4}:O\textsubscript{2} = 2:1  
• Reactions at 773 and 873 K                                                                                           | • Rh/SiO\textsubscript{2} was the only catalyst that showed direct partial oxidation to CO/H\textsubscript{2} and all the other catalysts showed reforming mechanism as studied by time-resolved FT-IR spectroscopy  
• CO\textsubscript{2} was observed on Ru catalysts and Rh supported on Al2O3 before formation of CO  
• Ru has more affinity for O\textsubscript{2} compared to Rh  
• Rh/Al\textsubscript{2}O\textsubscript{3} has more affinity for O\textsubscript{2} compared to Rh/SiO\textsubscript{2} and Rh\textsuperscript{0} are the active sites for syn-gas formation  
• Rh in Rh/SiO\textsubscript{2} is in metallic state under reaction conditions while all other catalysts are in oxidized state as seen by in situ raman spectroscopy | 20   |
| • 0.05% Rh on Al\textsubscript{2}O\textsubscript{3}  
Pulse reactions  
Reactions at 873K-1073 K                                                                                             | • Pulsing CH\textsubscript{4} in O\textsubscript{2} stream led to formation of complete oxidation products  
• Adsorption of CH\textsubscript{4} was slow on oxidized surface, removal of surface oxygen by various treatments enhanced the CH\textsubscript{4} adsorption rate  
• It is concluded that at high adsorbed O\textsubscript{2} concentration, complete oxidation takes place while direct partial oxidation is observed with low adsorbed O\textsubscript{2} on surface | 39   |
the catalyst bed during the reaction. The temperature of front part of the catalyst bed was higher than the latter part which reveals that exothermic and endothermic reactions taking place at the front and later part, respectively. It was concluded that the methane is completely oxidized at the initial catalyst contact, thus raising the temperature and the reforming reactions taking place with the unconverted methane to form syn-gas at the tail end of the catalyst bed. Syn-gas is the secondary product in this case. Temperature profile through the length of catalyst bed is shown in Figure 2.1.51

Direct partial oxidation of methane was studied by Hickman and Schmidt on Rh and Pt – coated monolith catalysts.41-43 A model involving adsorption, surface reaction, and desorption was proposed as follows:

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{C}_{(ads)} + 4\text{H}_{(ads)} & (2.6) \\
\text{C}_{(ads)} + [\text{O}]s & \rightarrow \text{CO}_{(ads)} & (2.7) \\
\text{CO}_{(ads)} & \rightarrow \text{CO}_{(g)} & (2.8) \\
2\text{H}_{(ads)} & \rightarrow \text{H}_2(g) & (2.9)
\end{align*}
\]

With direct partial oxidation of methane, syn-gas is the primary product. A temperature difference in the catalyst bed was also reported while using Pt and Rh. Temperature of Rh bed was lower than Pt bed showing endothermic reactions are of primary importance in the case of Rhodium catalyst. With Rh catalysts, syn-gas is the primary product.

2.1.2. Water-Gas Shift Reaction

Water-gas shift reaction on precious metal supported on ceria has long been studied and used for automotive catalyst for reduction of CO emission in exhaust. Recently water-gas shift reaction has generated lot of interest due to the need of CO free
hydrogen for fuel cells. The Pt catalysts used in PEM fuel cells are easily prone to poisoning with CO levels as low as 100 ppm. The commercial water-gas shift catalyst is Cu/ZnO which needs very careful reduction and regeneration/discharge due to its high pyrophoricity (tendency to combust instantaneously). This catalyst is not suitable for onsite hydrogen generation in fuel cells due to the complications in reduction and regeneration as well as fast start-up times required for fuel cells. Also Cu/ZnO is easily poisoned by any sulfur present in fuel or moisture/water vapor in fuel. A catalyst with high activity at low temperatures which is resistant to coking and sulfur content is desired for this application.

Metal supported ceria has been proved to be active for the water-gas shift reaction. There is a considerable debate over the role of ceria in the catalyst. The two mechanisms in debate are the formate mechanism and the redox mechanism. Researchers have used various spectroscopic and analytical tools to explain the role of ceria in the reaction. Nevertheless, there is one conclusion that the metal component is required for the reaction to proceed. Precious metals like Pt, Au, Rh, and Pd have been shown to be active for water-gas shift reaction. Ni and bimetallic Ni supported on CeO₂ have been shown to be comparable to noble metals supported on CeO₂. Due to the low cost of Ni and its high activity comparable to precious metal catalyst, it has generated considerable interest in water-gas shift catalyst researchers. The bimetallic catalyst containing Re which has promotion effect on sulfur and coke resistance is of particular interest. The literature survey on water-gas shift reaction on supported metal catalyst is summarized in Table 2.2 and activity data is summarized in Table 2.3.
Figure 2.2 Proposed reaction mechanism for water-gas shift reaction
(a) redox mechanism (b) formate mechanism
<table>
<thead>
<tr>
<th>Catalyst / Reaction Conditions</th>
<th>Key Observations</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| 3%Ni - 8%Mo on Al₂O₃, TiO₂ and ZrO₂  
• CO:H₂O = 1:1; 10% H₂S pretreatment  
• Reaction at 625 K | • Catalyst activity: TiO₂>Al₂O₃>ZrO₂  
• Addition of Ni to supported Mo catalyst increased the activity from 2-4 times on different supports  
• Addition of Ni enhances the reducibility of Mo supported catalyst and forms a Ni-Mo-S synergy on the catalyst surface which is highly dispersed | 76 |
| 5% Au on Zeolites (NaY, Na-mordenite, and Na-ZSM-5)  
• CO:H₂O = 12:1  
• Reaction at 323 K | • Surface formates are formed on Au⁺ sites and activity is related to amount of Au⁺ sites.  
• Zeolite surface hydroxyl groups are not needed to form the surface formates  
• Au⁺ and Au⁰ are both active sites for reaction which are formed by 3Au⁺→ 2Au⁰ + Au³⁺ especially NaY zeolite  
• Stable carbonates are formed with Na-ZSM-5 support  
• Catalyst activity: NaY>Mordenite>ZSM-5 | 77 |
| Pd, Co, Ni, Fe on CeO₂ prepared by decomposition.  
• CO:H₂O = 1:1  
• Varying reaction Temperatures (373-873 K) | • Peaks assigned as bidentate formate by Shido and Iwasawa is assigned as carbonates and bicarbonates on ceria based on similar peaks of metal carbonates and bicarbonates  
• The study strongly supports redox mechanism  
• Rate is half order in H₂O and zero order in CO  
• The O₂ evolves from reduction of ceria which is transferred to surface metal to react with adsorbed CO and the carbonates are readily adsorbed by reduced ceria  
• Catalyst activity: Pd:Ni>Co:Fe>CeO₂ | 56 |
| 1, 3, 5% Au on CeO₂  
• Varying temperatures  
• Varying CO:H₂O ratio | • 3% and 5% exhibited high activity and stability for the reaction at different temperatures and CO/H₂O ratios  
• Activity of 3% Au on ceria is higher than 5% and is stable over long period of time  
• Au particles decreased in size during reaction and the dispersion of gold and its contact with ceria is believed to facilitate the reduction of ceria | 52 |
| 3wt% Au/Ceria  
• Temp of studies (90, 300, 523, 573 K) | • The particle size of gold varies from 1 nm to 10 nm.  
• Au particles only smaller than 2 nm are covered by oxygen at the calcinations temperature of 573 K  
• Very small amount of step sites are available on particles of 10 nm size which are responsible for CO adsorption at low temperatures | 64 |
<table>
<thead>
<tr>
<th>Catalyst / Reaction Conditions</th>
<th>Key Observations</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Pd on ceria and alumina</td>
<td>After reduction the CO adsorption capacity increases</td>
<td>59</td>
</tr>
<tr>
<td>Catalyst poisoned with 1% SO₂ in He at 673 K</td>
<td>The reaction takes place at the boundary of Au particles and ceria interface where CO is adsorbed on Au and the water is dissociated on ceria surface</td>
<td></td>
</tr>
<tr>
<td>CO:H₂O = 2.5:1, 1:1</td>
<td>The formation of formate like bands confirm their role as reaction intermediate for WGS reaction</td>
<td></td>
</tr>
<tr>
<td>Varying temp (473-673 K)</td>
<td>The activation energies are same for poisoned Pd/CeO₂ and Pd/Al₂O₃, the activity of fresh Pd/CeO₂ is much higher than other two</td>
<td></td>
</tr>
<tr>
<td>1-8.3 atom% Au on ceria prepared by various methods and Cu on ceria</td>
<td>SO₂ reacts with ceria to form sulfate and the poisoned catalyst represent the activity of Pd itself</td>
<td></td>
</tr>
<tr>
<td>CO:H₂O = 1:5.4</td>
<td>Carbonates are formed only on reduced ceria and re-oxidation of ceria with O₂ or H₂O releases CO₂</td>
<td></td>
</tr>
<tr>
<td>Tested also under reformate conditions</td>
<td>The poisoned catalyst can be easily reduced by H₂ to CeO₂S₂ and can be easily oxidized by O₂, but cannot be oxidized by H₂O and hence is a irreversible poisoning for WGS reaction</td>
<td></td>
</tr>
<tr>
<td>Au and Pt on 10% La doped ceria</td>
<td>Presence of Au increases the oxygen storage capacity and reducibility of ceria catalyst</td>
<td>78</td>
</tr>
<tr>
<td>CO:H₂O = 1:1.36, reformate conditions</td>
<td>WGS activity of catalyst and availability of surface oxygen depends on the particle size of ceria</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au is present in metallic and ionic forms during reaction condition and the particle size of Au increased from 4.7 nm to 6.7 nm under reaction conditions</td>
<td></td>
</tr>
<tr>
<td>0.2% Rh on Ceria</td>
<td>The ceria prepared had mean size of 5 nm while the gold had particle size of approximately 5 nm.</td>
<td>55</td>
</tr>
<tr>
<td>H₂O vapor was used</td>
<td>Metallic gold when removed from the catalyst by cyanide leaching did not change activity of catalyst proving that ionic gold particles are active sites for WGS reaction</td>
<td></td>
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<tr>
<td></td>
<td>The reaction pathway for Au loaded ceria and leached ceria were different but the activity and activation energy were same</td>
<td></td>
</tr>
<tr>
<td></td>
<td>No loss of ceria was reported during leaching process and</td>
<td></td>
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<td></td>
<td>Similar observations were reported over leached Pt catalysts</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO adsorbs on terminal OH groups to form bidentate formate</td>
<td>68</td>
</tr>
<tr>
<td>Catalyst / Reaction Conditions</td>
<td>Key Observations</td>
<td>Ref.</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------------</td>
<td>-----</td>
</tr>
<tr>
<td>as water source</td>
<td></td>
<td>57</td>
</tr>
<tr>
<td>• Temp 373, 443 and 513 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bidentate formate decomposes to ( \text{H}_2 ) and unidentate carbonate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>In vacuum, only 35% of surface formates decompose to ( \text{H}_2 ) and ( \text{CO}_2 ); in presence of water 100% decompose to WGS products and the rate constant is 100 times faster than in vacuum</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Presence of water also decreases the activation energy</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Activation energy of decomposition of formate on CeO_2 is 4 times that of Rh/CeO_2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5%, 1%, 2.5%, and 5% Pt on ceria</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO:H_2O = 1:33.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst activity tested at 523 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reaction rate zero order in water due to excess water</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt on ceria enhances the reduction process of ceria; greater the Pt content, easier it is to reduce the ceria</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt also enhances decomposition rate of formates</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Particle size of ceria is 5-8 nm and that of Pt is 1-2 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>During reduction, surface bridging OH groups are formed which react with adsorbed CO to form formates</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Catalyst with high surface bridging OH groups have high intensity of formates</td>
<td></td>
</tr>
<tr>
<td></td>
<td>They support formate mechanism but do not rule out chances of redox mechanism</td>
<td></td>
</tr>
</tbody>
</table>
Table 2.3 Water-gas shift activity on various catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rate of formation μmole/(g s)</th>
<th>Relevant information</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Au/NaY zeolite</td>
<td>CO₂ formation rate 0.009 – 0.31 μmole/(g s)</td>
<td>The rate of CO₂ formation increased with increase in temperature and decreased with the increase in H₂O/CO ratio</td>
<td>60</td>
</tr>
<tr>
<td>Pd, Ni, Co, Fe on CeO₂ and Cu/ZnO</td>
<td>8-100 E-10 μmole/(g s) with Cu/ZnO being most active and Pd/CeO₂ is next most active catalyst</td>
<td>CO to H₂O ratio of 1 was used and the temperature varied from 100 – 500 C.</td>
<td>56</td>
</tr>
<tr>
<td>Cu and Au on various kind of Ceria</td>
<td>CO₂ formation rate 100-900 μmole/(g s)</td>
<td>CO to H₂O ratio of 5, and temperature varied from 100-350 C</td>
<td>78</td>
</tr>
<tr>
<td>Pt, Rh, Ru, and Pd on TiO₂</td>
<td>0.3-70 μmole/(g s) CO reacted</td>
<td>CO to H₂O ratio of 1:3, temperature range 150-500 C</td>
<td>61</td>
</tr>
</tbody>
</table>
2.1.2.1. Water-Gas Shift Reaction Mechanism

The literature review on water-gas shift mechanism reveals that there is considerable debate on the role of ceria in the water-gas shift mechanism. There are two mechanisms in debate, the redox mechanism and the formation of adsorbed formates on the surface leading to formation of end products.\textsuperscript{55, 56, 68, 69, 79-81} The redox mechanism was until late studied and supported by the kinetic analysis while the formate mechanism has been well supported by spectroscopic evidence of adsorbed species on the surface of the catalyst studied by Shido and Iwasawa.\textsuperscript{68, 79} Recently, Gorte and co-workers have published work involving in-situ spectroscopic evidence proving the formation of carbonates and the redox mechanism.\textsuperscript{56} These mechanisms are shown in Figure 2.2.

2.2. CO\textsubscript{2} Separation

Table 2.4 describes different ways to remove CO\textsubscript{2} from atmosphere and industrial process plants.\textsuperscript{82} It also shows the methods for recovery of this captured CO\textsubscript{2} and options for long term disposal. Some of these methods are economically feasible while others are just technically feasible at this point and require intensive research to make it attractive economically.

2.2.1. CO\textsubscript{2} Capture by Absorption in Aqueous Amine Solutions

The chemical absorption of CO\textsubscript{2} with aqueous amine solution is being used industrially to capture CO\textsubscript{2} from process streams like in natural gas liquefaction and ammonia synthesis process.\textsuperscript{83-85} This process is based on chemical absorption of CO\textsubscript{2} with aqueous monoethanolamine (MEA), diethanolamine (DEA), and mixture of amines to form aqueous carbamates and carbonates. These carbonate/carbamate species, on heating, decompose to CO\textsubscript{2} gas and the original amine is regenerated back for recycle.
The reaction of CO$_2$ with MEA is shown below and the typical process flow diagram for absorption with aqueous amines is shown in Figure 2.3.

\begin{align*}
2 \text{R}_1\text{R}_2\text{NH} + \text{CO}_2 & \rightleftharpoons \text{R}_1\text{R}_2\text{NH}^+ + \text{R}_1\text{R}_2\text{NCOO}^- \quad \text{(carbamate)} \quad 2.10 \\
\text{R}_1\text{R}_2\text{NH} + \text{H}_2\text{O} + \text{CO}_2 & \rightleftharpoons \text{R}_1\text{R}_2\text{NH}_2^+ + \text{HCO}_3^- \quad \text{(bicarbonate)} \quad 2.11
\end{align*}

Typically, 25 to 30 wt% of aqueous amine solution enters the top of absorption tower while the CO$_2$ containing gaseous stream is introduced at the bottom. In the tower, CO$_2$ containing gaseous streams contact amine solution and the CO$_2$ is chemically absorbed with amine. Desorption of absorbed CO$_2$ proceeds through a thermal regeneration or vacuum process. After regeneration the amine solution is recycled to the absorption tower for more CO$_2$ absorption.

CO$_2$ absorption by aqueous amine requires high temperature for regeneration of solvent and hence the process is energy intensive making it expensive to capture CO$_2$ from the power plant flue gas. Other problems associated with the process are amine degradation by oxidation leading to corrosion of process equipments.$^{86-88}$ The next few sections describe the amine degradation process, energy requirements, thermodynamics and reaction mechanism of this process.

2.2.2. Amine Degradation and Equipment Corrosion

Due to potential corrosion problems the amines are used as aqueous amines with concentration varying from 18 to 50 wt%. Oxidation of amines forms primary degradation products which reduce the absorption performance and further react to form secondary degradation products which cause corrosion resulting in system maintenance and equipment down time.$^{86,88}$ Primary amines are more reactive and hence have higher corrosion potential compared to secondary and tertiary amines. Higher concentration of
Table 2.4 Ways to remove CO₂ from atmosphere and process plants and recovery options for captured CO₂.

<table>
<thead>
<tr>
<th>Control Point</th>
<th>CO₂ removal options</th>
<th>Options for recovering captured CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>• Adsorption by solids</td>
<td>CO₂ captured by liquids</td>
</tr>
<tr>
<td></td>
<td>• Absorption by liquids</td>
<td>• Desorption by flashing or distillation</td>
</tr>
<tr>
<td></td>
<td>• Extraction by refrigeration</td>
<td>• Strip with gases like H₂, N₂ or steam</td>
</tr>
<tr>
<td></td>
<td>• Increase vegetation on land and ocean biota– photosynthesis</td>
<td>• Electrolytic decomposition of Na₂CO₃ to form NaOH, H₂, O₂, CO₂ using non</td>
</tr>
<tr>
<td></td>
<td>• Decomposition by low- and high-energy radiation</td>
<td>fossil fuel source</td>
</tr>
<tr>
<td>Oceans</td>
<td>• Strip CO₂ with H₂</td>
<td>CO₂ captured by solids</td>
</tr>
<tr>
<td></td>
<td>• Distillation or steam stripping</td>
<td>• Desorption by heating</td>
</tr>
<tr>
<td></td>
<td>• Acidification followed by degasification</td>
<td>• Desorption by pressure swing method</td>
</tr>
<tr>
<td></td>
<td>• Precipitation as carbonates, coral formation</td>
<td>• Decomposition by heating stripping using high pressure steam</td>
</tr>
<tr>
<td>Industrial Process Plants</td>
<td>• Adsorption by solids</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Absorption by liquids</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Extraction by refrigeration</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Use of alternative energy sources</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Advanced power cycle – air separation followed by combustion of fossil fuel with O₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>and recycle CO₂</td>
<td></td>
</tr>
</tbody>
</table>
Table 2.5 Typical values of overall forward reaction rate constant for CO$_2$-amine reactions.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Rate constant (mol/L-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>7600</td>
</tr>
<tr>
<td>DEA</td>
<td>1500</td>
</tr>
<tr>
<td>TEA</td>
<td>16.8</td>
</tr>
<tr>
<td>MDEA</td>
<td>9.2</td>
</tr>
</tbody>
</table>
## Table 2.6 Heats of vaporization and heats of reaction for various amine solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Concentration (wt %)</th>
<th>Heat of reaction (KJ/mol of CO$_2$)</th>
<th>Heat of vaporization (KJ/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>30</td>
<td>72</td>
<td>826</td>
</tr>
<tr>
<td>DEA</td>
<td>36</td>
<td>65</td>
<td>670</td>
</tr>
<tr>
<td>TEA</td>
<td>50</td>
<td>62</td>
<td>535</td>
</tr>
<tr>
<td>MDEA</td>
<td>50</td>
<td>53.2</td>
<td>550</td>
</tr>
</tbody>
</table>
secondary and tertiary amines can be used for absorption compared to primary amines. Primary amines are used in range of 18-30 wt% while secondary and tertiary amines are used with 30-50 wt% concentration.\textsuperscript{89}

The reactions involved in amine degradation are described in Figure 2.4.\textsuperscript{87} MEA reacts with CO\textsubscript{2} slowly to form MEA-carbamate, but the reaction rate is significant under process conditions. MEA-carbamate is further converted to 2-oxazolidone which is slowly converted to 2-hydroxyethyl-2-imidazolidone. This compound hydrolyzes to form N-(2-hydroxyethyl)-ethylenediamine which is less reactive compared to MEA and is also difficult to regenerate, resulting in fouling and corrosion of process equipment.

2.2.3. Energy Requirements and Thermodynamics

The energy costs involved in any absorption-desorption kind of process depends mainly on the regeneration of solvent. The total energy cost associated with the process can be approximately defined as

\[
\text{Total energy} = \text{Energy to blow the gas through scrubber} + \text{Energy to pump the liquid solvent} + \text{Heat required to regenerate the solvent}
\]

About 80\% of the total energy is consumed for solvent regeneration which is defined as reboiler duty and is calculated as

\[
\text{Regeneration duty} = \text{Heat of reaction} + \text{Sensible heat} + \text{Latent heat of vaporization of aqueous amine solution}
\]

The heat of reaction is equivalent to the energy required to break the chemical bond between amine and CO\textsubscript{2}. The energy required to bring the aqueous amine solution to reboiler temperature is called sensible heat. Latent heat of vaporization is addition of latent heat of vaporization of water and latent heat of vaporization of pure amine and
depends on wt% mixture. The heat of vaporization and heat of reaction for various amines is shown in Table 2.6.\textsuperscript{89}

Based on the heats of reaction and heats of vaporization, one can predict that MDEA would offer better energy efficiency compared to MEA. But if you compare the reaction kinetics, MDEA has far lower mass transfer rate compared to MEA. MEA being primary amine is more reactive with CO\textsubscript{2} compared to secondary and tertiary amines such as DEA, MDEA, and TEA.

2.2.4. Reaction Mechanism

The reaction between CO\textsubscript{2} and aqueous amine solutions advance at a finite rate and the rate is different for different kind of amines.\textsuperscript{89, 90} Some of the industrially important amines are MEA, DEA, TEA, di-isopropanolamine (DIPA) and methyl-di-ethanolamine (MDEA). Different wt% mixtures of these amines are used depending on the applications. From the literature review, it is found that not much data is available for tertiary amines and DIPA and hence a brief review of kinetics and reaction mechanism for primary and secondary amines is covered in this section.

The literature data on kinetics of CO\textsubscript{2} and alkanolamine reactions differ a lot, because the authors have used different experimental techniques, physico-chemical data and amine purities. The rate of reaction is invariably given as first order on CO\textsubscript{2} concentration in literature. Also the rate of reaction is found to be first order in MEA concentration regardless of experimental techniques and conditions used.\textsuperscript{90} Consequently, the reaction rate dependence on DEA vary widely in literature. For primary and secondary amines the following reactions occur with CO\textsubscript{2}.
Figure 2.3 Process diagram for typical aqueous amine CO$_2$ absorption plant
Figure 2.4 Reactions involved in MEA degradation leading to potential corrosion problems
where B is a base which can be another alkanolamine molecule, OH\(^-\) ion or H\(_2\)O and this base B is responsible for removal of proton. Based on this mechanism, Danckwerts derived the forward reaction rate at quasi-steady state. The rate expression was given by

\[
r = \frac{k_1[\text{CO}_2][\text{R}_1\text{R}_2\text{NH}_2]}{1 + k_{-1}/\Sigma k_b[B]}
\]  

(2.19)

Each of the above reactions (reactions 2.15 – 2.18) contributes to the overall reaction rate constant.\(^90\) For primary amines, reaction 2.17 is relatively faster than reaction 2.16 and term \(k_{-1}/\Sigma k_b[B]\)\(<\)1 and hence we get second order kinetics for reaction 2.15. Table 2.5 shows typical overall forward rate constants for CO\(_2\)-amine reactions.

2.2.5. CO\(_2\) Capture by Adsorption on Solid Sorbents

Solid amine based polymers/resins have been used for CO\(_2\) capture in closed environment like submarines and spacecrafts recently.\(^91,92\) These sorbents as such were not designed for large scale processes and high CO\(_2\) concentration found in power plant flue gases. The essence of designing a solid sorbent is high adsorption capacity and ease of regeneration. Also it should be able to adsorb in varying conditions, like different temperatures, moisture content, and CO\(_2\) concentrations in flue gases.
Table 2.7 CO\textsubscript{2} adsorption/absorption with amines and amine treated samples.

<table>
<thead>
<tr>
<th>Solvent / Sorbent</th>
<th>Reaction Conditions</th>
<th>Brief Conclusions</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine-Polyol sorbent</td>
<td>30°C, 50% humidity</td>
<td>Polyol-amine based sorbent capable of adsorbing and desorbing at room temperature. The amine concentration varies from 1-25 wt%.</td>
<td>91</td>
</tr>
<tr>
<td>Aminated molecular seives</td>
<td>Adsorption-30°C, desorption75°C</td>
<td>Sorbent has capacity to adsorb at low temperature (8-11°C) and in dry conditions or 80% relative humidity and low CO\textsubscript{2} concentrations.</td>
<td>93</td>
</tr>
<tr>
<td>Amine bonded silica gel</td>
<td>Adsorption at room temperature, desorption at 100°C</td>
<td>Amine is bonded on silica gel surface via 3-APTS. The sorbent can adsorb 10 STP cm\textsuperscript{3} per gm of sorbent. Adsorption of humid CO\textsubscript{2} produces small amount of HCHO. Suggesting activation of CO\textsubscript{2} molecule.</td>
<td>94</td>
</tr>
<tr>
<td>MgO, CaO on carbon based adsorbents</td>
<td>Adsorption at 28 and 300 °C. Pressure swing adsorption vacuum swing desorption</td>
<td>Individual oxides and mixed oxides on carbon based adsorbents were tried. The best results obtained were 0.28 mmol/g at 28°C and 0.22mmol/g at 300°C and 1bar.</td>
<td>95</td>
</tr>
<tr>
<td>Amine enriched fly-ash samples</td>
<td>Adsorption at 30°C with 10% CO\textsubscript{2} in He and desorption at 120°C.</td>
<td>Fly-ash samples containing about 50% C treated with amine enhance CO\textsubscript{2} capture capacity by a factor of 2. IR study show formation of bidentate and monodentate carbonate at 1148cm\textsuperscript{-1} and 1087 cm\textsuperscript{-1}.</td>
<td>96</td>
</tr>
<tr>
<td>EDA functional cross linked polymeric sorbents</td>
<td>Sorbent pretreated by heating before adsorption, pure CO\textsubscript{2} for adsorption and N\textsubscript{2} for purge</td>
<td>Primary amine binds 0.18 CO\textsubscript{2} molecules, secondary binds 0.07 while tertiary binds 0.2 CO\textsubscript{2} molecules. IR study show carboxylate bonds at 1650 and 1420 cm\textsuperscript{-1}.</td>
<td>97</td>
</tr>
<tr>
<td>MEA, MDEA and commercial solvents</td>
<td>18% CO\textsubscript{2}, 25-30 wt % amine solution, commercial solvent 50 wt%</td>
<td>Compares commercial solvents with MEA and MDEA and explains degradation of MEA and MDEA by oxidation.</td>
<td>87</td>
</tr>
<tr>
<td>MEA, DEA, MDEA, TEA, DIPA</td>
<td>Different wt % solution, CO\textsubscript{2} loading 0.4—0.5</td>
<td>Energy requirements for liquid solvent processes, reaction rate constants, heats of vaporization, enthalpy of solution and mass transfer enhancement.</td>
<td>89</td>
</tr>
<tr>
<td>MEA, DEA, DIPA, TEA</td>
<td>Different conditions</td>
<td>Reviews literature data on kinetics of CO\textsubscript{2} absorption by amine solutions and compares the data obtained by the author.</td>
<td>98</td>
</tr>
</tbody>
</table>
Recently amine treated solid sorbents and amine treated polymeric membranes have been researched for CO$_2$ adsorption and separation.\textsuperscript{85, 92, 99-107} It has also been estimated that cheap substrates like fly-ash and activated carbon can be used for CO$_2$ adsorption once or twice and then discarded, economically.\textsuperscript{82, 96}

Development of an economic CO$_2$ separation from flue gas requires a highly efficient CO$_2$ sorbent. It is desired that sorbent must possess high CO$_2$ capture and long term regeneration capacity at the level above 2000 $\mu$mol/g with a small difference in adsorption and desorption temperatures in the flue gas environment. One potential approach to prepare such a sorbent is to graft CO$_2$ adsorption sites on the high surface area supporting materials.

Table 2.7 summarizes the literature dealing with CO$_2$ capture and separation by absorption and adsorption. The literature predominantly contains information on absorption in aqueous amines, adsorption on amine treated surfaces and methods to modify the support surface with amine moieties. The modified amine sorbent literature is a new research area and most of the literature cited is from last 5 years.
CHAPTER III
EXPERIMENTAL

3.1. Experimental Apparatus

The experimental apparatus used for these studies is illustrated in Figure 3.1. It consists of three sections: 1) the feed and gas handling system, 2) the reactor system consisting of tubular reactor and Diffused Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) reactor, and 3) the analysis section. The actual set-up for each experiment might differ slightly from one study to another.

3.1.1. Feed and Gas Handling System

High quality 99+ % gases were used for all the experiments. The gas flow rates were controlled by Brooks 5850 series mass flow controllers. Step and pulse techniques were used for transient studies and pulse technique was also used to calibrate the mass spectrometer. The pulse and step studies were done using Valco 6 port and 4 port valves, respectively. The pulse and step techniques will be described later.

3.1.2. Reactor System

The reactor system consists of an in-situ DRIFTS reactor from Spectra-Tech, Inc and a stainless steel tubular reactor for packing of additional catalyst or sorbent to determine the change in concentration of the effluent on the mass spectrometer. The DRIFTS is a special accessory available commercially for FT-IR. It is used for reaction studies at high temperature, high pressure, as well as vacuum. It allows us to monitor the
Figure 3.1. Typical experimental setup for transient studies
changes on the surface of the catalyst or the sorbent during a reaction by IR spectroscopy. The DRIFTS and tubular reactor are described in detail in following sections.

3.1.2.1. Tubular Reactor

The tubular reactor used for these studies is constructed of stainless steel tube (3/8” OD and 0.305” ID). The catalyst is held as packed bed with help of two glass wool plugs on either side of the bed. The reactor is heated by wrapping Barnstead Thermolyne standard insulated samox heating tape around the tube which is insulated with standard insulation cloth available from Fischer-Scientific. The temperature is monitored with either a J or K type thermocouple and is controlled by Omega temperature controller CN 2011TC. The tubular reactor is used in series with DRIFTS reactor to increase the total product concentration in the effluent gases such that the changes in the reactant and product concentration can be determined accurately by the mass spectrometer. The DRIFTS reactor holds very small amount of sample/catalyst and hence we load the tubular in series with DRIFTS reactor.

3.1.2.2. DRIFTS Reactor

A Spectra Tech, Inc in-situ DRIFTS reactor assembly with high temperature and high pressure chamber was used for all the experiments. The DRIFTS assembly consists of the following components: 1) collector—a series of mirrors that reflects the IR beam from the source to the catalyst surface, and to the detector, 2) ceramic reactor equipped with a thermocouple and a dome for high pressure studies, and 3) temperature control unit. Figure 3.2 illustrates the ceramic reactor with dome. The dome covers the ceramic reactor which is sealed with a o-ring for high pressure studies. The dome is equipped with zinc selenide (ZnSe) windows that allow IR transmission from 4000-650 cm\(^{-1}\).
ZnSe windows are stable up to 300 °C in air and require cooling above 300 °C. A water jacket is coiled around the dome for water cooling. The reactant gases flow through the packed bed of catalyst or sorbent in the ceramic cup (which is also a heater). The temperature of the catalyst is monitored by K type thermocouple that penetrates through the side of ceramic heater and into the catalyst bed. The heater and thermocouple are connected externally to a temperature control unit from Spectra-Tech, Inc. with Omega temperature controller and a variac.

3.2. Catalyst Preparation

The most common methods used for catalyst preparation in laboratory are (i) incipient wetness impregnation, (ii) co-precipitation, and (iii) sol-gel method. The catalysts used in these studies were prepared by incipient wetness impregnation (IWI) method more commonly known as wetness impregnation method. The active component of catalyst is dispersed over high surface area material used as a support. The catalyst support and catalyst preparation methods used in the laboratory are described in this section. The method of preparation of the catalyst and its dispersion on the support plays an important role in the particle size and the distribution of the active component on the support.

3.2.1. Catalyst Preparation – Wetness Impregnation

An aqueous salt solution of nitrate or chloride of active metal is dispersed on the catalyst support drop by drop with constant stirring. Ideally, each drop should be totally dispersed and the catalyst should be dried before impregnating next drop of the solution. This procedure can take from few hours to days depending on the amount of catalyst prepared and the wt% of the active metal.
Figure 3.2. Schematic of high temperature-high pressure DRIFTS chamber
Once the impregnation is complete, the catalyst is dried at room temperature for 24 hours and calcined at 500 °C for 3-4 hours to remove all the nitrates, chlorides, and any volatiles present in the catalyst. The ramping rate is maintained at 2-3 °C/min to avoid sintering, plugging of the pores, and collapse the pore structure of the support in some cases. The calcined catalyst is reduced in flowing hydrogen at different temperatures ranging from 200 °C to 500 °C depending on the active metal. Some metals can be reduced at lower temperatures while some of them have to be reduced at higher temperatures.

3.2.2. Catalyst Support Preparation

The active component of a catalyst is dispersed on the high surface area materials. The most common support materials are Al₂O₃, SiO₂, TiO₂, and activated carbon. These support materials not only provide high surface area for dispersion but give mechanical stability and sometimes enhance the activity of the catalyst.

These catalyst supports are either prepared by heating their respective metal salts at temperatures above 500 °C, more commonly 1000 °C, or by precipitating the hydroxides at high pH using aqueous alkalis. The catalyst support used for these studies were Al₂O₃, CeO₂ and SBA-15. The Al₂O₃ and CeO₂ were purchased from commercial vendors while SBA-15, a high surface area mesoporous SiO₂ material, was prepared in the laboratory by the method described in the next section. Individual catalyst preparation will be described in detail in the respective chapters.

3.2.3. Synthesis of Mesoporous Material-SBA-15

The mesoporous silica like SBA and MCM family of materials have gained considerable interest recently for catalyst supports. In particular, SBA-15 and MCM-41
are of great interest due to their uniform hexagonal pore structure which have high hydrothermal stability and large surface areas which can be manipulated by changing the reaction conditions.

SBA-15 was synthesized using triblock-copolymer (Pluronic P123-EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) as a structure directing agent, tetraethylorthosilicate (TEOS) as a silica precursor, trimethyl benzene (TMB) as swelling agent, HCl for pH control. 4.0 g of Pluronic P123 was first dissolved in 30 g of water and 120 g of 2M HCl solution followed by addition of 30 g of (TMB). The resulting mixture was stirred at 35°C for 2 hr. The final solution was achieved by addition of 8.50 g of TEOS which was stirred at 35°C for 22 hr, and then kept at 100°C for 24 hr without stirring in a air tight bottle. The resultant precipitated residue was filtered, washed and dried at room temperature to obtain as-synthesized SBA-15. As-synthesized SBA-15 was calcined in air at 500°C for 6 hours by increasing the temperature from 25 to 500 °C at a rate of 2 °C/min.

3.3. Analysis Section

The analysis section includes IR spectrometer, a mass spectrometer (MS), and a gas chromatograph (GC). The IR spectrometer used for these experiments was either a 550 Nicolet Magna or/and 560 Nicolet Magna equipped with a MCT-B or MCT-A detectors at a resolution of 4 cm<sup>-1</sup>. Typically, 32 scans were co-added to obtain the spectrum. Both the spectrometers were connected to Gateway Pentium II computers which utilized OMNIC 5.1 or higher software.

One of the two mass spectrometers in the laboratory, Pfeiffer QMS 200 and Pfeiffer Omnistor , was used to monitor the effluents of the reactions. Both the mass spectrometers are quadrupole mass spectrometers with 6” quadrupole rod length used to
The Omnistar MS has electronic inlet valve controlled by computer while the QMS 200 is equipped with a manual inlet valve. The inlets of both MS are modified by capillary tubing and the orifice of the Omnistar was restricted to 0.01 mm from the manufacturer specification of 0.02 mm to reduce the total pressure due to the change in inlet tube from 1/16” capillary to 1/8” SS tube with a small piece of capillary welded at the inlet side. In either case, the effluent is fed into a capillary line and into the ionization chamber, where the operating pressure is around 5E-6 mbar. The dwelling time (time to scan and record) each m/e signal is typically less than 0.5 second, which can be modified from 0.1 sec up to 5 sec. Careful selection of the m/e ratios is required to prevent overlapping of the responses as a result of fragmentation in the ionization chamber. The MS data is acquired by QUADSTAR software using computers with Pentium II processors and serial ports.

3.4. Techniques

A variety of experimental techniques are used in catalysis research; few of them used in these studies are described here. These techniques involve a controlled perturbation (from a steady state condition) of the system, which leads to transient state. Through transient techniques, one can obtain information about reaction mechanism, surface properties of the catalyst, catalyst activity, poisoning, etc.

3.4.1. Step Input

Following a steady state condition, using a 4 port valve, a nearly instantaneous switch may be made from one gas flow to another. Generally this switch is made from an inert gas or mixture of gases to reactant gas or gases. This allows us to study the adsorbate and product formation on the catalyst surface via IR spectroscopy and product
formation via MS in the reactor effluent gases. The flow rates of the gases should be identical on both sides of the 4-port valve and the switch should be smooth and instantaneous for an effective step switch. If the flow rates are not identical and the switch is not smooth then problems, such as pressure changes, will complicate the interpretation of the data obtained from the MS.

3.4.2. Pulse Input

Using a 6-port valve, a known volume of gas can be “injected” into the reactor system. Refer to Figure 3.1 for the 4-port and 6-port valve descriptions. Gas A, the carrier gas, flows on one side while Gas B is flown on the other side of the valve filling a loop of known volume continuously. When the valve is switched, gas A flows through the pulsing loop and carries gas B along with it into the reactor system.

The transient state generated through this technique may lead to quantitative information about the reaction on catalyst surface when coupled with IR and MS. Catalyst dispersion, reaction rates, and poisoning information are few examples that can be obtained by this information. This pulse technique can also be used to calibrate certain equipments like MS or GC in which the known volume of gas to be calibrated is injected to MS or GC in bypass mode.

3.4.3. Temperature-Programmed Techniques

Temperature-programmed techniques such as temperature-programmed desorption, temperature-programmed reaction, temperature-programmed oxidation, and temperature-programmed reduction are most commonly used techniques for catalyst characterization and catalyst activity studies. In these techniques the catalyst is heated at a specific rate; the catalyst surface is monitored by in situ spectroscopic techniques and
the effluent of the reactor is monitored using GC or MS. The amount of oxygen uptake during temperature-programmed oxidation, or the amount of hydrogen uptake during temperature programmed reduction can yield us the catalyst oxidation state and the number of active sites on the surface making some simple assumptions. Temperature-programmed reaction could yield us the catalyst activity information at different temperatures.

3.4.4. Simplified Diffuse Reflectance Theory

When an infrared beam is focused onto a fine particulate matter, the incident beam may interact with the particles in one of several ways. First, the radiation can be reflected off the top surface of the particle without penetrating the particle. Second, the light can undergo multiple reflections off particle surfaces without penetrating into the particle. These reflections carry no characteristic information of the sample and is called specular reflectance. True diffuse reflectance occurs when the incident infrared beam penetrates one or more sample particles and subsequently scatters from the sample matrix.

When a beam of light impinges on a smooth mirror like surface, it is reflected and the reflected angle is equal to the incident angle. In diffused reflectance, the reflection angle of a series of reflected beams do not have any relationship with the angle of incidence. Along with diffuse reflectance, specular reflection also occurs and being highly focused, competes with diffused reflected beams. The specular component contains little information or no information about IR absorption characteristics of the sample, and seriously interferes with the spectrum giving distortions in the absorption bands.
The problem of specular reflectance may be overcome, at least in part, by diluting the sample with a non-absorbing material like KBr or CaF$_2$. Particle size is another factor which influences the quality of diffuse spectra. As the particle size increases, the absorbance bands become broader. For quality spectra, particle size should be $\leq 10 \ \mu$m in diameter.
CHAPTER IV

PARTIAL OXIDATION OF METHANE OVER Rh/Al₂O₃

4.1. Introduction

The recent advancements in the fuel cells due to its high energy efficiency have renewed the interest in hydrogen production technologies.¹,² Hydrogen is considered to be the fuel of the next century and is believed to change the current infrastructure dependant on the fossil fuels.³⁻⁶ The increase in the use of fossil fuels has also been linked to the increase in the atmospheric CO₂, a global warming gas.⁷⁻⁹ The use of hydrogen in fuel cells will not only improve the energy efficiency, but also reduce or maintain the atmospheric CO₂ levels.

Hydrogen can be produced by various ways as shown in Figure 4.1.¹⁰⁻¹⁴ The cleanest way would be using the solar water splitting or electrolysis using photovoltaic energy. There is considerable interest in production of hydrogen by biomass reforming. Nevertheless, these technologies have a very low overall efficiency to meet the demand for hydrogen.¹⁵ Most of the hydrogen has been produced by reforming and gasification of fuels (natural gas, gasoline, diesels, higher hydrocarbons, and coal).¹⁴ Reforming of hydrocarbons involve oxy-reforming (partial oxidation), steam reforming (with H₂O), and dry reforming (using CO₂).¹⁶ The stoichiometric reactions for partial oxidation and reforming using methane are described by the following reactions:
HYDROGEN
• Clean Energy Source

Figure 4.1. Hydrogen production technologies
a) \[ \text{CH}_4 + \text{H}_2\text{O} \xrightarrow{\text{steam reforming}} \text{CO} + 3\text{H}_2 \quad \Delta H = +49.2 \text{ kcal/mol} \]

b) \[ \text{CH}_4 + \text{CO}_2 \xrightarrow{\text{CO}_2 \text{ reforming}} 2\text{CO} + 2\text{H}_2 \quad \Delta H = +61.9 \text{ kcal/mol} \]

c) \[ \text{CH}_4 + \frac{1}{2} \text{O}_2 \xrightarrow{\text{partial oxidation}} \text{CO} + 2\text{H}_2 \quad \Delta H = -8.5 \text{ kcal/mol} \]

The steam and \( \text{CO}_2 \) reforming reactions (a, b) are highly endothermic reactions carried out above 800 °C, and the catalysts are prone to poison by small amounts of sulfur present in the fuel as well as the coke formation.\(^{17-20} \) On the other hand, partial oxidation is an exothermic reaction. Although partial oxidation is an exothermic reaction, it has to be carried out at high temperatures to avoid total oxidation reaction which is favorable at lower temperatures on the catalyst.\(^{16} \) Moreover, proper temperature control is required to avoid the hot spots and potential explosions that can be caused due to the methane.\(^ {16} \)

Catalytic partial oxidation of methane can be a one step process and has been reported in the literature.\(^{21-23} \) Supported Rh is one of the active catalysts for partial oxidation of methane to synthesis gas.\(^{23-31} \) Although Rh based catalyst can be expensive, advantage of using Rh is its long term stability due to the high resistance to deactivation and coking. There is considerable debate on the reaction mechanism for formation of hydrogen from partial oxidation of methane.\(^ {16, 23, 28, 30, 32} \) Two mechanisms are proposed of which one is direct partial oxidation while the other is reforming mechanism. In the reforming mechanism, it is believed that methane undergoes total oxidation (combustion reaction) to give \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) which further react with uncombusted methane to give \( \text{CO} \) and hydrogen. In partial oxidation mechanism, the \( \text{CH}_4 \) undergoes direct oxidation to \( \text{CO} \) and \( \text{H}_2 \) with low selectivity for \( \text{CO}_2 \). The mechanism of the \( \text{CH}_4 \) oxidation reaction depends on the catalyst as well as the reaction conditions.\(^ {29, 30, 32} \) An insight into the
reaction of methane with oxygen on the catalyst surface would allow us to understand the reaction pathway.

The objective is to investigate the mechanism for CH$_4$ oxidation on 2 wt% Rh/Al$_2$O$_3$ catalyst in the temperature range of 450-600 °C. The reaction mechanism can be studied using transient pulse and step techniques by monitoring the adsorbed species on the catalyst surface using IR spectroscopy and the product formation using mass spectrometry. Some of the experimental results of partial oxidation of methane on Rh/Al$_2$O$_3$ studied in our lab have been used in this chapter for comparison.$^{33}$

4.2. Experimental

4.2.1. Catalyst Preparation:

The 2 wt% Rh/Al$_2$O$_3$ catalyst was prepared by incipient wetness impregnation using an aqueous solution of RhCl$_3$•2H$_2$O (Alfa Chemicals) onto γ-alumina support (Alfa Chemicals, 100 m$^2$/g). The catalyst was dried overnight in air at room temperature and calcined by flowing air at 723 K for 6 hours. It was then reduced in flowing hydrogen at 723 K for an additional 6 hours and stored in sealed vials.

4.2.2. Experimental Apparatus

The experimental setup (Fig 3.1) for this study has been described in chapter III and the procedure will be described here in short. Approximately 130 mg of the catalyst was placed in the tubular reactor supported by glass wool and 30 mg of the catalyst was loaded in the DRIFTS. Unlike the other studies reported in this dissertation, the DRIFTS reactor for this study was placed downstream of the tubular reactor.

The gases used in the experiment were CH$_4$ (Praxair, UHP grade), O$_2$ (Praxair, UHP grade) and Ar (Praxair, 99.999%). Pulsing of O$_2$ (1cc) into flowing CH$_4$/Ar (3/37
over Rh/Al₂O₃ at 450, 500, 550 and 600 °C was done using a six-port switching valve with a 1 cc loop. Throughout the experiment, total gas flow rates were maintained at 40 cc/min. The transient response on the surface of the catalyst was recorded by DRIFTS; MS was used to record the product formation profile. The calibration factor for the MS was calculated by pulsing known amounts of CH₄, CO, CO₂, and H₂.

4.3. Results

4.3.1. Pulsing of O₂ into CH₄ at 500 °C

The catalyst was reduced with pure hydrogen at 500 °C for 2 hours before exposure to CH₄ and pulsing of O₂. After reduction, the catalyst was exposed to CH₄ until a steady state CH₄ flow was achieved as observed from MS baseline. Figure 4.2 shows DRIFTS IR spectra during CH₄ flow on Rh/Al₂O₃ at 500 °C after reduction. Exposure of Rh/Al₂O₃ to CH₄ led to the formation of CO₂ and adsorbed linear CO at 2008 cm⁻¹. Formation of linear CO at 2008 cm⁻¹ and lack in variation of the wavenumber with the intensity of adsorbed CO suggests highly dispersed Rh particles on the Al₂O₃ surface. The CO and CO₂ led to the formation of formate species as evidenced by the IR bands at 1379 and 1581 cm⁻¹. Prolonged exposure of the catalyst to CH₄ flow led to a shift in the band for linear CO from 2008 cm⁻¹ to 2063 cm⁻¹ and a decrease in the broad water band around 3500 cm⁻¹. The shift in the band from 2008 cm⁻¹ to 2063 cm⁻¹ indicates partial oxidation of Rh on surface. CO adsorbed on Rh⁺ sites appear above 2080 cm⁻¹ and hence we attribute these partially oxidized Rh atoms as Rh⁶⁺. The reduction in the water band is due to the reaction of CH₄ with water present on the Al₂O₃
surface. It is known that $\text{Al}_2\text{O}_3$ surface is not completely dehydrated until a temperature of $900 \, ^\circ\text{C}$.\textsuperscript{39}

Figure 4.3 shows IR spectra and MS profiles during the first $\text{O}_2$ pulse at $500 \, ^\circ\text{C}$ in steady state $\text{CH}_4$ flow. The DRIFTS reactor being downstream of the tubular reactor is exposed to the effluent from the tubular reactor. Figure 4.3(a) shows the IR bands for the adsorbed CO and the formates as seen in Figure 4.2. No product formation was observed upon pulsing of $\text{O}_2$ at $500 \, ^\circ\text{C}$ in flowing $\text{CH}_4$. The MS profiles [Fig. 4.3(b)] show increase in $\text{CH}_4$ from its steady state during $\text{O}_2$ pulsing. This is caused by displacement of adsorbed methane on the catalyst in tubular reactor by the incoming $\text{O}_2$ pulse as all of the $\text{O}_2$ was consumed in the tubular reactor. Since no product was observed on IR or MS, three more 1cc $\text{O}_2$ pulses were introduced. No product formation was observed until rapid pulsing of $\text{O}_2$.

After 4 single pulses and two rapid pulses, formation of CO, CO$_2$, and H$_2$ was observed on the MS as shown in Figure 4.4 (a). The formation of H$_2$ and CO was higher initially for initial few pulses which decreased later. All of the $\text{O}_2$ was consumed during each isolated and rapid pulse at $500 \, ^\circ\text{C}$ as no $\text{O}_2$ was observed in the effluent on the MS. A series of IR spectra were recorded during the rapid pulsing and the results are presented in Figure 4.4(b) and the IR intensity of certain species is plotted versus time in Figure 4.4(c). Exposure of the effluent from the tubular reactor to the DRIFTS catalyst surface led to the depletion of adsorbed CO at $2063 \, \text{cm}^{-1}$ and the formation of adsorbed CO band at $2018 \, \text{cm}^{-1}$ which is assigned to linear CO formed on Rh$^0$ sites.\textsuperscript{40} The disappearance of IR band at $2063 \, \text{cm}^{-1}$ and the formation of linear CO at $2018 \, \text{cm}^{-1}$ suggest the reduction of Rh catalyst by the H$_2$/CO produced by the partial oxidation and
Figure 4.2. DRIFTS spectra during Ar/CH\textsubscript{4} flow on 2wt\% Rh/Al\textsubscript{2}O\textsubscript{3} at 500 °C after reduction with pure H\textsubscript{2} at 500 °C
Figure 4.3. Results of first $O_2$ pulse in to steady state $CH_4$ flow at 500 °C
(a) DRIFTS spectra and (b) MS analysis
Figure 4.4. Results of rapid O₂ pulses in to steady state CH₄ flow at 500 °C (a) MS analysis, (b) DRIFTS spectra, and (c) IR intensity vs time of selected species.
Figure 4.5. Results of first O$_2$ pulse in to steady state CH$_4$ flow at 550 °C
(a) DRIFTS spectra and (b) MS analysis
the reforming reactions. The water formed during rapid pulsing by combustion reaction replenished the broad water band on the surface around 3500 cm\(^{-1}\). Pulsing of O\(_2\) also led to desorption of the formate species. The formates can desorb as CO\(_2\), H\(_2\), and H\(_2\)O.\(^{41}\) The water formed by combustion reaction is observed on the MS in Figure 4.4(a) which lags behind CO\(_2\). The water lagged behind other gaseous species is partly caused by adsorption and desorption of H\(_2\)O on the transportation tubing and partly due to replenishment of the dehydrated Al\(_2\)O\(_3\) surface.

4.3.2. Pulsing of O\(_2\) into CH\(_4\) at 550 °C and 600 °C

Subsequent to the study at 500 °C, the catalyst was heated to 550 °C in an inert (Ar) stream and then exposed to CH\(_4\) until a steady state flow was achieved. The exposure of catalyst to CH\(_4\) at 550 °C led to the formation of adsorbed CO at 2082 cm\(^{-1}\). Formation of adsorbed CO at 2082 cm\(^{-1}\) illustrate that the Rh is in partially oxidized state. At 550 °C, the very first pulse of O\(_2\) led to the formation of CO, CO\(_2\), and H\(_2\); the exposure of the DRIFTS catalyst to the effluent from the tubular led to the formation of a band at 2032 cm\(^{-1}\) for the linear CO on Rh\(^0\) sites as observed in Figure 4.5(a). The IR intensity of the linear CO formed matched closely to that of H\(_2\) profile on the MS which confirm that H\(_2\) leads to the reduction of the Rh surface during the reaction. The adsorbed CO desorbs from the surface as CO gas within a minute as seen on the Figure 4.5(a) and (b). Moreover, Figure 4.5(b) shows that the formation of CO and H\(_2\) lagged behind that of CO\(_2\) revealing that CO\(_2\) is a primary product while CO and H\(_2\) are secondary products. This observations lead to the conclusion that syngas is produced by CO\(_2\) reforming rather than direct partial oxidation.
The IR and MS results of rapid O₂ pulsing into steady state CH₄ flow at 550 °C are shown in Figure 4.6. Comparison of MS profiles in Figure 4.6(a) to that of Figure 4.4(a) shows that CO and CO₂ produced from the first rapid pulse is equivalent to the remaining 19 pulses at 550 °C. At 500 °C, the amount of CO and CO₂ increased with increase in the number of pulses and then decreased slightly. The DRIFTS spectra of rapid O₂ pulsing are similar to that at 500 °C but with decreased IR intensity for adsorbed CO. The decrease in the intensity is due to higher rate of desorption of linear CO than the rate of formation. The broad IR water band around 3500 cm⁻¹ increased due to the formation of water. The amount of H₂ formed decreased slightly with number of pulses of O₂ in to CH₄, while the formation of CO and CO₂ was constant. The decrease in formation of H₂ might be due to oxidation of H₂ to H₂O by the excess of O₂ on the surface as the amount of CO does not change with number of O₂ pulses.

At 600 °C, the conversion of methane decreased which led to a decrease in the formation of CO, CO₂, and H₂. Further, there was no evidence of linear CO species on Rh⁰ and a small band for linear CO on partially oxidized surface was observed at 2080 cm⁻¹ which disappeared with the O₂ pulse. The results of rapid fire pulsing were similar to that of single pulse; the reactant conversion and product formation was lower than that at 550 °C. The formation of CO, CO₂ and H₂ were in phase and the peak formation was observed at the same time on MS as shown in Figure 4.7. All of the O₂ was consumed during single and rapid pulses. The formation of CO, CO₂ and H₂ at the same time suggests that the partial oxidation and total oxidation reactions are taking place simultaneously.
Figure 4.6. Results of rapid O₂ pulses in to steady state CH₄ flow at 550 °C (a) MS analysis, (b) DRIFTS spectra, and (c) IR intensity vs time of selected species.
Figure 4.7. Results of first O$_2$ pulses in to steady state CH$_4$ flow at 600 °C
(a) DRIFTS spectra and (b) MS analysis
Figure 4.8. Results of first O\textsubscript{2} pulse in steady state CH\textsubscript{4} flow at 450 °C
(a) DRIFTS spectra and (b) MS analysis
Table 4.1. Methane conversion and product formation rates during $O_2$ pulsing at different temperatures

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>CH$_4$ conversion (%)</th>
<th>$X_{CH_4}$</th>
<th>H$_2$</th>
<th>CO</th>
<th>CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>76.8</td>
<td>21.9</td>
<td>5.5</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>43.4</td>
<td>3.5</td>
<td>1.2</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>43.7</td>
<td>17.3</td>
<td>3.57</td>
<td>3.4</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.9. Results of rapid O₂ pulses in to steady state CH₄ flow at 450 °C (a) MS analysis, (b) DRIFTS spectra, and (c) IR intensity vs time of selected species
4.3.3. Pulsing of $O_2$ into CH$_4$ at 450 °C

Subsequent to the reaction study at 600 °C, the tubular and DRIFTS reactor were cooled to 450 °C in an inert (Ar) environment. At 450 °C, there were no adsorbed CO species formed during steady state CH$_4$ flow. Figure 4.8 shows IR and MS results for the first pulse of O$_2$ into CH$_4$ flow at 450 °C. The formation of linear CO at 2032 cm$^{-1}$ is observed after the DRIFTS catalyst is exposed to the products from the effluent. The linear CO formed on the surface does not desorb completely as seen from the top spectrum in Figure 4.8(a). A close look at the MS analysis [Fig. 4.8(b)] and calculation of the products formed shows that the amount of CO and H$_2$ formed at 450 °C is higher than that at 600 °C and lower than that at 550 °C. Table 4.1 shows product analysis and methane conversion at each temperature during O$_2$ pulsing.

The IR and MS results during rapid O$_2$ pulsing is shown in Figure 4.9. The MS analysis in Figure 4.9(a) shows O$_2$ breakthrough after 4 rapid pulses. The formation of CO$_2$ and conversion of methane is almost constant while the formation of CO and H$_2$ decreases gradually. The IR analysis during rapid pulsing shows a very strong IR band for adsorbed CO at 2006 cm$^{-1}$ which is observed only on highly dispersed Rh$^0$ atoms and was observed on fresh catalyst after reducing with H$_2$ at 500 °C with CH$_4$ flow. The intensity of linear CO observed is highest at 450 °C and the amount of CO in effluent is higher at 450 °C compared to that at 600 °C and lower than that at 550 °C. The adsorbed linear CO stays on the Rh$^0$ surface. Figure 4.9(c) shows the IR peak height versus time for some selected species observed on IR. It is observed that adsorbed linear CO is formed on the surface with 5$^{th}$ O$_2$ pulse during rapid pulsing and the intensity of linear
CO increases with increase in number of pulses. The peak height of linear CO is highest when the peak height of CO\textsubscript{2} and methane is lowest (i.e. when methane resumes near its steady state value).

4.4. Discussion

The objective of pulsing O\textsubscript{2} in to CH\textsubscript{4} stream is to probe the role of adsorbed oxygen in the formation of CO/H\textsubscript{2}. The amount of adsorbed oxygen present on the catalyst surface during reaction controls the selectivity of the reaction. Moreover, the strength of adsorbed oxygen can lead to the formation of either partial or total oxidation products.\textsuperscript{16, 30} It has been reported that strongly adsorbed oxygen activates partial oxidation and the weakly adsorbed oxygen leads to the activation of total oxidation route.\textsuperscript{42} Although IR spectroscopy cannot determine the nature of adsorbed oxygen species, the nature of Rh sites can be determined by looking at the wavenumber of adsorbed CO.\textsuperscript{43} Raman spectroscopy has been used actively to determine the kind of adsorbed oxygen on the surface. At 450 °C, the presence of linear CO at 2006 cm\textsuperscript{-1} suggests highly dispersed Rh\textsuperscript{0} on the surface. Moreover, the intensity of the adsorbed CO changes during rapid oxygen pulsing, but the wavenumber of adsorbed CO remains the same. It has been revealed that wavenumber of linear CO changes with intensity of adsorbed CO on neighboring Rh atoms due to dipole-dipole coupling\textsuperscript{40, 43}. This confirms that CO is adsorbed on highly dispersed Rh\textsuperscript{0} atoms. The high dispersion of Rh particles might be a result of multiple oxidation-reduction cycles during O\textsubscript{2} pulsing at different temperatures. It is well known that the metal particles on the support can be well dispersed by oxidizing and reducing the catalyst for several times.
Figure 4.10. Results of first O$_2$ pulse in steady state CH$_4$ flow at 550 °C from a previous study with tubular downstream of DRIFTS reactor (a) IR spectra and (b) MS analysis.
In this study, during steady state CH$_4$ flow, a band above 2063 cm$^{-1}$ was observed at all temperatures except for 450 °C. This band has been assigned to CO adsorbed on partially oxidized Rh$^{5+}$ sites. The hydrogen formed in the tubular reactor reduces the catalyst in the DRIFTS. Further linear CO is formed on the surface which might be due to (i) adsorption of gas phase CO from the effluent on the reduced catalyst, (ii) CO formed from reforming of CH$_4$ by CO$_2$ on the DRIFTS catalyst, and (iii) both of the above. From the IR analysis, it is likely that adsorbed linear CO is formed by reforming of CH$_4$ as adsorbed CO is seen after catalyst is exposed to CO$_2$. A rise in temperature was also observed at the front end of tubular during each O$_2$ pulse in the reactor suggesting the exothermic complete oxidation reaction. This is clearly evidenced by previous study on CH$_4$ partial oxidation by O$_2$ pulsing with DRIFTS reactor upstream of the tubular reactor.\textsuperscript{33} Since DRIFTS is upstream of tubular reactor, the catalyst in the DRIFTS is exposed to O$_2$ pulse rather than the effluent from the tubular reactor.

Figure 4.10 shows DRIFTS spectra and MS analysis during 1cc O$_2$ pulse in CH$_4$ flow at 550 °C. During this study, the DRIFTS reactor was placed before the tubular reactor. This time resolved IR spectra clearly show that CO$_2$ is formed on the catalyst surface which then leads to the formation of linear CO on the surface which eventually desorbs as CO gas. At 450 °C, the results are similar to that observed in these studies where linear CO is accumulated on the surface which suggests that the rate of formation of CO is much higher than the rate of desorption at 450 °C. The rate of CO desorption increases with an increase in the temperature. At 600 °C, no linear CO was observed on the catalyst surface.
On the basis of the observed lead-lag relationships and the active intermediates on the catalyst surface, following series of overall reactions are proposed.

\[
\begin{align*}
\text{CH}_4 + \text{O}_2 & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{CH}_4 + \text{CO}_2 & \rightarrow 2\text{CO} + 2\text{H}_2 \\
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2 \\
2\text{CO} + \text{O}_2 & \rightarrow 2\text{CO}_2
\end{align*}
\]

The above overall reactions are results of the following postulated elementary steps: (i) dissociative adsorption and activation of CH\(_4\) and O\(_2\) on the Rh surface, (ii) reaction of adsorbed CH\(_x\) with adsorbed O to form CO\(_2\), (iii) activation and reaction of CO\(_2\) with adsorbed CH\(_x\) to form adsorbed CO on the surface, (iv) desorption of linear CO to CO gas, and (v) combination of adsorbed H to form H\(_2\).

A partial oxidation study with 1 wt% Rh supported on SiO\(_2\) and Al\(_2\)O\(_3\) using FT-IR by Weng et al showed that Rh on SiO\(_2\) is in reduced state while Rh on Al\(_2\)O\(_3\) has partially oxidized Rh surface under reaction conditions. They observed direct partial oxidation mechanism on Rh/SiO\(_2\) while reforming mechanism was observed on Rh/Al\(_2\)O\(_3\). It has been reported by several researchers that the support plays an important role in reaction pathway for methane partial oxidation. Our studies on 2 wt% Rh/Al\(_2\)O\(_3\) show that the formation of CO\(_2\) lagged behind that of CO and H\(_2\) revealing that CO and H\(_2\) are secondary products formed by CO\(_2\)/H\(_2\)O steam reforming of CH\(_4\). The observation of linear CO at all temperatures reveal that the Rh is present as Rh\(^0\) (reduced form) or in partially oxidized state (Rh\(^{\delta+}\)) on the catalyst. This is further confirmed by the absence of any gem-dicarbonyl CO species which is observed on oxidized Rh\(^+\) surface.
4.5. Conclusions

In situ IR spectroscopy studies reveal that linear CO is formed on the catalyst surface during the reaction in the presence of hydrogen. The presence of linear CO at 2063 cm\(^{-1}\) suggests that Rh is in partially oxidized state on Al\(_2\)O\(_3\) catalyst during reaction conditions. The amount of adsorbed CO on the catalyst surface decreases as temperature of the reaction increases which suggest the rate of desorption of CO is higher than the rate of formation at higher temperatures. The intensity of adsorbed CO observed at 450 °C was highest and most of the adsorbed CO remained on the surface at 450 °C. The formation of CO\(_2\) before that of CO, as observed from time-resolved FT-IR spectroscopy as well as the MS profiles, reveal that CO is secondary product while CO\(_2\) is the primary product. The lead-lag relationship observed from IR and MS suggest a reforming mechanism for partial oxidation of CH\(_4\) on 2 wt% Rh/Al\(_2\)O\(_3\) between 450 and 600 °C.
CHAPTER V

WATER-GAS SHIFT REACTION OVER Ni/CeO$_2$ and Ni-Re/CeO$_2$

5.1. Introduction

Polymer electrolyte membrane (PEM) fuel cells utilize nearly pure hydrogen as a fuel. Hydrogen containing CO concentration as low as 10 ppm can poison the anode catalyst of the fuel cell.$^{1, 2}$ Typically, production of hydrogen involves: (i) reforming of CH$_4$ to syngas at temperatures above 800 °C, (ii) high and low temperature water-gas shift to convert CO to CO$_2$ and generate additional H$_2$ from water, (iii) preferential oxidation of the remaining CO to CO$_2$ over noble metal catalysts, and (iv) separation of H$_2$ from CO$_2$.$^{2-5}$

For PEM fuel cells, it is desired to produce hydrogen on-site due to the unavailability of proper H$_2$ storage and transportation options.$^6$ It is possible to produce H$_2$ by natural gas reforming in the fuel cell compartment using commercial catalysts. Commercially CH$_4$ undergoes steam reforming on Ni/Al$_2$O$_3$ catalyst to produce syngas (CO and H$_2$). The syngas undergoes high temperature shift on Fe$_3$O$_4$/Cr$_2$O$_3$ catalysts and low temperature shift on Cu/ZnO based catalyst. The industrial catalysts based on Cu/ZnO requires long reduction times and special handling due to the pyrophoric nature of the catalyst.$^{7, 8}$ This would lead to long start-up times; furthermore, careful passivation (oxidation) of catalyst is required during shut-down. Also, the Cu/ZnO catalysts are
easily poisoned by any sulfur present in the reactants. The problems associated with Cu/ZnO based catalysts have led to a search for more versatile water-gas shift catalyst.

Recently, CeO$_2$ based noble metal catalysts have gained considerable interest as low temperature water-gas shift catalysts. There is a considerable debate on the mechanism of water-gas shift reaction with metal supported CeO$_2$ catalysts. Two reaction mechanisms have been proposed. A formate mechanism, initially proposed by Shido and Iwasawa, suggests reaction of CO with terminal OH groups on CeO$_2$ to form adsorbed formates which later decompose to H$_2$ and unidentate carbonate in presence of water. A ceria mediated redox mechanism proposed by several researchers suggests adsorption of CO on metal sites, reaction of adsorbed CO with oxygen from CeO$_2$ to reduce it to Ce$^{+3}$ which is later oxidized to Ce$^{+4}$ by H$_2$O. The metal component is required in former case to generate terminal hydroxyl groups while it is required in redox mechanism for CO adsorption. Although noble metal catalysts are active for water-gas shift reaction, they add to the cost of fuel cell and an alternative cheaper metal catalyst is desired.

Ni based CeO$_2$ catalyst are active for water-gas shift catalyst but are easily deactivated by coking and sulfur poisoning. It has been known that the sulfur content as lows as 20 ppm poisons the ceria based catalyst in automobile exhaust catalyst. In the catalytic hydrocarbon processing, the addition of rhenium in the bimetallic Pt-Re catalyst enhances the coke resistance and the sulfur resistance of the catalyst. Addition of Re disperses the Pt clusters which reduces the coke formation while the sulfur is selectively adsorbed on Re particles which enhances the deactivation resistance of the catalyst.
The objective of this study was to investigate the effect of Re on the bimetallic Ni-Re supported on CeO$_2$ catalyst for water-gas shift reaction. The sulfur effect was studied by reducing the Ni and Ni-Re catalyst with H$_2$ and a mixture of 0.1% H$_2$S in H$_2$. The reaction was carried out in the range of 100-600 °C using equimolar ratios of CO and water. Isotopic reaction studies were done using transient isotopic switch using H$_2$O and D$_2$O.

5.2. Experimental

The two catalysts used for these studies were 5 wt% Ni and 5wt% Ni-2 wt% Re supported on CeO$_2$. CeO$_2$ was purchased commercially from Alfa Aesar. 5 wt% Ni was impregnated on 10g of CeO$_2$ using an aqueous Ni(NO$_3$)$_2$.6H$_2$O solution by incipient wetness impregnation method. The impregnated catalyst was dried for 24 hours. 5g of Ni impregnated CeO$_2$, prior to calcination or reduction, was further impregnated with 2 wt% Re using an aqueous solution of NH$_4$ReO$_4$ (ammonium rhenate). The solubility of NH$_4$ReO$_4$ in water is small (87 g/L) and an excess amount of water is required to dissolve the NH$_4$ReO$_4$ equivalent to 2 wt%. The catalyst was dried for 24 hours and then both the catalysts were simultaneously calcined in air at 500 °C and then reduced using pure hydrogen at 500 °C.

The experimental set-up used for this study was similar to that shown in Figure 3.1. The only difference was both the streams A and B were Argon (Ar) flowing through H$_2$O and D$_2$O saturators. The reactant, CO, was mixed directly with one of the Ar streams depending on the position of the 4-port valve and then exposed to the catalyst in the DRIFTS and the tubular reactor. The reactant feed was 4% CO and 4% H$_2$O/D$_2$O balanced in Ar.
Approximately, 300 mg of catalyst was loaded in tubular reactor as packed bed between glass wool plugs and an additional 100 mg was loaded in DRIFTS reactor. In this study the DRIFTS reactor was placed upstream of the tubular reactor. The catalyst was reduced in situ by using a mixture of Ar/H\textsubscript{2} (23/7 cc) or Ar/0.1\% H\textsubscript{2}S-H\textsubscript{2} (23/7 cc). The activity of the catalyst for water-gas shift reaction was studied at different temperatures. The products were analyzed by quadrupole MS and the surface species were monitored by DRIFTS placed in Nicolet Magna 560 FT-IR.

5.3. Results and Discussion

5.3.1. Catalyst Characterization

Figure 5.1 shows XRD characterization spectra of Ni and Ni-Re supported on CeO\textsubscript{2}. Both the catalysts show diffraction peaks for CeO\textsubscript{2} at 2\theta = 29, 33, 48, 56, and 59 degrees. The peak at 2\theta = 37.5\textdegree is the instrumentation peak. A small peak for Ni was observed on both catalysts at 2\theta = 44\textdegree while there were no peaks observed for Re phase in Ni-Re catalyst. This might be caused either due to high dispersion of Re metal component or the metal loading is below the detection limit of the instrument. Typically, 2wt\% metal loading should be easily detectable by a XRD instrument which leads to the conclusion that Re is highly dispersed on the CeO\textsubscript{2} catalyst.

Comparison of the XRD spectra for the two catalysts show broadened peaks for Ni/CeO\textsubscript{2} catalyst while sharp peaks are observed for Ni-Re/CeO\textsubscript{2} catalyst. Using Scherrer equation, the size of Ni and CeO\textsubscript{2} particles on Ni-CeO\textsubscript{2} catalyst was calculated to be 19.1 nm and 13.6 nm, respectively. The size of Ni and CeO\textsubscript{2} in Ni-Re catalysts was calculated to be 38.2 nm and 11.3 nm. The calculation of the particle size using XRD analysis is shown in Appendix. Sharp diffraction peaks are observed for highly
crystalline material while broadening of the peaks is observed due to smaller particles or amorphous nature of the material.

IR spectra of the Ni/CeO$_2$ catalyst exposed with CO at 30 °C are shown in Figure 5.2. Exposure of CO to Ni/CeO$_2$ catalyst led to the formation of an intense band at 2056 cm$^{-1}$ for gas phase nickel carbonyl, Ni(CO)$_4$, species. Ni(CO)$_4$ can be formed easily by reaction of CO with metallic Ni at various conditions.$^{29,30}$ These species are highly toxic and care should be taken while running reactions that can form Ni(CO)$_4$ species. A possible leak and improper ventilation can be fatal if Ni(CO)$_4$ is vented in to the atmosphere.$^{29}$

5.3.2. Water-Gas Shift Activity

Figure 5.3 shows the IR results of water-gas shift reaction on Ni/CeO$_2$ catalyst at 150 and 250 °C. There was no catalytic activity for water-gas shift reaction below 150 °C as seen from Figure 5.3(a). Exposure of the catalyst above 200 °C led to the formation of CO$_2$ and H$_2$. At 250 °C, the formation of CO$_2$ was clearly visible on IR spectra as seen in Figure 5.3(b). These results show that the reaction water-gas shift reaction proceeds above 200 °C on the Ni/CeO$_2$ catalyst. Although there is formation of CO$_2$ and H$_2$ as observed from IR and MS, IR was not able to detect any adsorbed intermediates on the catalyst. There were no adsorbed intermediates observed on Ni-Re/CeO$_2$ and Ni/CeO$_2$ catalyst even at higher temperatures. Since IR was not able to detect adsorbed intermediates, only MS data is reported hereafter. Moreover, the activity of the catalyst increased with the increase in temperature and hence further isotopic studies were done between the temperatures of 500 and 600 °C.
Figure 5.1. XRD patterns of Ni and Ni-Re supported on CeO$_2$. 
Figure 5.2. IR spectra during CO exposure on Ni/CeO$_2$ catalyst at 30 °C after reduction with H$_2$. 

2056 cm$^{-1}$
Figure 5.3. IR spectra during water-gas shift reaction on Ni/CeO$_2$ (a) at 150 °C and (b) 250 °C
Figure 5.4. MS profiles during water-gas shift activity on Ni/CeO$_2$ catalyst at 500 °C after reduction with (a) pure H$_2$ and (b) 0.1%H$_2$S in H$_2$. 

(a) 

(b)
Figure 5.5. MS profiles during water-gas shift activity on Ni-Re/CeO$_2$ catalyst at 500 °C after reduction with (a) pure H$_2$ and (b) 0.1\%H$_2$S in H$_2$.
Figure 5.4 shows the MS profiles during water-gas shift reaction using $\text{H}_2\text{O}$ at 500 °C on Ni/CeO$_2$ reduced with (a) pure H$_2$ and (b) 0.1% H$_2$S in H$_2$, respectively. Exposure of the catalyst reduced with pure H$_2$ to the reactants (CO and H$_2$O) led to instantaneous formation of the CO$_2$ and H$_2$. The activity and conversion of pure H$_2$ reduced catalyst was much higher than the catalyst reduced with 0.1% H$_2$S/H$_2$. The huge negative peak and a small positive peak observed in Fig. 5.4(a, b) is due to the disturbance from the switch with two 3-way valves. Figure 5.5 shows the MS profiles during water-gas shift reaction using H$_2$O at 500 °C on Ni-Re/CeO$_2$ reduced with (a) pure H$_2$ and (b) 0.1% H$_2$S in H$_2$. Comparison of the Ni-Re catalyst reduced with pure H$_2$ shows higher activity compared to that reduced with 0.1% H$_2$S/H$_2$. Moreover, the activity of H$_2$ reduced Ni-Re catalyst is higher than Ni reduced with H$_2$. These results show that Re promotes the water-gas shift reaction. In both cases, the activity of sulfided catalyst was lower than that of the H$_2$ reduced catalyst, but the activity of sulfided Ni-Re was much higher than that of sulfided Ni. The CO conversion and products formation rate at different temperatures during steady state water-gas shift reaction is shown in Table 5.1. The activity of the Ni-Re catalyst reduced with H$_2$ is the highest while the activity of sulfided Ni catalyst is the lowest. The activity data clearly shows that the Re enhances the water-gas shift activity and sulfur poisoning resistance.

It has been reported that addition of Re in Pt-Re catalyst used in catalytic hydrocarbon reforming enhances the sulfur resistance and prevents coking.$^{25-27, 31-33}$ Re is believed to disperse the Pt particles such that the ensemble of Pt atoms promoting coke formation is not formed.$^{26, 27, 31}$ There was no coke formation observed on either catalyst.
With metal catalysts, coke can be formed by dissociative adsorption of CO on metal by the following reaction:\(^{34}\)

\[
\text{CO} + 2\ast \rightarrow \ast\text{C} + \ast\text{O}
\]

Also, it has been reported that Re selectively adsorbs sulfur and increases the stability of Pt-Re supported catalysts.\(^ {26, 27, 33}\) In our case, the activity of sulfided Ni-Re/CeO\(_2\) catalyst was lower than that of pure hydrogen reduced catalyst. With Pt-Re catalyst, the sulfur (an electron acceptor) adsorbs selectively on Re due to very low electron affinity compared to that of Pt. The electron affinities of Pt, Ni, and Re are 2.12, 1.15, and 0.16 eV, respectively.\(^ {35}\) From comparison of electron affinities, the adsorption of sulfur is more likely on Ni compared to that of Pt. It is possible that sulfur adsorbs on Ni as well as Re, decreasing the activity of Ni-Re catalyst when reduced with 0.1%H\(_2\)S/H\(_2\) compared to that reduced with just H\(_2\). H\(_2\)S can also adsorb on the CeO\(_2\) support to form sulfates as reported in one study using SO\(_2\).\(^ {36}\) Further characterization of catalyst is required to postulate the exact position of sulfur on the catalyst.

### 5.3.3. H\(_2\)O/D\(_2\)O Isotopic Exchange Studies

Figure 5.6 shows MS profiles resulting from isotopic exchange of H\(_2\)O and D\(_2\)O at 500 °C on sulfided Ni/CeO\(_2\) and sulfided Ni-Re/CeO\(_2\) catalyst. Isotopic exchange from H\(_2\)O to D\(_2\)O led to a decrease in the formation of H\(_2\), and an increase in the formation of D\(_2\) and HD. The formation of HD is at a maximum when the H\(_2\) and D\(_2\) intersect. An exchange of H\(_2\)O with D\(_2\)O also led to a decrease in the formation of CO\(_2\). The decrease in the formation of CO\(_2\) due to the isotopic switch from H\(_2\)O to D\(_2\)O is because of an isotopic effect. D\(_2\)O being much heavier than H\(_2\)O would result in a slower rate of dissociation of D\(_2\)O on catalyst surface and recombination of adsorbed D atoms to
Table 5.1. CO conversion and product formation rate on Ni and Ni-Re supported on CeO$_2$ catalysts at varying conditions

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Ni/CeO$_2$</th>
<th>Ni/CeO$_2$</th>
<th>Ni-Re/CeO$_2$</th>
<th>Ni-Re/CeO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$</td>
<td>H$_2$</td>
<td>H$_2$</td>
<td>H$_2$</td>
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<tr>
<td></td>
<td>$X_{CO}$</td>
<td>H$_2$</td>
<td>CO$_2$</td>
<td>$X_{CO}$</td>
</tr>
<tr>
<td>CO conversion (%) and Production formation (μmole/g·sec)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temp (°C)</td>
<td>500</td>
<td>6.17</td>
<td>7.63</td>
<td>0.1% H$_2$S in H$_2$</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>9.59</td>
<td>11.82</td>
<td>H$_2$</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>18.08</td>
<td>16.38</td>
<td>H$_2$</td>
</tr>
</tbody>
</table>
Figure 5.6. MS profiles during water-gas shift reaction with isotopic exchange from H$_2$O to D$_2$O at 500 °C on (a) sulfided Ni/CeO$_2$ catalyst (b) sulfided Ni-Re/CeO$_2$ catalyst
Figure 5.7. MS profiles during water-gas shift reaction with isotopic exchange from H$_2$O to D$_2$O at 550 °C on (a) sulfided Ni/CeO$_2$ catalyst (b) sulfided Ni-Re/CeO$_2$ catalyst
Figure 5.8. MS profiles during heating of Ni/CeO$_2$ catalyst from 550 to 600 °C (a) catalyst reduced with H$_2$ and (b) catalyst reduced with 0.1% H$_2$S/H$_2$. 
Figure 5.9. MS profiles during heating of Ni-Re/CeO$_2$ catalyst from 550 to 600 °C (a) catalyst reduced with H$_2$ and (b) catalyst reduced with 0.1% H$_2$S in H$_2$.
form D₂. This results in a slower reaction rate; this effect is termed as kinetic isotope effect. Furthermore, the comparison of Ni/CeO₂ with Ni-Re/CeO₂ shows that the HD and D₂ profile drags on Ni/CeO₂ catalyst while the steady state is achieved much quicker. This shows the rate of reaction is faster on Ni-Re/CeO₂ catalyst. Figure 5.7 shows an isotopic exchange from D₂O to H₂O at 550 °C on sulfided Ni/CeO₂ and Ni-Re/CeO₂ catalyst. Isotopic switch from D₂O to H₂O led to increase in H₂ and CO₂ and a decrease in D₂ formation. The rate of formation of CO₂ is higher in Figure 5.7 than that observed in Figure 5.6 because of the higher temperature (550 °C) and the kinetic isotope effect due to the step switch from D₂O to H₂O.

Figure 5.8 and 5.9 show MS profiles of CO₂, H₂, and CO when the catalyst is heated from 550 to 600 °C in steady state CO/H₂O flow. With Ni/CeO₂ catalyst reduced with H₂ [Fig. 5.8(a)] and with H₂S/H₂ [Fig. 5.8(b)], the increase in temperature led to an increase in the formation of CO₂ and H₂. The amount of increase with the increase in temperature observed with Ni-Re catalyst (Fig 5.9) was much lower compared to that of Ni/CeO₂ catalyst. When these catalysts were heated from 500 to 550 °C, the change in catalyst activity was comparable. These results show that the activity of Ni-Re does not change significantly with the change in temperature.

The commercial water-gas shift reactor involves a two step process for removal of CO: (i) high-temperature shift with low cost Fe-Cr catalyst (>350 °C) and (ii) low-temperature shift (<250 °C) with Cu-ZnO catalyst. Both the catalysts deactivate on exposure to air and are poisoned by sulfur in the feed. The Ni-Re/CeO₂ catalyst developed in this research is sulfur tolerant and active at high temperatures while the conversion of CO is only 25%. The conversion of CO is more than 50% with the
commercial Fe-Cr catalyst. Hence the activity of Ni-Re/CeO$_2$ needs to be improved further. More over addition of Re would increase the cost of base Ni/CeO$_2$ catalyst and hence the activity of Ni-Re/CeO$_2$ should be much higher compared to that of Fe-Cr catalyst to be cost-effective.

Current on-board fuel cell reformers utilize Pt based catalysts for water-gas shift reaction. The mixed oxide based Pt and CeO$_2$ based Pt catalysts are able to convert CO to less than 1% in a single step process which reduces the size of the reformer. The use of Pt based catalyst increases the overall cost of the reformer. Commercial units for fuel cell applications are available on demand from major catalyst companies for natural gas reforming to hydrogen with CO content of less than 100ppm. The units are available upon signing an understanding that no tests or characterization of the catalysts may be performed for confidential reasons.

5.4. Conclusions

Ni supported on CeO$_2$ is active for water-gas shift reaction above 200 °C. XRD characterization of the catalysts showed highly crystalline structure for CeO$_2$ impregnated with Ni-Re compared to that of Ni. Adsorption of CO at room temperature on reduced Ni/CeO$_2$ catalyst led to the formation of toxic Ni(CO)$_4$ species. The Ni/CeO$_2$ and Ni-Re/CeO$_2$ catalyst prepared by incipient wetness impregnation on commercial ceria showed no adsorbed reaction intermediates using DRIFTS spectroscopy.

Isotopic studies with H$_2$O and D$_2$O showed kinetic isotope effect at different temperatures. Addition of Re enhanced the activity of the catalyst when reduced with pure H$_2$. The activity of the sulfided Ni-Re catalyst was lower compared to that of non-sulfided catalyst. Moreover, the activity of Ni-Re remains stable with an increase in the
temperature while the activity of Ni/CeO$_2$ catalyst increases with an increase in the temperature. Catalyst characterization with EXAFS or a similar technique would lead to a better understanding of the bimetallic interaction and the sulfur co-ordination with the active metal component and/or the CeO$_2$ support.
6.1. Introduction

Concerns about the link between increases in CO\textsubscript{2} concentration in the atmosphere and global climate changes have led to extensive research in the approaches for limiting the emission of greenhouse gases. Increased CO\textsubscript{2} emission is a result of fossil fuel usage to meet our growing energy needs. One of the largest sources of CO\textsubscript{2} emission are coal-fired power plants which contribute to 36\% of the anthropogenic CO\textsubscript{2} emission in the United States and a similar percentage is applicable worldwide.\textsuperscript{1} The capture of CO\textsubscript{2} from the coal fired plants, stationary sources, is technically feasible as compared with that of CO\textsubscript{2} from mobile sources.

Depending on the operating conditions, the concentration of CO\textsubscript{2} in the coal-fired power plant flue gas varies from 10-15\%.\textsuperscript{2} The first step to sequester CO\textsubscript{2} is the separation of CO\textsubscript{2} from the flue gas.\textsuperscript{3-5} The available approaches for CO\textsubscript{2} capture and separation include the use of solid sorbents for pressure swing adsorption (PSA), temperature swing adsorption (TSA), and concentration swing adsorption (CSA), the employment of liquid amines for absorption and membrane separation process. These approaches have been used for removal of CO\textsubscript{2} from closed environments and the natural gas liquefaction process.\textsuperscript{6-9}
The PSA process has been used to capture CO\textsubscript{2} from closed environments like space shuttles and submarines where the concentration of CO\textsubscript{2} is low (i.e., less than 1% CO\textsubscript{2}).\textsuperscript{6} PSA operates at isothermal condition. The driving force in the PSA process is the difference in total pressure during adsorption and desorption. TSA has been used for the separation of CO\textsubscript{2} from natural gas in liquefaction processes and SO\textsubscript{2} removal from sulfuric acid plant flue gases.\textsuperscript{10} Desorption in TSA process takes place at a temperature much higher than adsorption while the total pressure is maintained constant. The difference in temperature during the adsorption and desorption cycle is the driving force for the TSA process. External heat is required to break the bonds during desorption and to regenerate the sorbent. A less common adsorption process is the concentration swing adsorption (CSA) which has been used to capture gasoline vapors from carburetor and gas tank in automobiles.\textsuperscript{10} In the CSA process, adsorption and desorption takes place at the same temperature and total pressure. The driving force in CSA is the partial pressure difference between the inlet gas carrying the adsorbate (i.e., adsorbing gas) and the purge gas where the adsorbate concentration is mostly zero.

Aqueous alkanolamines have been used in natural gas processing industry for the sweetening process (removal of acid gases). Primary aqueous alkanolamines react with CO\textsubscript{2} by the following reaction:

\[
\text{C}_2\text{H}_4\text{OHNH}_2 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_4\text{OHNH}_3^+ + \text{HCO}_3^- \tag{6.1}
\]

Separation of chemically reacted CO\textsubscript{2} and regeneration of the amines require an expensive distillation process. Adsorption processes with solid sorbents would be preferred over the liquid amine process due to the inherent properties associated with ease in handling of solids and corrosion problems caused by the liquid amines.\textsuperscript{11-13} All of
the sorbents for CO$_2$ capture and separation were designed for low levels of CO$_2$; the use of these sorbents for CO$_2$ separation from flue gas (10-15% CO$_2$) will make power generation from coal prohibitively expensive. The cost of CO$_2$ capture can be drastically reduced if effective low cost sorbents are designed which have CO$_2$ adsorption capacity of more than 1000 μmole/g sorbent and long term regeneration capacity.

Our strategy to develop a high CO$_2$ adsorption capacity sorbent is to graft amine functional group(s) containing species on the high surface area supports like SBA-15 by the silanation approach.$^{14-18}$ A high surface area support will allow us to graft more number of active amine sites per gram of support. The nature of the grafted amine functional groups (primary or secondary amine) will determine the amount of CO$_2$ adsorbed and the energy required for regenerating the sorbent. The interaction between the CO$_2$ and NH/NH$_2$ groups is expected to be stronger than van der Waals forces but weaker than a covalent/ionic bond such that the CO$_2$ bound to the amino groups can be released with the low pressure steam available in the power plants. CO$_2$ is a weak acid while amines are weak bases; this weak acid-base interaction with binding energy in the range of 50-100 kJ/mol has been used to design solid sorbents for CO$_2$ capture from various sources.$^6, 14, 15, 19-23$

Our previous results have shown that grafting of monoamine (3-APTS containing one amine group) on SBA-15 showed CO$_2$ adsorption capacities up to 408 μmole/g sorbent with adsorption at 25 °C and regeneration at 120 °C.$^{14}$ The adsorption capacity can be further increased if the surface density of amine functional groups per gram of sorbent is increased. One way to improve the surface density of amine functional groups is to graft a diamine containing two amine groups per molecule. Diamine contains both
primary amine (R-NH₂) and secondary amine (R-CH₂-NH-CH₂-R') which may interact with surface OH during grafting and other species such as H₂O, limiting their CO₂ capture capacity.

The objectives of this paper are to investigate the grafting of diamine on the high surface area mesoporous silica material, SBA-15, and determine the CO₂ adsorption capacity of the diamine-grafted SBA-15. The diamine grafting has been studied by transmission infrared (IR) spectroscopy; adsorption capacity of the sorbent has been studied using temperature-programmed desorption technique (TPD) monitored by diffused reflectance Fourier transform infrared spectroscopy (DRIFTS) coupled with mass spectrometry (MS). Diamine-grafted SBA-15 showed high adsorption capacity and was further explored for concentration swing adsorption (CSA) process with DRIFTS coupled with MS.

6.2. Experimental

6.2.1. Preparation of SBA-15 and Diamine-Grafted SBA-15 Sorbent:

SBA-15 was prepared by using Pluronic 123 as a structure directing agent, HCl solution for pH control, 1,3,5-trimethyl benzene as a pore expander, and tetraethylorthosilicate as a silica precursor. The specific steps are described in details elsewhere.¹⁴ Amine grafted SBA-15 was prepared by (i) heating 1g of SBA-15 at 110 °C in vacuum (150mm of Hg) for 6 h, (ii) impregnating 2.4 ml of N-(2-aminoethyl) 3-aminopropyltrimethoxysilane (i.e., diamine) in 4 ml toluene solution onto the pretreated SBA-15, and (iii) heating the impregnated SBA-15 at 150 °C for 20 h in vacuum (150mm of Hg).
Figure 6.1. Experimental apparatus for CO$_2$ adsorption study
6.2.2. In Situ IR study of Grafting of Diamine on SBA-15

A SBA-15 disc weighing 10 mg was placed in a stainless steel IR cell with CaF$_2$ windows on each end. The schematic and details of the IR cell are presented elsewhere. The disc was pretreated in flowing He at 150 °C for 2 h and was exposed to diamine vapor by injecting a diamine/toluene solution (0.6/1 volume ratio) in flowing He at 25 °C. The IR cell was heated to 100 °C for 3 h to drive off the excess solvent. The surface interaction between the diamine and SBA-15 was monitored by in situ transmission IR spectroscopy.

6.2.3. Concentration Swing Adsorption/Desorption and Partial Pressure Studies

Figure 6.1 shows the experimental setup which includes a 4-port valve, a 6-port valve, a DRIFTS reactor filled with 30 mg of sorbent followed by a tubular reactor filled with 300 mg of sorbent, and a mass spectrometer. The tubular reactor allowed packing of a sufficient amount of sorbent for adsorbing CO$_2$, giving the change in the CO$_2$ effluent concentration for mass spectrometric measurement. The surface adsorbed species were monitored by the DRIFTS reactor (Thermo Nicolet) placed inside a Nicolet 560 FT-IR bench and the effluent of the reactors was simultaneously analyzed with a Pfeiffer QMS 200 quadrupole mass spectrometer (MS).

Prior to adsorption, the sorbent was pretreated in flowing He at 30 °C to remove the excess moisture and obtain a clean background spectrum. CO$_2$ adsorption was carried out by switching the inlet flow from He to 10% CO$_2$ in He and Ar (tracer) using a 4 port valve. The adsorbing gas stream and the He stream were bubbled through a water saturator at room temperature corresponding to a partial pressure of 30 mm of Hg (equivalent to 4%) in the gas streams. The presence of water enhanced the CO$_2$
adsorption capacity. The 4-port valve allows replacement of one flow stream by another while maintaining the total flow rate across the valve constant. The concentration swing adsorption/desorption cycle (CSA) was carried out by switching the inlet flow from an inert gas stream to the adsorbing gas stream containing CO$_2$. Upon saturation of the sorbent with adsorbing gas, the inlet stream was switched back to the inert gas stream (He saturated with water). The difference in partial pressure of CO$_2$ between the adsorbing stream and the inert stream creates a driving force to desorb weakly adsorbed CO$_2$. The change in concentration of CO$_2$ in the effluent flow was monitored by MS. The cycle was repeated twice to determine the reproducibility of the sorbent. The effect of partial pressure on CO$_2$ adsorption capacity of the sorbent was studied by varying the partial pressure of CO$_2$ (5%, 10%, 25% and 50%) in the adsorbate stream for each cycle.

6.2.4. Temperature-Programmed Desorption Study

Following the adsorption step, the sorbent was regenerated by temperature-programmed desorption (TPD) technique by heating the sorbent to 120 °C in flowing He at a rate of 10 °C/min. The CO$_2$ concentration profile during adsorption and desorption was monitored by the MS and the amount of CO$_2$ was quantified by calibrating the MS for CO$_2$ gas (m/e=44). The calibration factor was obtained by injecting 1 cm$^3$ of 10% CO$_2$ pulse in flowing He stream using the 6-port valve and calculating the area corresponding to the amount of CO$_2$ injected.

IR spectra in this work were collected in 3 different ways: (i) transmission mode, (ii) diffuse reflectance Fourier transform infrared spectroscopy (DRFITS) mode, and (iii) single beam DRIFTS mode. DRIFTS is more suitable for IR study of CO$_2$
adsorption/desorption on diamine-treated sorbent particles than the transmission IR, in particular for reaction studies at high temperature and high pressure. The DRIFTS reactor gives precise control of temperature and the sealed chamber is suitable for gas-solid systems. Despite the above mentioned advantages of the DRIFTS, DRIFTS is not applicable for in-situ studies involving liquids. Transmission IR spectroscopy was used to study grafting of amines in toluene on the SBA-15 disc.

For the in situ grafting study in transmission cell, the background spectrum of dry He pretreated SBA-15 disc was used as the reference and the data was reported in the form of absorbance [$A = -\log \left( \frac{I}{I_0} \right)$, where $I$ and $I_0$ are spectra and background IR intensities]. During the DRIFTS study, the spectrum of pretreated diamine-grafted sorbent was used as the reference spectrum and the data was reported in the form of absorbance. The single beam spectrum is the reference (i.e., background) spectrum which contains the characteristics of the IR source and IR bands of the sample placed in the path of the IR beam. The CaF₂ windows used in the transmission reactor cuts off the spectrum below 1100 cm⁻¹ while the Zn-Se windows in DRIFTS cuts off at 650 cm⁻¹.

6.3. Results and Discussion

6.3.1. IR Study of Diamine Grafting on SBA-15

Figure 6.2 shows the transmission IR spectra of the SBA-15 disc during heating from 25 °C to 150 °C in flowing He; a spectrum at 25 °C in He environment was used as the background spectrum. The IR absorbance intensity of the 3388 cm⁻¹ broad band and the 1630 cm⁻¹ intense band decreased with the increase in temperature and the time exposed to flowing He at 150 °C due to dehydration of the surface. These bands can be attributed to hydrogen bonding in molecular H₂O and H-O-H bend, respectively.²⁴
Figure 6.2. Transmission IR spectra during heating of SBA-15 from 25 to 150 °C
Figure 6.3. Transmission IR spectra of SBA-15 disc during grafting of amine with amine/toluene mixture at 100 °C.
sharp band at 3750 cm\(^{-1}\) for isolated hydroxyl groups is similar to that observed on the silica materials degassed at high temperatures.\(^{24}\) The isolated hydroxyl groups (silanol groups) which can react with a variety of functional groups can be used to tailor the surface chemistry of silica and glass materials.

Figure 6.3 shows the transmission IR spectra during grafting of diamine onto the SBA-15 surface. Exposure of the SBA-15 disc to a diamine/toluene mixture at 100 °C produced IR bands at 1457, 1596, 2844, 2941, 3300 and 3377 cm\(^{-1}\). The band assignments are shown on the Figure 6.3.\(^{14, 23, 25}\) IR spectrum of the diamine/toluene mixture is included in the Figure 6.3 for comparison; toluene gives IR bands at 1492 cm\(^{-1}\) and 3026 cm\(^{-1}\). The IR bands for CH\(_3\) and NH\(_2\) on the surface of SBA-15 are similar to the bands observed for diamine in toluene (top spectra in Figure 6.3) suggesting that NH\(_2\) functional groups of diamine do not react with the hydroxyl groups on the surface. The decrease in isolated surface hydroxyl groups (IR band at 3745 cm\(^{-1}\) band) suggests the reaction of surface hydroxyl groups (Si-OH) with highly active methoxy groups of diamine compound by the following reaction:

\[
(CH_3O)_3SiCH_2CH_2CH_2NHCH_2CH_2NH_2 + x \text{Si-OH} \rightarrow (\text{Si-O})_x\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2 + x CH_3\text{OH}
\]  

This is further confirmed by a small amount of CH\(_3\)OH formed which is evidenced by the OH bending vibration of methanol at 1346 cm\(^{-1}\).

6.3.2. Effect of Pretreatment on Diamine-Grafted SBA-15

Figure 6.4 compares the DRIFTS spectra of SBA-15, diamine-impregnated SBA-15 and diamine-impregnated SBA-15 treated in flowing He for 1 h at 25 °C. Exposure of the grafted sorbent to dry flowing He for 1 h resulted in the formation of prominent IR
bands at 2930 for asymmetric C-H, and 3290 and 3358 cm\(^{-1}\) for symmetric and asymmetric N-H stretch, respectively. The broad water band at 3400 cm\(^{-1}\) observed in the diamine-grafted SBA-15 disappears during dry He purge suggesting desorption of molecular water from the surface of the sorbent. This observation indicates that the molecular water is weakly adsorbed on the silica surface as well as on the diamine-grafted silica surface. The decrease in IR intensity of 3747 cm\(^{-1}\) band of diamine-grafted SBA-15 compared to SBA-15 further confirms the depletion of isolated OH groups by reaction with methoxy groups of diamine species.\(^{14}\)

6.3.3. IR and MS Study during CO\(_2\) Adsorption on Diamine-Grated SBA-15 by CSA Process

Figure 6.5 shows MS intensity profiles of CO\(_2\) and Ar (tracer) during CSA cycles. Each adsorption cycle started with a step switch from water saturated He (30 cm\(^3\)/min) to water saturated He/CO\(_2\)/Ar (25/2/3 cm\(^3\)/min) stream. The step switch produced a sudden change in the concentration of CO\(_2\)/Ar. The sudden change in concentration created the CO\(_2\) and Ar fronts which traveled through the DRIFTS, the sorbent bed in the tubular reactor and then to the MS detector. The Ar profile showed a sharp response on MS while the response of CO\(_2\) was delayed due to the adsorption of CO\(_2\) on the sorbent. Upon reaching steady state, the CO\(_2\) and Ar profiles attained a stable MS base line. The desorption cycle was initiated by a step switch from He/CO\(_2\)/Ar to He, the MS intensity of Ar showed a sharp decrease while the intensity of CO\(_2\) lagged behind due to desorption of weakly adsorbed species from the sorbent. The MS intensity of Ar was normalized to the height of CO\(_2\); the amount of CO\(_2\) adsorbed and desorbed was
calculated from the area between the MS profiles of CO$_2$ and Ar using the calibration factor of CO$_2$.

The residual CO$_2$ on sorbent in each adsorption/desorption cycle is the difference between the total amount of CO$_2$ adsorbed and the amount of CO$_2$ desorbed during each cycle. In the first adsorption cycle, the amount of CO$_2$ desorbed was more than the amount of CO$_2$ adsorbed. This was due to the CO$_2$ adsorbed on the sorbent from the atmosphere prior to the study. In the subsequent cycles, the amount of CO$_2$ adsorbed was more than that of the amount desorbed, thus increasing the residual CO$_2$ loading on sorbent after each cycle. The residual CO$_2$ on the sorbent is strongly bound to the surface by chemical reaction and has to be desorbed by a stronger force than the partial pressure driving force in the CSA process. This can be accomplished by temperature-programmed desorption.

DRIFTS IR spectra during adsorption are shown in Figure 6.6. The spectra shown after each adsorption cycle are relative to the starting point A, before adsorption. The interaction of CO$_2$ with diamine-grafted species produced bidentate bicarbonate species at 1628 cm$^{-1}$, monodentate bicarbonate at 1470 and 1422 cm$^{-1}$, and bidentate carbonate at 1541 cm$^{-1}$. The bands at 929 and 819 cm$^{-1}$ may be attributed to NH$_3$ rocking vibrations while the band at 1287 cm$^{-1}$ may be assigned to carbamic acid species. The decrease in IR band at 3303 cm$^{-1}$ for N-H stretch is due to the depletion of NH$_2$ bands by the reaction of CO$_2$ with amine species. The residual CO$_2$ on the sorbent increased with the number of adsorption/desorption cycles which is clearly evidenced by the increase in intensity of IR bands at 1628, 1541 and 1422 cm$^{-1}$ corresponding to the species produced by the interaction of CO$_2$ with diamine.
Figure 6.4. DRIFTS background spectra of (i) SBA-15, (ii) Di-amine grafted SBA-15, and (iii) Di-amine grafted SBA-15 pretreated in dry He flow for 1 h at 25 °C
Figure 6.5. CO$_2$ MS (m/e = 44) intensity during adsorption desorption cycles on amine treated SBA-15 with Ar (m/e=40) as a tracer.
6.3.4. Effect of Partial Pressure on CO\(_2\) Adsorption Capacity of Diamine-Grafted SBA-15

The effect of partial pressure of CO\(_2\) in adsorbate stream on adsorption capacity of the sorbent is shown in Figure 6.7. An increase in partial pressure of CO\(_2\) led to a sharp increase in the total adsorption capacity of the sorbent; at 50% CO\(_2\) partial pressure, the adsorption capacity of sorbent was more than 3500 μmole/g sorbent. Further increase in the partial pressure would lead to saturation of the sorbent.

6.3.5. TPD Study on Diamine-Grafted SBA-15 Adsorbed with CO\(_2\)

Figure 6.8 and Figure 6.9 show the MS intensity and DRIFTS IR spectra during TPD of CO\(_2\) over diamine-treated sorbent, respectively. The TPD study was carried out after the CSA study using 50% partial pressure of CO\(_2\). The amount of CO\(_2\) desorbed from the sorbent was 786.5 μmole/g as calculated from MS intensity profile of CO\(_2\) during TPD. The amount of TPD desorbed CO\(_2\) is at the levels of the commercial polymer amine sorbent used for CO\(_2\) capture in submarines and space shuttles and other amine based sorbents reported in literature as shown in Table 6.1. The presence of IR bands corresponding to monodentate and bidentate bicarbonate and monodentate carbonate at 120 °C on the sorbent surface reveals that not all the adsorbed CO\(_2\) is desorbed at peak temperature of 120 °C, and higher temperature is required to desorb the strongly adsorbed CO\(_2\). The peak intensity of adsorbed species at 120 °C is almost half to that of adsorbed species at 40 °C. Assuming a linear relationship between the amount of adsorbed CO\(_2\) and the IR peak intensity, we can conclude that the amount of CO\(_2\) present on the surface of the sorbent when it first reaches a temperature of 120 °C is half of its total adsorption capacity at 40 °C. Using 120 °C as the CO\(_2\) desorption peak
Table 6.1. CO$_2$ capture capacity of amine based solid sorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>CO$_2$ Capture Capacity (μmole/g sorbent)</th>
<th>Adsorption/Desorption Technique</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoamine treated mesoporous silica (MCM-48)</td>
<td>1136</td>
<td>TGA and Temp. Prog. Des.</td>
<td>12</td>
</tr>
<tr>
<td>Amine treated mesoporous silica (SBA-15)</td>
<td>400</td>
<td>MS and Temp. Prog. Des.</td>
<td>13</td>
</tr>
<tr>
<td>Polymer amine based sorbent (HSC+)</td>
<td>909</td>
<td>TGA</td>
<td>3</td>
</tr>
<tr>
<td>Amine treated silica gel</td>
<td>898</td>
<td>GC</td>
<td>4</td>
</tr>
<tr>
<td>Diamine treated mesoporous silica (SBA-15)</td>
<td>768</td>
<td>MS and Temp. Prog. Des.</td>
<td>This Study</td>
</tr>
</tbody>
</table>
Figure 6.6. DRIFTS IR spectra during CO$_2$ CSA cycles on amine treated SBA-15 sample.
Figure 6.7. CO$_2$ adsorption capacity of amine treated SBA-15 as a function of partial pressure of CO$_2$
Figure 6.8. CO$_2$ MS profile during desorption of CO$_2$ by TPD technique.
Figure 6.9. DRIFTS IR spectra during desorption of CO$_2$ by TPD technique
Figure 6.10. IR band peak intensities during temperature programmed desorption
temperature, the binding energy was calculated to be 47.8 kJ/mol which can be considered as the minimum average binding energy of CO$_2$ on diamine-treated sorbent.$^{26}$

Figure 6.10 shows the absolute IR peak intensities of adsorbed CO$_2$ during TPD. The sharp decrease in peak intensity of IR band at 1628 cm$^{-1}$ with increase in temperature, compared to the IR band at 1534 cm$^{-1}$, indicates that the bidentate carbonate has lower binding energy than bidentate bicarbonate. Similar results were observed during temperature-programmed desorption of monoamine-treated SBA-15. The species formed due to interactions of CO$_2$ with monoamines are similar to that of CO$_2$ with diamine species.

Comparing the intensity ratios of the peaks at 1541 cm$^{-1}$ and 1628 cm$^{-1}$ in Figure 6.6 and Figure 6.9 reveals that bidentate carbonate plays a key role during CSA while monodentate and bidentate bicarbonates play a significant role during TSA. This is evidenced by the extent of change in the IR intensity of these species during CSA and TSA. The bidentate carbonate can desorb more than 50% during CSA at 25 °C suggesting that that CO$_2$ adsorbed as bidentate carbonate species is weakly bound on the surface and can be flushed off by partial pressure driving force.

IR study of CO$_2$ adsorption on monoamine-treated SBA-15 compared to diamine-treated SBA-15 reveals that the species formed by interaction of CO$_2$ with the type of amine functional group (mono or diamine) are indistinguishable. This suggests that the interaction of CO$_2$ with diamines is similar to that of monoamines. Furthermore, the amount of CO$_2$ adsorbed per gram of sorbent during the TPD at 120 °C for diamine-treated SBA-15 (786.5 μmole/g) is about twice the amount for monoamine-treated SBA-15 (408 μmole/g). These results suggest that the diamine-grafted SBA-15 provides
almost twice as much effective amine functional groups as that of monoamine-grafted SBA-15 for CO₂ capture.

6.3.6. Economic Analysis of Sorbent for Power Plants

The use of solid sorbent could be a low cost alternative to capture CO₂ from power plant flue gases because of its high CO₂ adsorption capacity, low heat capacity, and the simplicity of operation. The economic potential of a CO₂ capture process can be determined by the total capital cost and the utility cost.³⁷ The capture of CO₂ by the solid sorbent involves the direct adsorption of CO₂ on the amine surface functional groups; the capture of CO₂ by aqueous amines involves the mass transfer from gaseous CO₂ through the gas-liquid interface to the bulk liquid for the reaction with aqueous amines. The rate limiting step for adsorption on solids is the diffusion of CO₂ from the flue gas bulk stream to the inside pore of the SBA-15, while for the aqueous amine process the rate limiting step is the CO₂ diffusion across gas-liquid interface. The rate of the former is normally three orders of magnitude higher than the latter.³⁸ The high adsorption capacity and high rate of mass transfer will lead to a small adsorption bed, resulting in significant savings in construction and equipment costs.

The major utility cost is resulted from the energy consumption in stripping of CO₂ from CO₂-rich amine solution for aqueous amine process and desorption of CO₂ from the solid sorbents for solid adsorption process.³⁹ Considering the heat capacity of sorbent as 0.8 kJ/kg·K (SiO₂) and that of solvent to be 4 kJ/kg·K (30 wt% MEA), adsorption capacity of 0.036 kg CO₂/kg solvent and 0.044 kg CO₂/kg sorbent and the regeneration temperature of 120 °C for both processes, the regeneration energy required per kg of CO₂ captured is 40,000 kJ for liquid amine process compared to 6,600 kJ for solid sorbents.
Although the operating (i.e., utility) cost for TSA process with solid amine based sorbent is significantly lower than aqueous amine process, the durability and cost of the solid amine sorbent remains to be further improved to reach the DOE target of $9/ton for CO$_2$ sequestration.

6.4. Conclusions

The present study provides an insight on the mechanism of diamine grafting on SBA-15 with in situ IR spectroscopy. The isolated surface hydroxyl groups are active moieties on the SBA-15 surface for reaction with methoxy groups of diamine containing silanes. CO$_2$ adsorbs on the primary and secondary amine groups forming carbonate, bicarbonate and carbamic acid species. The major species formed by the adsorption of CO$_2$ on the surface are monodentate bicarbonate, bidentate bicarbonate and bidentate carbonate. The bidentate bicarbonate species bind stronger to the diamine-grafted SBA-15 than bidentate carbonate. The amount of CO$_2$ desorbed from the carbonate and bicarbonate between 30–120 °C is two times more than that of CO$_2$ adsorbed/desorbed during each cycle of the concentration swing adsorption/desorption.

The CO$_2$ capture capacity of diamine-grafted SBA-15 is two times of monoamine-grafted SBA-15 with TSA at desorption temperature of 120 °C. Although TSA is an energy intensive and costly process, use of a low cost solid sorbent with TSA using low pressure steam from reboiler could be a cost-effective alternative to capture CO$_2$ from power plant flue gases.
7.1. Introduction

The increase in the atmospheric CO$_2$ over past centuries is a result of the increase in the use of fossil fuels. The CO$_2$ concentration in the atmosphere has increased from 280 ppm during the pre-industrial time to 365 ppm in 1998. The CO$_2$ concentration is expected to continue to increase before a non-carbon containing fuel takes over as the dominant energy source. The continuous rise in CO$_2$ concentration and its linkage to global warming demands cost-effective approaches to stabilize the CO$_2$ concentration in the atmosphere.

Examination of various sources of CO$_2$ emission revealed that more than 33% of global CO$_2$ emissions is from coal fired power plants which represent the largest stationary source of CO$_2$. The direct capture of CO$_2$ from the highly concentrated and large volume CO$_2$ stationary source is technically feasible and could be cost-effective for sequestrating CO$_2$. Depending on operating conditions and the type of coal burned, the CO$_2$ concentration in the power plant flue gas varies from 10-15%, NO from 1500-2500 ppm, and SO$_2$ from 500-800ppm. The NO is removed by the selective catalytic reduction while the SO$_2$ is captured by the wet lime scrubber and the CO$_2$ is vented out in the atmosphere.
The available approaches for CO₂ capture and separation include absorption of CO₂ in aqueous amines, membrane separation, and adsorption on solid sorbents.⁶⁻¹⁵ The absorption of CO₂ is carried out in a packed column where the CO₂ stream is injected at the bottom of the column while the aqueous amine is sprayed from the top of the column at 40 °C. CO₂ is absorbed in the aqueous amines to form carbamates and bicarbonates by the following reactions:

\[
2 \text{R}_1\text{R}_2\text{NH} + \text{CO}_2 \leftrightarrow \text{R}_1\text{R}_2\text{NH}^+ + \text{R}_1\text{R}_2\text{NCOO}^- \quad \text{(carbamate)} \quad (1)
\]

\[
\text{R}_1\text{R}_2\text{NH} + \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{R}_1\text{R}_2\text{NH}_2^+ + \text{HCO}_3^- \quad \text{(bicarbonate)} \quad (2)
\]

In absence of water, one mole of CO₂ reacts with two moles of amine to form carbamate by reaction 1; in presence of water, one mole of CO₂ reacts with one mole of amine to form bicarbonate by reaction 2. The CO₂ containing aqueous amine is regenerated by distillation at about 110 °C.

The CO₂ separation by the membrane process involves use of either polymer membranes or amine modified inorganic oxide membranes.⁷,¹⁶ The membrane process is based on the high permeability of CO₂ through the membrane compared to the other gases. The membrane process is efficient in separating CO₂ from the gas stream with a small volumetric flow rate and a low CO₂ concentration.⁷ As the amount (i.e., flux) of CO₂ required for permeating through membrane increases, the membrane efficiency for the CO₂ separation decreases due to the insufficient flux and selectivity and its rate of degradation accelerates due to contaminants in the feed stream.⁷,¹⁶,¹⁷

Solid sorbents based on amine-treated polymers have been used for years to capture CO₂ from closed environments containing less than 1% CO₂ such as space shuttles and submarines.¹³,¹⁸ A feed stream containing CO₂ is pumped through a packed
bed of solid sorbent; CO\textsubscript{2} adsorbs on the sorbent by interaction with the amines\textsuperscript{19}. The sorbent is regenerated by temperature swing adsorption or pressure swing adsorption or a combination of both processes\textsuperscript{13}.

The current aqueous amine and membrane technologies are cost-effective for separation of CO\textsubscript{2} from natural gas in liquefaction process and ammonia synthesis process due to the high value of end products\textsuperscript{9, 20, 21}. These current technologies when applied for CO\textsubscript{2} capture from coal fired power plants, increases the cost of electricity by more than 70\%\textsuperscript{2}. The cost of CO\textsubscript{2} sequestration can be reduced if an effective CO\textsubscript{2} capture sorbent is developed which has (i) high CO\textsubscript{2} adsorption capacity (> 1000 μmole/g), (ii) long term regeneration capacity in power plant flue gas environment, and (iii) low energy requirement for regeneration compared to large amount of energy required for aqueous amine process\textsuperscript{22}.

Our previous study has shown that the amine-grafted SBA-15 has one of the highest CO\textsubscript{2} adsorption capacities compared to the solid sorbents reported in literature\textsuperscript{8, 11, 13, 22, 23}. The key issues that need to be addressed for development of an effective solid amine sorbent for CO\textsubscript{2} capture include:

- Effect of nature of amine and adsorbed CO\textsubscript{2} species on the CO\textsubscript{2} adsorption capacity of the sorbent
- Effect of SO\textsubscript{2} on CO\textsubscript{2} adsorption capacity of solid amine sorbent
- Thermal stability and long term CO\textsubscript{2} adsorption/regeneration capacity.

The objectives of this study are (i) to evaluate the nature of adsorbed CO\textsubscript{2} on the amine-grafted SBA-15 sorbent and a commercial polymer amine based sorbent (ii) to evaluate the SO\textsubscript{2} capture capacity of amine-grafted SBA-15 sorbent and its effect on CO\textsubscript{2}.
adsorption capacity, and (iii) to determine the thermal stability of the sorbent. SBA-15 was used as the support due to its high hydrothermal stability as well as large pores and surface area for amine grafting. The CO$_2$ and SO$_2$ adsorption/desorption is studied by transient technique and temperature-programmed desorption with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) coupled with mass spectrometry (MS). The thermal stability of the sorbents is studied by temperature-programmed degradation with DRIFTS and MS.

7.2. Experimental

7.2.1. Preparation of SBA-15 and Amine-Grafted SBA-15 Sorbent

SBA-15 was prepared by using TEOS (tetraethylorthosilicate) as a silica precursor, Pluronic P123 (PEO$_{20}$PPO$_{70}$PEO$_{20}$, tri-block copolymer) as a template, 1,3,5-trimethylbenzene as an expander, and HCl to control pH. The specific steps for preparation of SBA-15 are described elsewhere.$^8$

APTS-SBA-15 (i.e. SBA-15 grafted with \(\gamma\)-aminopropyltriethoxysilane) was prepared by impregnating 5.4 mL of APTS/toluene solution on to 1 g of SBA-15. The volumetric ratio of APTS to toluene was 1:3.35. The impregnated sample was heated at 150 °C for 20 h in a vacuum oven to obtain APTS-SBA-15. The commercial sorbent SA9-T based on immobilized amines on polymer support, utilized in CO$_2$ capture from closed habitats, was used as a reference case.$^{13,18,24}$

7.2.2. Adsorption Studies:

The experimental setup is similar to that shown in Figure 6.1. It consists of (i) a gas manifold which includes a 4-port valve, a 6-port valve, and mass flow controllers, (ii) a DRIFTS reactor filled with 30 mg of sorbent followed by a tubular reactor filled with
300 mg of sorbent, and (iii) a mass spectrometer for effluent analysis. The tubular reactor was packed with additional amount of sorbent in line with DRIFTS for sufficient change in MS signal of CO$_2$ in the effluent.

The adsorption of CO$_2$ was carried out by switching the inlet flow from an inert gas stream (100% Ar) to adsorbing gas stream (10% CO$_2$ in Ar) using a 4 port valve. The 4-port valve allows a smooth switch from one flow stream to another. Upon saturation of the sorbent with adsorbing gas, the inlet stream was switched back to the inert gas stream. The gases were bubbled through a D$_2$O saturator at room temperature corresponding to 4% D$_2$O in the gas streams during adsorption, desorption and degradation. D$_2$O was used to trace the role of water during CO$_2$ adsorption. The SO$_2$ adsorption was carried out in a similar way with 2% SO$_2$ in He and H$_2$O saturator. The surface adsorbed species during adsorption/desorption and degradation were monitored by the DRIFTS reactor (Spectra-Tech) placed inside a Nicolet 560 FT-IR bench. The change in concentration of adsorbing gas in the effluent of the reactors was simultaneously analyzed with a Pfeiffer QMS 200 quadrupole mass spectrometer (MS).

7.2.3. Temperature-Programmed Desorption

The sorbent was regenerated by temperature-programmed desorption (TPD) by heating the DRIFTS and the tubular reactor simultaneously from room temperature to 120 °C in Ar stream at a rate of 10°C/min. The CO$_2$ concentration profile during TPD was monitored by the MS and the amount of CO$_2$ was quantified by calibrating the CO$_2$ (m/e=44) on the MS. The calibration factor was obtained by injecting 1 mL of CO$_2$ gas in flowing Ar stream using the 6-port valve and calculating the area corresponding to the amount of CO$_2$ injected. SO$_2$ TPD was carried out in a similar way and the calibration
factor was obtained by injecting 1 mL of SO$_2$ in flowing He stream and monitoring SO$_2$ (m/e=64) on the MS.

7.2.4. Thermal Stability Studies

The thermal stability of the sorbent was studied by heating the DRIFTS and the tubular reactor from 30 °C to 500 °C with a rate of 10 °C/min in the presence of air. The surface of the sorbent during decomposition of the amines was monitored by DRIFTS and the effluent of the reactors was simultaneously monitored by MS for the possible decomposition products.

IR spectra in this work are reported in 2 ways: DRIFTS single beam and DRIFTS absorbance. The single beam (i. e. background spectra) of the sorbent contains the characteristics of the source and the sample placed in the path of the IR beam and is similar to transmission spectrum. The DRIFTS absorbance spectra are obtained by subtraction of the background spectrum from spectra during the reaction. The absorbance is given by: $A = -\log \left( \frac{I}{I_0} \right)$, where $I$ and $I_0$ are spectra and background IR intensities.

7.3. Results and Discussion

7.3.1. Characterization of Sorbent

The DRIFTS single beam spectra of APTS-SBA-15 and SA9-T are shown in Figure 7.1. APTS-SBA-15 shows asymmetric and symmetric N-H stretch at 3358 and 3300 cm$^{-1}$, and asymmetric and symmetric C-H stretch at 2946 and 2827 cm$^{-1}$, respectively. The N-H and C-H band region on APTS-SBA-15 is overlapped by a broad water band between 2000 and 3600 due to hydrogen bonding of molecular water present on the SBA-15 surface. The presence of N-H and C-H vibrational frequencies
on APTS-SBA-15 spectrum shows that APTS was successfully grafted on SBA-15 surface. The SA9-T spectrum shows only one mode of N-H stretching vibration at 3312 cm\(^{-1}\) suggesting the presence of secondary amine. The absence of the broad band of hydrogen bonding on the SA9-T surface reveals the hydrophobic nature of the polymer support. The presence of C-N-C band at 1158 cm\(^{-1}\) further confirms the presence of secondary amine structure on polymer surface. The intense IR bands for C-H, CH\(_2\) and C=C are from the hydrocarbon chain of amines and the polymer support.

7.3.2. CO\(_2\) Adsorption and TPD studies on APTS-SBA-15

Figure 7.2 shows the DRIFTS absorbance spectra during CO\(_2\) adsorption on the APTS-SBA-15 in presence of D\(_2\)O. The exposure of APTS-SBA-15 to CO\(_2\) produced bidentate carbonate species at 1543 and 1363 cm\(^{-1}\), and monodentate bicarbonate species at 1472 and 1428 cm\(^{-1}\).\(^8\) The increase in the carbonates and bicarbonates intensity was accompanied by a slight decrease in the C-H bands at 2936 and 2876 cm\(^{-1}\).

Comparison of the carbonate and bicarbonate species produced on the surface of the sorbent in presence of H\(_2\)O (top spectra) and in the presence of D\(_2\)O show an isotopic shift in their vibrational frequencies. The proposed structure of carbonate and bicarbonate species is shown in Table 1. The D atom on the amino group causes isotopic shift in the carbonate and bicarbonate vibrational frequency. An isotopic shift caused by an isotope on a neighboring atom or a remote atom is termed as secondary isotopic shift. In the proposed carbonate and bicarbonate structure (as shown in Table 1), the D atom is present on the amino group (NH\(_2\)D\(^+\)) and hence shows secondary isotopic shift in the carbonate (NH\(_2\)D\(^+\)CO\(_3\)^\(^-\)) and bicarbonate (NH\(_2\)D\(^+\)HCO\(_3\)^\(^-\)) structures.
Figure 7.1. DRIFTS single beam spectra of commercial sample SA9-T and amine-grafted APTS-SBA-15 sample
Figure 7.2. DRIFTS absorbance spectra during CO$_2$ adsorption on APTS-SBA-15 in presence of D$_2$O and H$_2$O
Figure 7.3. DRIFTS absorbance spectra of adsorbed CO$_2$ on APTS-SBA-15 during TPD study with a heating rate of 10 °C/min in flowing Ar/D$_2$O (4 % D$_2$O)
Figure 7.4.  MS intensity profile of CO$_2$ (m/e=44) during TPD of APTS-SBA-15
Figure 7.3 and Figure 7.4 shows the DRIFTS absorbance spectra of adsorbed CO$_2$ and MS intensity profile of CO$_2$ during TPD. The spectrum at 30 °C shows significant decrease in C-H band intensity compared to that in Figure 7.2 which is due to prolonged exposure of the sorbent to the adsorbing stream. The decrease in the C-H IR band intensity is consistent with our previous studies and is a result of a decrease in the dipole moment of C-H bonds due to the formation of bulky carbonates and bicarbonates on the surface.$^{26}$ The increase in the temperature led to a decrease in adsorbed carbonate and bicarbonate species at 1543, 1363, and 1428 cm$^{-1}$ and an increase in C-H vibrational frequency at 2925 and 2838 cm$^{-1}$. The increase in C-H stretching vibrations is due to the decrease in the surface density of the carbonate and the bicarbonate species exposing the C-H bands of the propyl amine. Desorption of the carbonate and the bicarbonate species led to the formation of gas phase CO$_2$ as observed from the MS intensity for CO$_2$. The CO$_2$ adsorption capacity of APTS-SBA-15 was calculated to be 728 μmole/g sorbent at a desorption temperature of 120 °C from the MS TPD profile of CO$_2$. The presence of IR bands for carbonate and bicarbonate species on the spectrum at 120 °C (5 min, see the bottom spectrum of Figure 7.3) reveals that not all of the CO$_2$ is desorbed from the surface and a higher desorption temperature is required to remove the residual CO$_2$. From the degradation study (discussed later), it was revealed that all of the CO$_2$ is desorbed at a temperature of 150 °C.

7.3.3. CO$_2$ Adsorption and TPD studies on SA9-T

Figure 7.5 shows DRIFTS absorbance spectra during CO$_2$ adsorption on SA9-T in presence of D$_2$O. Before exposure to CO$_2$, the sample was exposed to Ar/D$_2$O stream. Exposure of SA9-T to D$_2$O led to formation of IR bands 1624 and 1705 cm$^{-1}$ due to
Figure 7.5. DRIFTS absorbance spectra during CO$_2$ adsorption on SA9-T in presence of D$_2$O
Figure 7.6. DRIFTS absorbance spectra of adsorbed CO$_2$ on SA9-T during TPD study with a heating rate of 10 °C/min in flowing Ar/D$_2$O (4% D$_2$O)
scissoring modes. Exposure of the sample to CO$_2$ stream produced prominent IR bands at 1564 and 1373 cm$^{-1}$ for bidentate carbonate, 1475 and 1409 cm$^{-1}$ for monodentate bicarbonate, and 1313 for monodentate carbonate. The IR intensity of the adsorbed carbonate and bicarbonate species increased with the increase in CO$_2$ exposure time. The formation of carbonates and bicarbonates led to a decrease in N-H and C-H band intensity similar to that observed for APTS-SBA-15. The shift in the frequency for adsorbed carbonate and bicarbonate species on SA9-T compared to the species on APTS-SBA-15 is due to the secondary and primary amine species grafted on these sorbents.

Figure 7.6 and Figure 7.7 shows DRIFTS absorbance spectra and MS intensity of CO$_2$ during TPD study on SA9-T. Upon switching to inert flow, comparison of DRIFTS spectra from Figure 7.5 to the spectrum at 30 °C in Figure 7.6 shows dramatic decrease in the IR intensity of adsorbed carbonate and bicarbonate species. The decrease in the IR intensity suggests that the CO$_2$ was weakly bound to the surface and upon switching to an inert gas, most of the CO$_2$ desorbed from the surface. The increase in the temperature led to an initial increase in the bands at 1624 and 1564 cm$^{-1}$ which eventually decreased and completely disappeared shortly after reaching 120 °C. The bands at 1409 and 1313 cm$^{-1}$ for adsorbed carbonates decreased with increase in temperature and disappeared above the temperature of 70 °C. The MS intensity of CO$_2$ in Figure 7.7 shows the desorption peak intensity at 70 °C, a shoulder at 100 °C; and almost all of the CO$_2$ desorbed when the temperature of the sorbent reached 120 °C. The two desorption peaks show two different adsorbed species with different binding energies. The monodentate carbonate and bicarbonates have lower binding energies and desorbs at 70 °C while the bidentate carbonate species desorb at a temperature above 100 °C which is consistent with our
previous data. The CO$_2$ adsorption capacity of SA9-T was calculated to be 440 μmole/g sorbent.

7.3.4. SO$_2$ Adsorption and TPD studies on APTS-SBA-15

The DRIFTS IR spectra during SO$_2$ adsorption in presence of H$_2$O are shown in Figure 7.8. Adsorption of SO$_2$ on the amine impregnated SBA-15 led to an increase in IR bands at 1108, 1200, 1250, 1342, 1533 and 1633 cm$^{-1}$ and a decrease in IR bands at 2867, 2993, 3308 and 3358 cm$^{-1}$. The bands at 1200 and 1250 are assigned to S=O stretching vibration of sulfates and sulfites formed on the surface of APTS-SBA-15. The sharp decrease in the IR bands at 3308 and 3358 cm$^{-1}$ for N-H symmetric and asymmetric stretch and the IR bands at 2867 and 2933 cm$^{-1}$ for C-H symmetric and asymmetric stretch is due to the reaction of surface amine with SO$_2$ and the formation of sulfates and sulfites on the surface. The bands at 1533 and 1633 can be attributed to N-O stretching vibrations as there are no IR bands in this region that can be attributed to H-S or S-O vibrations.

Figure 7.9 and Figure 7.10 shows DRIFTS IR spectra and MS intensity during TPD study of the adsorbed SO$_2$ on APTS SBA-15 in the presence of H$_2$O. The increase in temperature led to a minor decrease in all the sulfate/sulfite IR bands while there was no significant change in the N-H and C-H stretching bands indicating a strong irreversible interaction between SO$_2$ and surface amine species. The amount of SO$_2$ desorbed from surface was calculated to be more than 1000 μmole/g sorbent as calculated from the MS intensity profile of SO$_2$ (m/e=64) during TPD. The SO$_2$ desorbed from the surface only after the sorbent temperature reached 60 °C and the peak desorption temperature was at 120 °C. The visual analysis of sample after the TPD study showed
Table 7.1. Proposed carbonate and bicarbonate structures formed by CO$_2$ adsorbed on APTS-SBA-15

<table>
<thead>
<tr>
<th>Monodentate carbonate</th>
<th>Bidentate carbonate</th>
<th>Monodentate bicarbonate</th>
<th>Bidentate bicarbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Monodentate carbonate" /></td>
<td><img src="image2" alt="Bidentate carbonate" /></td>
<td><img src="image3" alt="Monodentate bicarbonate" /></td>
<td><img src="image4" alt="Bidentate bicarbonate" /></td>
</tr>
<tr>
<td>1543, 1363 cm$^{-1}$</td>
<td>1472, 1428 cm$^{-1}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 7.7. MS intensity profile of CO$_2$ (m/e=44) during TPD of SA9-T
Figure 7.8. DRIFTS absorbance spectra during SO$_2$ adsorption on APTS-SBA-15 in presence of H$_2$O
Figure 7.9. DRIFTS absorbance spectra of adsorbed SO$_2$ on APTS-SBA-15 during TPD study with a heating rate of 10 °C/min in flowing
Figure 7.10. MS intensity profile of SO$_2$ (m/e=64) during TPD of APTS-SBA-15.
Figure 7.11. IR peak intensity of species during CO$_2$ adsorption on SA9-T
Figure 7.12. MS intensity profiles during degradation of APTS-SBA-15 in presence of air
the change in the color of sample from white to yellow which might be due to the formation of irreversible sulfates/sulfites on the surface. CO$_2$ adsorption on this sample after regeneration from SO$_2$ study showed negligible CO$_2$ adsorption capacity revealing that no free surface amine species were available for bonding with CO$_2$. If amine treated sorbents are to be used for CO$_2$ adsorption, the adsorption towers need to be placed down stream of SO$_2$ scrubber. Large amount of SO$_2$ in flue gas will poison the sorbent and hence a provision for CO$_2$ adsorber bypass should be made in case of failure of SO$_2$ scrubber.

7.3.5. Comparison of APTS-SBA-15 and SA9-T

The growth of IR peak intensities versus time was plotted during CO$_2$ adsorption on APTS-SBA-15, SA9-T, and during SO$_2$ adsorption on APTS-SBA-15. A typical plot of the IR peak intensities of adsorbed CO$_2$ species on APTS-SBA-15 is shown in Figure 7.11. The peak height of adsorbed carbonates and sulfates increased with increase in exposure of the sorbent surface with CO$_2$ and SO$_2$, respectively. The rate of adsorption of bidentate carbonate species was higher than monodentate bicarbonate for APTS-SBA-15 and SA9-T. The relative rate of adsorption of carbonates and bicarbonates on both the sorbents was about the same. Compared to the rate of adsorption of carbonate and bicarbonates, the relative rate of adsorption of SO$_2$ to adsorbed sulfate/sulfite species was much lower. Although the rate of adsorption of CO$_2$ is much faster than SO$_2$ on the amine sorbents, the adsorbed carbonates and bicarbonates can be decomposed while adsorbed sulfates/sulfites form stable compounds and the sorbent cannot be regenerated at low temperatures.
7.3.6. Temperature-programmed degradation study of APTS-SBA-15

Figure 7.12 shows the temperature-programmed degradation study of APTS-SBA-15 in the presence of air. The ratio of air to He was maintained at 1:2 with a total flow rate of 30 mL/min. The MS profile during degradation show that the increase in temperature over 270 °C led to the consumption of oxygen from air and simultaneous decomposition of surface NH$_2$ groups in the form of NH$_3$. The combustion of surface hydrocarbons to CO$_2$ was not observed until after 325 °C. It is interesting to note that the peak intensity of NH$_3$ is right around the temperature of 325 °C where the combustion of hydrocarbons starts. This observation suggests that the surface NH groups are decomposed followed by the combustion of hydrocarbon backbone of the silane. A similar study with APTS on MCM-48 support was carried out by Huang et al. and the amine species were stable up to 225 °C.\textsuperscript{11} Another study by Zhen et al. with Ethylene diamine supported on SBA-15 showed amine loss at 300 °C.\textsuperscript{6} The amine species on the SBA-15 support in this study are stable up to 250 °C and any further increase in temperature would lead to decomposition of amine and the combustion of hydrocarbon species above 325 °C.

7.4. Conclusions

The APTS grafted SBA-15 shows high CO$_2$ adsorption capacity in presence of water and the difference in the nature of CO$_2$ adsorbed species in presence of D$_2$O and H$_2$O reveal that water plays an important role during CO$_2$ adsorption. The CO$_2$ adsorbs on the surface as carbonates and bicarbonates on APTS-SBA-15 and the commercial sample SA9-T. The rate of adsorption of carbonate species was higher than bicarbonate
species on both the sorbents. Temperature-programmed desorption studies revealed that
the nature of amine on the surface affects the regeneration temperature of the sorbent.
The SA9-T sample with secondary amine can be regenerated at a lower temperature
while the APTS-SBA-15 requires a temperature above 120 °C for complete regeneration.

SO$_2$ adsorbs strongly on the APTS-SBA-15 sample and the exact structure of the
adsorbed SO$_2$ species needs to be determined. The rate of adsorption of SO$_2$ is slower
than CO$_2$ on APTS-SBA-15 sample. The sample shows high SO$_2$ adsorption capacity but
it cannot be regenerated for CO$_2$/SO$_2$ adsorption. Temperature-programmed degradation
of the APTS-SBA-15 revealed that the amine species are thermally stable up to 250 °C in
air and degrades above this temperature while the combustion of hydrocarbon chain
begins at 325 °C.
CHAPTER VIII

CONCLUSIONS

The research in this dissertation employed in situ IR and MS techniques to investigate the partial oxidation mechanism on Rh/Al$_2$O$_3$, water-gas shift reaction on a novel sulfur tolerant Ni-Re/CeO$_2$ catalyst, and CO$_2$ adsorption on new amine based solid sorbents.

8.1. Partial Oxidation of Methane

Hydrogen production by partial oxidation of methane to syngas over Rh/Al$_2$O$_3$ is preferred due to its high activity and resistance to deactivation by coking. The syngas production can follow the direct partial oxidation pathway or the reforming mechanism depending on the catalyst composition. The objective of this study was to investigate the reaction mechanism and the oxidation state of Rh atoms during the catalytic methane oxidation reaction. The reaction was studied by pulse transient technique using in situ IR spectroscopy (DRIFTS) coupled with mass spectrometry.

It was hypothesized that the syngas production on 2wt% Rh/Al$_2$O$_3$ follows a two-step mechanism involving total oxidation and reforming. The in-situ IR spectroscopy results showed that Rh was present in the partially oxidized and reduced form (Rh$^{5+}$ and Rh$^{0}$) during methane flow. The mass spectrometry results clearly showed that CO and H$_2$ were produced after the formation of CO$_2$ on the catalyst surface. This was well supported by observing the gas-phase CO$_2$ on IR which later led to the formation of the
linear CO observed on the reduced Rh$^0$ surface. The lead-lag relationship observed between CO, H$_2$, and CO$_2$ reveals that syngas was generated by reforming mechanism. Methane was totally oxidized by O$_2$ pulse to CO$_2$ and H$_2$O which led to CO$_2$ and steam reforming of the methane to generate syngas.

The key contribution of this study in the area of methane partial oxidation is the understanding of the reaction mechanism on 2wt% Rh/Al$_2$O$_3$ and the results are very well supported by the in-situ techniques. This study shows that 2 wt% Rh/Al$_2$O$_3$ is a good reforming catalyst compared to the direct partial oxidation and the Rh is present in form of partially oxidized as well as reduced state. Further in-situ studies are recommended using various support for Rh as it has been reported that syngas production pathway greatly depends on the metal-support interaction.

8.2. Water-Gas Shift Reaction

Production of CO-free H$_2$ onboard is desired for the fuel cell powered automobiles. The commercial water-gas shift catalysts require special startup/shutdown procedures and are easily poisoned by the presence of sulfur compounds in the reformate stream. Hence, there is a need for the development of a low cost-sulfur resistant water-gas shift catalyst for automobile fuel cell applications. The objective of this study was to investigate the effect of Re on sulfur tolerance of the Ni/CeO$_2$ catalyst.

It was hypothesized that addition of Re to the Ni/CeO$_2$ catalyst would impart sulfur resistance and resistance to coking. The effect of coking was not observed at the reaction conditions employed in this study while the addition of the Re to the Ni/CeO$_2$ catalyst enhanced the activity of the catalyst by a factor of three when the catalyst was reduced with pure H$_2$. The activity of 0.1%H$_2$S/H$_2$ reduced Ni/CeO$_2$ catalyst decreased
by 50% compared to that of pure H₂ reduced Ni/CeO₂. The activity of Ni-Re/CeO₂ catalyst decreased by only 20% when reduced with 0.1%H₂S/H₂ compared to that reduced with pure H₂. These results show that Re not only improves the activity of the catalyst but also imparts sulfur resistance to the catalyst. In case of Pt-Re catalyst used for catalytic reforming of napthas, Re imparts sulfur resistance and improves the coke resistance of the Pt catalyst by dispersing the Pt on the surface. The affinity of sulfur adsorption increases as Re > Ni > Pt. It is postulated that most of the sulfur is adsorbed on the Re atoms and the bimetallic Ni-Re interaction enhances the activity of the water-gas shift reaction. Steady state isotopic exchange studies with H₂O and D₂O showed kinetic isotope effect due to the slower dissociation rate of D₂O and surface recombination of D₂. As no adsorbed intermediates were observed with DRIFTS, IR studies did not reveal any information except for the formation of toxic Ni(CO)₄ at room temperature over Ni/CeO₂ catalyst.

This study showed that the Re in the novel Ni-Re/CeO₂ catalyst acts as a promoter as well as enhances the sulfur resistance of the catalyst. Further studies are recommended for the optimization of the metal content and characterization of the catalyst.

8.3. CO₂ Adsorption

Various CO₂ sequestration schemes are being considered for the reduction of CO₂ in the atmosphere. CO₂ needs to be separated from the process streams before it can be sequestered in deep oceans/aquifers. The cost of separation of CO₂ is estimated to be 70% of the total cost of sequestration scheme due to the current expensive aqueous amine technology. There is considerable interest in solid sorbents for CO₂ capture due to the
low capital, equipment, and operation cost. The objectives of this study were to synthesize a novel CO$_2$ adsorption sorbent and to investigate the effect of SO$_2$ on the CO$_2$ adsorption capacity of the sorbent.

For CO$_2$ adsorption research, it was postulated that increasing the number of amine functional groups in the grafted molecule will increase the CO$_2$ adsorption capacity. It was also postulated that other acid gases like SO$_2$ and H$_2$S can be adsorbed using this solid sorbent. A comparison study of monoamine and diamine-grafted SBA-15 showed that diamine-grafted SBA-15 adsorbed twice as much CO$_2$ as the monoamine-grafted SBA-15. Furthermore, SO$_2$ poisoned the sorbent by adsorbing on the amine-grafted sorbents irreversibly.

The grafting of amine on SBA-15, CO$_2$ adsorption/desorption, and SO$_2$ adsorption/desorption was studied using IR spectroscopy, mass spectrometry, and temperature-programmed desorption techniques. CO$_2$ is adsorbed on amine modified sorbents as carbonates and bicarbonates. Furthermore, the amine grafted sorbents had higher CO$_2$ adsorption capacity than the commercial polymer amine based sorbent used in space shuttles and submarines. Adsorption of SO$_2$ on mono-amine grafted SBA-15 showed that SO$_2$ adsorbs very strongly on the sorbent. Upon regeneration, the CO$_2$ adsorption capacity of the sample was found to be negligible. Furthermore, the decomposition study of the monoamine-grafted SBA-15 showed that the surface amine functional groups are stable up to a temperature of 250 °C.

This study led to the synthesis of a novel amine based sorbent for CO$_2$ capture. Furthermore, it revealed that the increase in the density of surface amine functional groups enhances the CO$_2$ adsorption capacity. It also revealed that SO$_2$ can be adsorbed
Figure 8.1. Scheme for production of clean hydrogen
on the amine based sorbent, but it poisons the sorbent and it cannot be used further for CO₂ adsorption. Further studies required for commercialization of the sorbent include long term adsorption/regeneration of the sorbent in the simulated process streams and in a pilot plant.

Results of these studies may be used to develop an integrated process for production of clean hydrogen as shown in Figure 8.1. The results of the methane partial oxidation research provide the fundamental understanding of the catalytic reaction mechanism which can be used for an effective design of the catalyst and the reactor. The results of water-gas shift reaction provide a basis for the development of an effective sulfur tolerant catalyst for fuel cells using onboard reforming of hydrocarbons. Although the employment of Re metal would increase the cost of the water-gas shift catalyst, it would be beneficial on long term basis due to high durability and long-term operation. Although the CO₂ adsorption sorbents were developed for CO₂ adsorption from power plant flue gases and closed habitats like submarines and space crafts, they may be employed for CO₂ adsorption from process streams and for generation of pure hydrogen. The solid sorbents are advantageous for CO₂ separation from process streams due to low initial capital cost and low cost of operation.
CHAPTER I


**CHAPTER II**


CHAPTER 4


CHAPTER V


CHAPTER VI


CHAPTER VII


APPENDIX A

SOLID OXIDE FUEL CELLS

Introduction

Fuel cells have gained interest due to their high efficiency and low emissions. Various fuel cells are being developed depending on the end applications. Depending on the type of the fuel cell, there is a change in the operating conditions and the principle of operation. Figure A1 shows the principle of operation of various fuel cells. All the fuel cells consist of an anode and a cathode separated by an electrolyte which may be in a solid or a liquid form. Fuel is supplied on anode side and air or oxygen is supplied on cathode side. Out of the various fuel cells, the polymer electrolyte membrane (PEM) and solid oxide fuel cells (SOFCs) have been developed the most and are also commercialized. The costs of these fuel cells are still high and are not affordable for every day use.

SOFCs are being developed primarily for stationary power generation while the PEM fuel cells are being developed for mobile applications. Each of the fuel cells uses some kind of membrane that separates the anode and cathode compartment of the fuel cell. As the name suggests, PEM fuel cells have a polymer membrane that allows diffusion of protons. In case of SOFCs, the membrane is a solid oxide which allows diffusion of oxygen anions at high temperatures (>600 °C – depending on the oxide). The most stable oxide currently used for SOFC is 8% yttria stabilized zirconia.
Figure 1.1 Fuel cells of various kinds, their anode and cathode reactions
commonly known as YSZ. Other oxides under research consist of gadolina doped ceria (GDC), samaria doped ceria (SDC) and bismuth containing oxides.

The SOFCs based on YSZ operate at temperatures higher than 800 °C which requires use of highly stable mechanical components and interconnects. Along with the mechanical components, the thermal expansion coefficient of the anode and cathode materials needs to be considered. A thermal expansion coefficient mis-match would lead to poor structure of anode and cathode layers and might eventually crack the electrolyte disc. Table A2 shows thermal expansion coefficient of various materials used in SOFC.

The most common anode for SOFC is Ni supported on YSZ, although there are some papers published with Cu as an anode. For cathode, lanthanum strontium manganese oxide is used predominantly. Other cathode materials being researched are perovskite materials containing mixture of oxides which form oxygen deficient vacancies. The cathode catalyst is responsible for converting $O_2$ gas from air to oxygen anions that diffuse through electrolyte layer.

The SOFC fuel cell project was initialized from scratch. The reactor design was adapted from the work described by Prof. Gorte at University of Pennsylvania. During the initial phases following problems occurred and the solutions are described after the description of the problem:

- the anode layer would not adhere to the electrolyte disc – different temperatures and heating rate were employed. The anode layer would adhere on a acetone cleaned disc above 950 °C with a ramping rate of 5 °C/min or less.
• thin electrolyte discs would fracture while applying anode and cathode layer – a fast heating rate develops stress due to thermal mis-match coefficient between electrolyte layer and anode/cathode. A slower heating rate of less than 1 °C/min was employed to reduce the effect of thermal mis-match. A thinner anode/cathode layer would further help in reducing the thermal mis-match coefficient.

• the Pt grid (electron collector) would not adhere to anode and cathode layers as described in the literature – Pt ink was purchased from Engelhard that would bond to YSZ. A layer of Pt ink was applied to anode/cathode, the Pt grid was placed on the ink layer and some more Pt ink was applied over it. A small amount of YSZ powder was sprinkled over the ink and calcined above 900 C. This was a standard procedure there after to adhere the Pt grid to the disc firmly.

• the ceramic seal used to adhere the fuel cell electrolyte disc to the alumina tube would not seal properly – a ceramic seal that has a material of thermal expansion coefficient near the alumina and YSZ disc material was purchased from Aremco which reduced the problem. The Aremco seal was not leak proof which made it unsuitable for reaction studies and mass balance – a hermatite seal was purchased from Aremco. A layer of hermatite seal was applied over the previous ceramic seal and heated above 900 C to make a leak proof seal.

• the Pt wire cracked inside the tube at high temperature during reaction – the reactor design was changed, the Pt wire leads from anode and cathode
were pulled out near the edge of the alumina tube, rather then through the alumina tube.

- after facing the above problems we still were not able to get high power density – we are now working on manufacturing thin electrolyte discs and anode supported electrolyte discs that would enhance the current density close to that published in the literature.
APPENDIX B

XRD ANALYSIS

X-Ray diffraction is a very common technique used for catalyst characterization. This technique yields the catalyst particle size, the phase of the catalyst in bulk, and the dispersion of the active component on the support. Below is a method described to calculate the size of particles from XRD pattern. The size of Ni and CeO$_2$ for the water-gas shift catalysts has been calculated by this method.

The XRD spectra are reported in the form of intensity of x-ray radiation as a function of angle of diffracted beams from the surface. The crystallite size of the particle is calculated by the following equation known as Scherrer equation:

\[
D = \frac{K \lambda}{\beta \cos \theta}
\]

where,

- $D$ = average crystal dimension
- $\lambda$ = wavelength of the x-ray (Cu$k\alpha$ = 1.54178 Å)
- $\theta$ = angle of diffraction called Bragg angle
- $K$ = shape factor (close to unity)
- $\beta$ = width at half maxima (FWHM) in radians

Refer to the figure on the next page for an illustration.
\[ \beta = \frac{2 (\theta_1 - \theta_2)}{2} \times \frac{2\pi}{360} \]

\[ D \text{ (in nm)} = \frac{1 \times 15.4178}{\beta \times \cos \theta} \]
APPENDIX C
CANDIDACY EXAM

Task # 1 Survey the literature which relates to the use of Raman spectroscopy to study metal oxide catalysis for partial oxidation of hydrocarbons.

Introduction to Raman Spectroscopy

When a monochromatic beam of photons interacts with the material, the molecules of the material are excited to higher energy virtual states. The excited molecules can decay back to the original electronic ground state or higher energy electronic ground state thus losing some energy. If the excited molecule decays without any energy loss of the photons, it is called Rayleigh scattering. If the excited molecule decays to higher electronic ground state, the photons lose some energy ($\Delta \nu$) and gives rise to Stokes scattering. On the other hand a molecule at higher ground state can be excited by incident photons and can return to ground state gaining some energy ($\Delta \nu$). This is called anti-Stokes scattering. Figure 1 shows the principle of Rayleigh, stokes and anti-stokes scattering (1). The intensity of Rayleigh scattering is much higher compared to Stokes scattering which is higher than anti-Stokes scattering. The Stokes and anti-Stokes scattering is called Raman scattering and they are equally spaced on each side of Rayleigh scattering wavelength. A high energy laser source is used to excite the molecules and get higher Raman scattering. A Raman spectrum is plotted as intensity of scattered radiation against the difference in frequency of the laser radiation and Raman
scattering radiation called Raman Shift ($\text{cm}^{-1}$). The instrument filters the Rayleigh scattering to reduce the interference in spectrum and plots show only the Stokes frequency as the intensity of anti-Stokes scattering is very low and has exactly same Raman shift frequency as Stokes with negative sign.

Metal Oxides in Catalysis

Transition metal oxides and mixed metal oxides supported on inorganic oxides like $\text{Al}_2\text{O}_3$, $\text{SiO}_2$, and $\text{TiO}_2$ are being widely used in industry to manufacture number of important commodity and specialty chemicals as well as pollution control industries (2,3,4). The structure of surface metal oxide species differ from the bulk oxide and it can change with varying reaction conditions which can alter the reaction chemistry (5). The molecular structure of these catalysts have been characterized by different spectroscopic techniques such as, EXAFS-XANES, UV-vis-Near-IR DRIFTS, XPS, IR, and Raman spectroscopy (6). The transition metal atom under reaction conditions can be in different oxidation state and coordination environment. In situ Raman spectroscopy has been identified as a promising technique due to its ability to discriminate the transition metal oxide on the surface and supported metal oxide catalysts on the support (1,2,4-18). Most of the metal-oxygen vibrational bands are below $1000 \text{ cm}^{-1}$ and heavy metal oxide bonds are more covalent in nature and hence give strong Raman signals. The intensity of absorption bands for IR depend on the change in dipole moment while for Raman, it depends on the change in polarizability of the molecule (4). In general, an ionic bond gives strong IR signal while a covalent bond gives strong Raman signal. It is important to know the molecular structure of the catalyst during reaction conditions for proper structure-activity relations which can help to enhance the selectivity for particular
reaction and to elucidate the reaction mechanism. In situ Raman spectroscopy technique can be useful to study selective oxidation of hydrocarbons on supported metals and metal oxides as it can also determine different kind of oxygen species present on metal/metal oxide surface during the reaction condition. The active sites responsible for partial oxidation can then be tailored using surface chemistry approaches to enhance the activity and selectivity of the reaction.

**Raman Spectroscopy and Metal Oxide Catalysis**

Raman spectroscopy has been used to study the transformation of metal oxide structure during reaction, interaction of metal oxide with the support, structure of terminal metal-oxygen bonds and adsorbed oxygen species on the surface of metal oxide catalysts. Oxygen can adsorb on metal or metal oxide surface in various ways. Some of the identified adsorbed oxygen species and the mechanism of adsorption are shown in the scheme A below (19).

![Scheme A. Various forms of adsorbed oxygen species observed in catalysis](image)

In earlier work of Haber J. (5), he explained that O$^{2-}$ or O$^{-}$ activated oxygen species are responsible for total oxidation while lattice oxygen species are responsible for partial oxidation of hydrocarbon molecule. In one of the work by Gasior and Grzybowska (8), it was shown that during oxidation of o-xylene on V$_2$O$_5$/TiO$_2$ catalyst system, the catalyst changed from V$^{5+}$ oxidation state to V$^{4+}$ and V$^{3+}$ as the reaction proceeded. This was monitored in situ by Raman spectroscopy and the oxidation states
were confirmed by XPS of V₃d electrons. The Raman spectra of fresh catalyst and in reaction conditions are shown in Figure 2.

Selective oxidation of methane to produce hydrogen and synthesis gas is well adapted in industry. Figure 3 on the next page shows Raman studies of partial oxidation of methane on La₂O₃ at 970 K (9). After initial exposure of catalyst to O₂ at 970 K lead to formation of Raman band at 863 cm⁻¹ which is assigned to peroxide ions on the surface. Upon introduction of CH₄ diluted in He, the band disappeared within 80 s. This shows that the peroxide ion is responsible for the partial oxidation of methane on La₂O₃ catalyst. Furthermore, when O₂ was reintroduced with CH₄/He, the band at 863 cm⁻¹ reappeared showing that La₂O₃ can catalytically activate O₂ to peroxide ions and catalyze the partial oxidation of CH₄.

In one of the other examples, oxidation of methanol on MoO₃/SiO₂ was studied using Raman spectroscopy (4). The spectra of the dehydrated catalyst exposed to He/O₂ showed bands at 978 cm⁻¹ for isolated metal oxide bonds on the surface as shown by spectrum “a” in Figure 4. Upon exposure of catalyst to He/O₂/CH₃OH the band at 978 cm⁻¹ was converted to sharp bands at 842 and 768 cm⁻¹ responsible for crystalline β-MoO₃ phase. This structural transformation tells us that during reaction conditions it is β-MoO₃ phase which is responsible for catalytic oxidation of methanol.

Metal oxides on support can be present as mono-, di- and tri-oxo species. In situ Raman spectroscopy combined with ¹⁸O isotopic labeling can determine the structure of these species on surface (6). Supported metal oxide catalysts prepared by standard techniques can be reduced and re-oxidized using ¹⁸O₂ gas leading to various labeled species on surface. If the supported metal oxide is mono species the isotopic labeling
Rayleigh Scattering
no change in energy
$\nu_{in} = \nu_{out}$

Raman Scattering
net change in energy
$\nu_{in} \neq \nu_{out}$

Figure 1 Principles of Raman Spectroscopy
Figure 2  Raman Spectra of fresh $\text{V}_2\text{O}_5$/TiO$_2$ catalyst and in reaction condition for 1h
Figure 3  Raman studies of La$_2$O$_3$ during partial oxidation of CH$_4$ at 973 K
Figure 4 Raman spectra of MoO$_3$ monitored during oxidation of methanol at
Figure 5  Possible Metal-Oxygen Species on Support (Monoxo, Dioxo and Trioxo)
Figure 6  Raman Spectra of 3 wt% WO$_3$/ZrO$_2$ - Redox cycles with Isotopic labeling
Figure 7. Raman Spectra of MoO$_3$/Al$_2$O$_3$ as function of metal oxide coverage
Figure 8 Raman study for interaction of metal oxide and its support
would give rise to two bands in Raman spectra. On the other hand if the surface oxide specie is di-oxo it will give us 3 bands and tri-oxo species will lead to 4 bands in Raman spectra by the species as shown in Figure 5.

Figure 6 shows the Raman spectra of 3% WO$_3$ on ZrO$_2$ support during reduction and $^{18}$O$_2$ oxidation cycles using 514.5 nm Ar ion laser(6). The first spectrum in the figure labeled as dehydrated is the spectrum taken after calcination of catalyst in $^{16}$O$_2$ at 550 °C. The subsequent spectra show the spectrum after each reduction and then oxidation with $^{18}$O$_2$. Isotopic substitution of $^{16}$O with $^{18}$O in the M=O bonds shifts the frequency to lower wave number. From the figure we see that the new bands formed after oxidation with $^{18}$O$_2$ are formed at the expense of reduction of intensity in M=$^{16}$O bands and the M-O-M band in the oxide catalyst. This suggests that the oxide studied in this example has mono-oxo species on ZrO$_2$.

When metal oxides on support surface have coverage of more than a monolayer, it can form a microcrystalline phase. The vibrations of microcrystalline phase occur at different frequency then isolated monolayer metal oxide species (4). Figure 7 shows series of Raman spectra as a function of surface coverage of MoO$_3$ on Al$_2$O$_3$ surface. Figure shows that up to 20 % metal loading there is a prominent band at around 1000 cm$^{-1}$. When the metal oxide loading is increased to 25%, there is another prominent band formed at 815 cm$^{-1}$ which represents crystalline MoO$_3$ phase (4).

The interaction of catalyst with its support plays an important role in catalytic reaction. Wachs et al. showed that interaction of WO$_3$ with Al$_2$O$_3$ support can be studied and the phase transformations of WO$_3$ can be determined during the calcination of 10
wt% WO₃ on Al₂O₃ (17). Figure 8(a) shows the spectra during this study and Figure 8(b) shows the schematic of interactions and transformations of the catalyst/support.

As the temperature rises up from 550 °C to 950 °C the high surface area γ-Al₂O₃ change to low surface area θ-Al₂O₃, increasing the surface density of WO₃. Further heating the catalyst/support to 1000 °C reduces more surface area forcing some of the WO₃ to form a crystalline WO₃ phase as seen by the bands developed at 808, 711 and 273 cm⁻¹ for crystalline WO₃. On further heating to 1050 °C, the crystalline WO₃ reacts with the support to form Al₂(WO₄)₃ which is the only thermally stable compound at 1050 °C for the W-Al-O system.

In conclusion, Raman spectroscopy can be used to study the phase transformation, metal oxide loading, metal oxide-support interactions, type of adsorbed oxygen species on surface or number of terminal metal oxide bonds giving us the information about the oxidation state of metal.

**Task # 2 Identify the grand challenge in partial oxidation and select the key model reaction for investigation of the partial oxidation.**

**Grand Challenge in Partial Oxidation of Hydrocarbons**

Partial oxidation of hydrocarbons is used in industry to produce important commodity chemicals such as ethylene oxide, propylene oxide, anhydrides, aldehydes, ketones and many other bulk and specialty chemicals. The grand challenge in partial oxidation industry is to obtain high selectivity for partial oxidation product with high conversion. The competing thermodynamically favorable reaction to partial oxidation is total oxidation. The selectivity of catalytic partial oxidation can be improved if we have proper understanding of active sites and catalyst structure which promotes partial
oxidation and total oxidation. To increase the selectivity we can selectively poison the total oxidation site to enhance the conversion for partial oxidation product.

**Key Model Reaction: Propylene to Propylene Oxide**

A key model reaction for this study would be direct partial oxidation of propylene with $O_2$ to form propylene oxide (PO) on Rh/Al$_2$O$_3$. PO is currently produced by chlorohydrin and hydro peroxide process in industry. All the efforts to develop successful catalyst for direct oxidation suffer from low selectivity at high conversion because it is easier to oxidize the $\alpha$-hydrogen of the allyl methyl group to aldehydes (3). Industrially, there are processes to directly oxidize propylene to make acetone and acrolein on suitable catalyst with high selectivity and conversion.

The chlorohydrin process (Eq. 1) currently used for manufacturing PO was initially used to produce ethylene oxide from ethylene, but after the successful development of Ag/Al$_2$O$_3$ to directly oxidize ethylene with $O_2$ to ethylene oxide, the chlorohydrin plants became more useful for propylene oxidation. In the chlorohydrin process, propylene is treated with aqueous chlorine at around 50 °C and a pressure of 2-3 bars to form a mixture of a- and b-chlorohydrin which is then dehydrochlorinated using dilute alkali such as lime or sodium hydroxide solution. All the chlorine is lost as CaCl$_2$ and cannot be recovered. This process suffers from large amount of chlorine loss and waste water disposal as 10% dilute alkali solution is used.

$$\begin{align*}
2 \text{H}_3\text{C} \equiv \text{C} \equiv \text{CH}_2 + 2 \text{HOCl} &\rightarrow \text{H}_3\text{C} \equiv \overset{\text{OH}}{\text{C}} \equiv \text{CH}_2\text{Cl} + \overset{\text{Cl}}{\text{H}_3\text{C}} \equiv \text{CH}_2\text{OH} \\
\text{Ca(OH)}_2 &\rightarrow 2 \text{H}_3\text{C} \equiv \text{C} \equiv \text{CH}_2 + 2\text{H}_2\text{O} + \text{CaCl}_2
\end{align*}$$

...............(1)
In the hydro peroxide process (Eq. 2), the peroxide oxygen of an alcohol or an acid is used to selectively oxidize the propylene to PO. In this process large amount of cooxidates are produced in quantities more than PO itself and hence production of PO by this process is somehow related to the demand of the cooxidates in the industry along with PO. There are large varieties of peroxy alcohols and acids that can be used to produce the cooxidates of industrial interest.

\[
\text{H}_3\text{C}–\text{C}═\text{CH}_2 + \text{ROOH} \xrightarrow{\text{catalyst}} \text{H}_3\text{C}–\text{C}═\text{CH}_2^\text{O} + \text{ROH} \hspace{1cm} \text{(2)}
\]

A direct oxidation route (Eq. 3) in which propylene can be oxidized using air or oxygen is preferred due to the disadvantages of the above processes as well as the simplicity of direct oxidation process to give propylene oxide. All the efforts in producing PO by direct oxidation suffer from either low selectivity or low conversion for the process to be economical.

\[
\text{H}_3\text{C}–\text{C}═\text{CH}_2 + \frac{1}{2} \text{O}_2 \xrightarrow{\text{catalyst}} \text{H}_3\text{C}–\text{C}═\text{CH}_2^\text{O} \hspace{1cm} \text{(3)}
\]

In one of the recent combinatorial studies by Senkan et al. (20) more than 400 catalyst combinations were screened and in conclusion it was found that Rh and bimetallic catalyst containing Rh are highly selective catalysts for formation of PO. In these studies, 3 different concentrations of Rh metal loading (0.1%, 1% and 10%) were used and it was found that 1% Rh metal loading in single component catalyst system was most active for PO production along with total combustion to CO2 which increased with metal loading. Further addition of Ag, Zn or Cr decreased the formation of CO2 and increased the formation of PO. In his conclusion, he suggests further characterization of catalyst to improve the selectivity and activity of these catalysts. A good idea would be
to study Rh/Al₂O₃ catalysts using transient techniques and characterize the catalyst ex situ as well as in situ for propylene oxidation study.

**Task # 3 Propose an experimental approach involving Raman spectroscopy to study the mechanism of the proposed model reaction.**

Rh supported on Al₂O₃ can be studied using Raman spectroscopy to characterize the catalyst as well as to study the in situ oxidation of propylene. I propose to study the effect of metal loading which effects the CO₂ production as metal loading is increased. At 0.1% or 1% metal loading it is expected that Rh metal will be well dispersed and isolated but at 10% loading it might be a monolayer or some of the Rh might cluster together on the surface enhancing the total combustion and decreasing the number of sites responsible for catalyzing the formation of PO. Raman spectroscopy can be used to just characterize the catalyst to see the structure of metal oxygen bonds on the surface and their relative density on the surface.

Further more, reaction of propylene with oxygen can be studied in situ by Raman spectroscopy along with some complimentary techniques to focus on mechanism of the reaction and to determine the type of adsorbates, active and spectator species. This could help us in improving the activity and selectivity of propylene oxidation on Rh/Al₂O₃. I propose to study this reaction by transient technique using Raman spectroscopy in line with mass spectrometry. This can give us the information of the reactants and products on the catalyst surface which might be present as isolated metal oxide, clustered metal oxide or might be reduced to Rh⁰ during reaction conditions. This can be determined by Raman spectra which might differ from initial metal oxide on the surface and the type of
adsorbates present on the surface during reaction conditions. Mass spectrometry can help us to identify the products produced from the reaction and quantification.

An experimental approach to study this kind of reaction is shown in Figure 8. The apparatus will consist of 3 sections: (a) Gas handling system (b) Reactor system and (c) Analysis section. The gas handling system will consist of the required gases, their mass flow controllers and a set of 4 port and 6 port valves. Step and pulse techniques will be used to study the transient kinetics. The step input will be accomplished with a 4-port valve while a 6-port valve can be used for pulse input which will also be used to calibrate the MS. This kind of reactor system has been described in literature (21). The reactor system will consist of a home made quartz tub reactor which will sit in the Raman bench. The catalyst will be loaded in the quartz reactor and will be supported on quartz wool on both sides. The reactant gases will enter from one side of the quartz tube, while the products will leave from other side of the reactor and go to mass spectrometer where the effluent gases will be analyzed and quantified using calibration factor for the mass spectrometer for each gas. To just characterize the catalyst, the catalyst will be filled in the quartz tube and spectra will be recorded to obtain the surface structure information.

The information obtained from this study can help to shed light on the structural changes due to metal loading of catalyst as noted by Senkan et al. Also this study can help us to study the kind of adsorbates and note any changes in structure of catalyst during the reaction by in situ monitoring. The information obtained can help us in determining a possible reaction mechanism for propylene oxidation on Rh/Al₂O₃. If active sites for the partial oxidation to PO and total oxidation to CO₂ are determined, it
can help us to design the catalyst so as to selectively poison the total oxidation sites to enhance the selectivity for partial oxidation of propylene to PO.

References

