ELECTROCHEMICAL AND PHOTOCATALYTIC OXIDATION OF CARBON AND HYDROCARBONS

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Dissertation

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Development of novel technologies for the conversion and storage of energy has been actively investigated in recent years. The use of a combined approach consisting of direct electrochemical and photocatalytic oxidation reactions could allow the efficient utilization of energy resources. Direct electrochemical oxidation in a fuel cell could offer significant advantages over conventional combustion technologies, in light of their increased energy efficiency, reduction in emission of toxic pollutants, and overall process simplicity. The majority of fuel cell research has focused on the use of hydrogen, an environmentally friendly fuel characterized by high energy density and production of H$_2$O byproduct. Despite these advantages, commercialization of hydrogen powered fuel cells is currently limited by difficulties in hydrogen production and storage.

The high operation temperature of the solid oxide fuel cell (700-1000 °C) facilitates the direct use of hydrocarbon and carbon fuels, avoiding the complex and expensive reforming processes for the generation of concentrated H$_2$ fuel. Exposure of gaseous hydrocarbons to the fuel cell at these high temperatures provides a thermodynamically favorable pathway for formation of carbon deposits (i.e., coking) which can lead to rapid and irreversible anode electrode degradation. This dissertation presents a study of the use of a novel Cu/Ni-YSZ anode electrode that reduces the
formation of coke deposits and allows the energy efficient operation of the solid oxide fuel cell in hydrocarbon and carbon fuels. The microstructure of the Cu/Ni-YSZ anode electrode is extensively characterized by scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). The performance of the Cu/Ni-YSZ anode and the energy efficiency during the operation on carbon (i.e., coke, a devolatized form of coal) is experimentally measured with the aid of in situ electrochemical analysis and, mass spectrometry (MS) and gas chromatograph (GC), demonstrating higher energy efficiencies compared with combustion technologies.

Photocatalytic reactions over semiconductor catalysts such as TiO$_2$ have received significant attention due to their potential applications for conversion and storage of solar energy to chemicals and the degradation of harmful pollutants present in air streams and wastewaters. Excitation of photocatalysts by exposure to light of appropriate energy causes promotion of electrons from the valence band to the conduction band, resulting in the generation of electron/ hole pairs that can initiate redox reactions with species adsorbed on the surface of the photocatalyst. Hydrogen can be produced by the photocatalytic reduction of water (i.e. splitting reaction). Addition of alcohol molecules have been shown to improve the photocatalytic evolution of H$_2$ from H$_2$O due to hole scavenging oxidation reactions that limit electron/hole recombination. Detail knowledge of the mechanisms governing the photocatalytic oxidation of alcohols could facilitate the development of highly efficient photocatalysts for water splitting and degradation of volatile organic compounds (VOC).

The photocatalytic evolution of H$_2$ from aqueous solutions containing methanol (CH$_3$OH) hole scavenging reagents was studied by tracing the reaction of D$_2$O over a
Cu/S-TiO₂ catalyst under UV illumination. Use of D₂O/CH₃OH produced higher formation rates of HD and D₂ than that of H₂. The low H₂ formation rates indicate that the direct reaction of CH₃OH with photogenerated holes does not proceed to an appreciable extent in the presence of high concentrations of D₂O. The role of CH₃OH in accelerating hydrogen formation can be attributed to its ability to produce an electron donor, injecting its electrons to the conduction band.

The photocatalytic oxidation of alcohols was further studied at 30 °C and 1 atm by in situ infrared methods, using ethanol as a model compound. Results from these studies have shown ethanol adsorbs on TiO₂ in the presence of high contents of water as molecularly adsorbed ethanol (CH₃CH₂OHₐd), which exhibit a lower initial C-H scission and CO₂ formation rate than ethoxy CH₃CH₂Oₐd produced from ethanol adsorbed low water content TiO₂ catalysts. CH₃CH₂OHₐd photooxidation produced formic acid (HCOOHₐd) and formate (HCOO⁻ₐd) species, whereas CH₃CH₂Oₐd reactions proceed via formation of acetaldehyde (CH₃CHOₐd) and acetate (CH₃COO⁻ₐd). CH₃CHOₐd was found to react on TiO₂ via hydrogen abstraction of the α-Carbon producing CH₃COO⁻ₐd which can be further oxidized to HCOO⁻ₐd and CO₂. The rate of ethanol photooxidation was found to decrease due to the accumulation of CH₃COO⁻ₐd species on the TiO₂ surface. In the presence of excess H₂O, weakly adsorbed species (i.e., acetic acid CH₃COOHₐd) can be redistributed in the surface and dissociated producing acetate.
DEDICATION

A mis padres que me han apoyado desde siempre, mi hermana Maria Jimena, y a mi querida Camila, Por su constante afecto e inspiracion.
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CHAPTER I
INTRODUCTION

The installment of more stringent regulations on the emission of pollutants and the increase in world energy demand, which has been projected to grow 55% over the next 20 years [1], provide the motivation for the development of alternative technologies for energy generation and storage. In that respect, electrochemical and heterogeneous photocatalytic reactions could provide novel approaches for the utilization of conversion of energy resources, resulting in higher efficiency and lower environmental impact than current combustion processes.

Electrochemical reactions involve a series of electron transfer processes that take place at the interface of an electron conductor (i.e., a metal or metal oxide electrode) and an ionic conductor (i.e., electrolyte). Unlike conventional chemical reactions, the electrochemical oxidations of a fuel is not accompanied by the release of large amounts of heat; instead, the conversion of reactants result in the generation of an electric current that can be used to perform work. Thus, these reactions could facilitate the efficient generation of power, avoiding the thermodynamic efficiency limitations encountered with heat engines (i.e., Carnot efficiency).
Heterogeneous photocatalytic reactions comprise a series of reduction and oxidation steps resulted from generation of charged species upon adsorption of light, providing a route for the direct conversion of solar energy into chemical energy. Heterogeneous photocatalytic reactions can be used for the complete oxidation of organics or the reduction of oxidized species such as H$_2$O and CO$_2$ to valuable feedstocks (i.e., water splitting: H$_2$O $\rightarrow$O$_2$ + H$_2$). The use of a combined approach in which fuels are electrochemically oxidized producing electric power and the resulting byproducts (i.e., H$_2$O and CO$_2$) are photocatalytically converted into valuable chemicals, constitutes a highly desirable route for efficient energy utilization. Development of such approach requires detailed knowledge of the key fundamental principle shared by electrochemical and photocatalytic reactions: the electron transfer.

The objective of this dissertation is to study the electron transfer processes occurring during electrochemical and photocatalytic reactions, using the conversion of hydrocarbons and carbon as model reactions. The use of carbon and hydrocarbons can be illustrated by considering Figure 1.1. The continuous electrochemical oxidation involves the use fuel cells, which to a large extent, have been developed for the conversion of hydrogen. Production of hydrogen at industrial scale quantities involves converting carbon and hydrocarbon feedstocks into hydrogen by means of reforming reactions. These reforming reactions increase the complexity of the process, and impose significant energy and cost penalties that limit the fuel cell commercialization. The direct electrochemical oxidation of hydrocarbons and carbon feedstocks would avoid the use of reforming units, simplifying the process and increase the fuel cell energy efficiency.
Photocatalytic conversion of carbon and hydrocarbons would provide the route for (i) complete oxidation of unreacted fuel and undesired byproducts and (ii) synthesis of valuable chemicals (i.e., alcohols, aldehydes, H₂ or CH₄) that could be electrochemically oxidized.

1.1 Photocatalytic oxidation

Photocatalytic reactions on semiconductor TiO₂ powders have attracted research interest due to their potential applications for the destruction of organic compounds on polluted air and wastewaters [2] and conversion and storage of solar energy [3]. Recent investigations have shown that the photocatalytic oxidation (PCO) rates for the gas phase elimination of certain volatile organic compounds (VOCs) can be higher than those observed for the photocatalytic degradation in aqueous solutions[4, 5]

Driven by the promise of potential applications on the treatment of enclosed atmospheres, there has been an increased interest in the development of more active catalysts based on semiconductor TiO₂. The development of photocatalytic oxidation catalysts with high photocatalytic oxidation rate, limited production of harmful intermediate species (i.e., traces of COCl₂ produced during PCO of 4-chlorophenol, pentachlorophenol, trichloroethylene [6]), and enhanced resistance to deactivation requires a better understanding of the mechanisms of photocatalytic reactions. Infrared (IR) spectroscopy is very effective technique for the detection of gas phase and surface bound species, providing relevant and detailed information of the chemical nature and structure of intermediate species.
Figure 1.1 Electrochemical and photocatalytic reactions for the efficient generation and utilization of energy.
Development of efficient photocatalyst requires a better understanding of photocatalytic reactions. This dissertation presents a fundamental study of the photocatalytic reactions occurring on the surface of conventional TiO$_2$ photocatalyst, focusing on the photocatalytic oxidation of $\alpha$-carbon alcohols such as ethanol and methanol as a model compounds.

1.2 Electrochemical oxidation

Electrochemical oxidation can be carried out in a continuous mode using a fuel cell. Fuel cells are devices composed of two electrodes, anode and cathode, separated by an ion conducting electrolyte. The nature of the electrolyte has often been used as a criterion for distinguishing the different types of fuel cells, including the Proton Exchange Membrane Fuel Cell (PEMFC), the Molten Carbonate Fuel Cell (MCFC), the Alkaline Fuel Cell (AFC), and the Solid Oxide Fuel Cell (SOFC). During fuel cell operation, the fuel and the oxidant (usually oxygen from air) are continuously fed to the anode and cathode compartment. Electrochemical reactions occur at the electrodes resulting in the generation of a flux of ionic species through the electrolyte and a corresponding electric current drawn from an external circuit. The nature of the ionic species generated during the electrochemical oxidation depends on the type of electrolyte.

Majority of research efforts focusing on the electrochemical oxidation of hydrocarbons have been directed towards the development of processes that convert the fuels to hydrogen for its electrochemical oxidation. Although hydrogen possesses several advantages for electrochemical oxidation such as rapid electro kinetics rates of reaction, high energy density, and formation of non polluting H$_2$O byproducts; the generation and
storage of hydrogen face challenging problems. Hydrogen can be generated at an industrial scale from fossil fuels by the catalytic steam reforming. Catalytic steam reforming is an endothermic reaction that involves the conversion of hydrocarbons and water into hydrogen, carbon monoxide (i.e., synthesis gas), as shown in reaction (1.1). The steam reforming reaction is usually accompanied by the slightly exothermic water gas shift (WGS) reaction (1.2).

\[
C_nH_{m+n} + nH_2O \rightarrow nCO + \left( \frac{n+m}{2} \right)H_2 \quad (\Delta H_{298} > 0) \quad (1.1)
\]

\[
CO + H_2O \rightarrow CO_2 + H_2 \quad (\Delta H_{298} = -412 kJ/mol) \quad (1.2)
\]

The synthesis of hydrogen for electrochemical oxidation applications requires the use of catalytic reforming units that inevitably reduce between 20 and 30 % the fuel value, and increase the cost due to sophisticated and expensive and purification modules.

Fuel cells that operate at low temperature such as the PEMFC are poisoned by small amounts of CO and require extremely high purity hydrogen in order to operate. In contrast, high temperature fuel cells offer the possibility of running directly on carbon and hydrocarbons. Driven by the promise of higher energy efficiency and low cost, researchers have slowly started to investigate the direct electrochemical oxidation of carbon and hydrocarbons using high temperature fuel cells including molten carbonate (MCFCs) and solid oxide (SOFCs).
1.2.1 Direct electrochemical oxidation of hydrocarbons

The direct electrochemical oxidation of hydrocarbons has been investigated using solid oxide fuel cells (SOFCs). SOFCs consist of a solid electrolyte material made from an inorganic oxide that can conduct oxygen ions at temperatures between 600 and 1000 °C, in contact with an anode and cathode electrode. During the operation of a SOFC, the cathode electrode catalyze the reduction of oxygen by electrons resulting in the formation of oxygen ions (i.e., $O^{2-}$), which are then transported through the electrolyte layer to a fuel rich anode electrode where they can react, giving up electrons to an external circuit. Figure 1.2 presents a schematic representation of the operation of a solid oxide fuel cell.

![Figure 1.2 Schematic representation of a solid oxide fuel cell (SOFC).](image)
The elevated operation temperature of the SOFC imposes a number of requirements on the materials suitable for the electrolyte, the anode and cathode electrode, as well as interconnects and fuel cell housing. Research and development efforts made over the last two decades have resulted in the use of Yttria stabilized Zirconia (YSZ) electrolytes; Lanthanum doped Strontium Manganese (LSM) cathode electrodes, and a Nickel (Ni-YSZ) anode electrode due to their stability under operation conditions, high ionic/electronic conductivity, and matching thermal expansion coefficients.

SOFCs can operate on hydrocarbons by either internal reforming or direct utilization. During internal reforming, a mixture of hydrocarbon fuel and steam is introduced to the SOFC where it is catalytically converted to hydrogen and carbon monoxide, and then the hydrogen and carbon monoxide are electrochemically oxidized to water and carbon dioxide. During direct utilization, the hydrocarbon fuel is sent to the SOFC where it is electrochemically converted to carbon dioxide without the presence of significant amounts of water or oxygen. An important aspect of the operation of SOFCs with hydrocarbon fuels, regardless of the amount of steam present, is that the fuel cell is not deactivated by the deposition of carbon residues on the anode electrode. At the high operation temperature of the SOFC, hydrocarbons can react on the surface of the anode, and even in the housing material surrounding the cell. Hydrocarbons can also react in the gas phase via free radical cracking [7] forming tars that can deposit on the anode surface.

The use of state of the art Ni-YSZ anode electrocatalysts for the direct utilization of hydrocarbon fuels on the SOFC has been shown inconvenient since metallic Ni is a highly active catalysts for the formation of carbon fibers. The formation of carbon fibers
on the Ni anode catalysts involves the deposition of carbon at the Ni surface, dissolution of the carbon into the bulk of Ni, and the precipitation of carbon as a fiber, removing Ni particles embedded in the carbon deposit causing the mechanical failure of the SOFC. The limitation of the Ni-YSZ anode during the operation on hydrocarbon has inspired a number of investigations focusing on the development of alternative electrodes for the operation of hydrocarbon SOFCs.

Research studies have been directed towards the development of novel anode electrodes that can catalyze the electrochemical oxidation of carbon and hydrocarbons, as it is briefly summarized in chapter II. Despite the improvements achieved in recent years, the need for highly active, stable and low cost electrodes remains. Our experimental results have shown Cu-Ni alloys constitute highly active and stable electrodes for the electrochemical oxidation of hydrocarbons and carbon.

1.2.2 Electrochemical oxidation of carbon

The development of fuel cells that can carry out the direct electrochemical oxidation of carbon is supported on the prospects of: (i) higher energy efficiency, (ii) the use of low cost readily available fuel source, (iii) the generation of a nearly pure CO\textsubscript{2} byproduct stream ready for sequestration, and (iv) the reduction in the formation of undesired by products such as nitrous oxides. The improved energy conversion efficiency of carbon fuel cells lies on the favorable thermodynamics of the carbon/oxygen reaction, which have the advantage of a nearly zero entropy change, resulting in theoretical conversion efficiencies approaching 100\% [8].

\[ C + O_2 \rightarrow CO_2, \ \Delta S = 1.6 J/K \text{ mol at 873 K} \] (1.3)
Early attempts to convert carbon and hydrocarbons into electricity date to the nineteenth century. Becquerel and Jacques described the use of carbon rods immersed in molten $\text{K}_2\text{NO}_3$ and $\text{NaOH}$ electrolytes [9, 10]. Owing to undesirable side reactions, Baur and co-workers [11, 12] investigated the replacement of alkali electrolytes by molten salts. Decades later, in 1937, Baur and Preis[13] suggested that the condition for a chemically stable electrolyte can only be met by an ionically conducting solid electrolyte.

More recently researchers have attempted the direct conversion of carbon fuels to electricity using molten salt electrolytes (e.g., molten carbonates, and molten hydroxides)[8, 14]. Results from those studies have shown the electrochemical oxidation of carbon can proceed at temperature close to 800 $^\circ$C, generating current densities between 40 and 100 mW/cm$^2$. The main barriers encountered during their development efforts include the buildup of ash in the molten carbonate electrolyte, low anode reaction rates, and high cost of carbon electrode manufacture. The disadvantages found with molten electrolyte fuel cells were discussed by Baur, who suggested for the first time the use of solid electrolytes[13]. Unlike molten electrolyte fuel cells; Solid electrolyte cells are not affected by the build-up of ash, and can be easily and inexpensively fabricated according to conventional processing ceramic techniques such as tape casting and screen printing.

Despite the advantages of the solid electrolytes, the difficulty of ensuring appropriate contact between the carbon particles and the surface of the anode catalyst discouraged researchers from developing these type of fuel cells for many years. However, recent investigations conducted by Gür and Huggins[15], demonstrated the feasibility of direct electrochemical conversion of carbon to electrical energy using a two
compartment cell fabricated with an YSZ electrolyte. Their experimental apparatus consisted of a sealed quartz tube connected to a tubular YSZ membrane coated with Pt electrodes that allowed the independent control of the temperature of the electrolyte and the carbon fuel. Results from their study reported open circuit voltages close to theoretical values and current densities of 20 mA/cm$^2$ at 0.2 Volts. Although the cells fabricated by Gür and Huggins fail to achieve the performance needed for practical applications, their results are encouraging, and provide valuable insights on the potential for developing solid electrolyte fuel cells for conversion of carbon.

Advances in solid oxide fuel cell technology have allowed researchers at Stanford University to design a novel solid electrolyte fuel cell for the direct electrochemical oxidation of carbon. The fuel cell described in their publications follows the design introduced by Huggins, modified by the incorporation of screen printed LSM cathode electrodes and Ni-YSZ electrodes. Carbon is introduced in sealed compartment where CO$_2$ is introduced at high flow rates with the purpose of generating a fluidized environment. Inspection of the performance of the fuel cell revealed improvements on the rate of electrochemical oxidation of different types of carbonaceous materials (i.e., current densities of 50 mA/cm$^2$ at 0.2 V when operating on coal[16]), with respect to previous attempts. However, the operation temperature of the cells required to carry on the electrochemical oxidation remain relatively high (i.e., 900 °C). High operation temperatures facilitate the anodic formation of carbon monoxide, according to the equilibrium Boudouard reaction.

$$C + CO_2 \rightarrow CO$$ (1.4)
Formation of carbon monoxide in the anode compartment of the fuel cell reduces the overall efficiency of the electrochemical oxidation since the oxidation of carbon to CO$_2$ produces four electrons, whereas the electrochemical oxidation of carbon monoxide yields only 2 electrons. Details on the definition of the fuel cell efficiency can be found on Chapter II. Inspection of the current status of the electrochemical oxidation of carbon and hydrocarbons indicate the need of a breakthrough on the anode electrocatalyst in order to achieve a high energy efficient conversion of carbon to electricity. This study presents a novel approach to address the current limitations on the electrochemical oxidation of carbon.

1.3 Hypothesis, objective and scope

The hypothesis and objectives for the electrochemical oxidation of coke and methane and the photocatalytic oxidation of ethanol, which are the focus if this dissertation, are discussed in the following sections.

1.3.1 Electrochemical oxidation of carbon and hydrocarbons

Previous investigations have shown the feasibility of developing solid electrolyte fuel cells that can carry out the electrochemical oxidation of carbon and hydrocarbons. The current limitations observed on the electrochemical oxidation of hydrocarbon are related to the low catalytic activity of the anode electrode and its tendency to form carbon deposits leading to fuel cell deactivation. Similarly, the major difficulties found on the electrochemical oxidation of carbon on solid electrolyte fuel cells lie on the low activity
of the electrocatalyst, and the large ohmic resistance of the solid electrolyte, which impose higher operating at higher temperatures (>900 °C) resulting in low energy conversion efficiencies.

Methane Steam reforming reactions on Ni supported catalysts and its deactivation process due to formation of carbon deposits have been extensively investigated. Previous studies have shown the mechanism of coking on the Ni during reforming reactions proceeds through decomposition of CH₄ producing CHₓ species and molecular hydrogen. Molecular hydrogen species (H) combine at the surface producing H₂ while the CHₓ species further dissociates generating carbon deposits on the catalyst. Conventional methane steam reforming and electro catalytic oxidation of carbon containing fuels on the anode electrode of the fuel cell have similar reaction conditions and catalyst. Therefore the mechanism of coking during electro catalytic oxidation could be the same as in reforming reactions

The hypothesis proposed in this study include: (i) The Ni-YSZ catalyst can be modified for the electrochemical oxidation of hydrocarbons, (ii) The modified Ni-YSZ electrocatalyst could facilitate the operation of the fuel cell with carbon fuels such as coke derived from coal, resulting in higher energy efficiencies compared to conventional H₂ fuel cell, (iii) Approaches for avoiding coking on conventional CH₄ reforming reactions could be used to prevent coking on the hydrocarbon and carbon fuel cell. The scope of this research verified the hypothesis that Ni-YSZ anode electrocatalyst can be modified for carbon and hydrocarbon fuel cell. Ni-YSZ and bimetallic Cu/Ni-YSZ were fabricated and tested. Cu/Ni-YSZ bimetallic anode electro catalysts were be fabricated by introducing Cu nitrate species into Ni-YSZ electrocatalyst alloying under H₂ atmosphere
at 800°C. The hypothesis was verified by comparing the current-voltage performance of the fuel cell during electrochemical oxidation of H₂, CH₄ and coke at 800 °C. The deactivation of the anode electrocatalyst due to formation of carbon deposits was analyzed from the current-voltage performance of the fuel cell as well as from impedance spectroscopy analysis. The formation of carbon deposits on the anode electrocatalyst was studied by SEM, XRD and EDS. The efficiency of the fuel cell will was calculated by analyzing the composition of the gases at the outlet of the fuel cell using MS, GC and simultaneously measuring the current-voltage performance of the fuel cell. Figure 1.3 presents the diagram block of the experiments to verify the hypothesis.

1.3.2 Photocatalytic oxidation of ethanol

Elucidation of the reaction mechanism of photocatalytic oxidation on the surface of the TiO₂ catalyst would facilitate optimizing the activity and long term stability of photocatalysts. Previous studies have revealed the dynamic behavior of electron/hole pairs[6, 17, 18] The generation of electrons and holes has been shown to occur on the TiO₂ catalyst at a time scale of femtoseconds (1 x 10⁻¹⁵ sec), and the interfacial charge transfer from the TiO₂ surface to adsorbed species occurs in the time scale of nanoseconds. In contrast, the time scale for the electron recombination process can vary from 100 ps to days, depending on the surface state of the TiO₂ semiconductor [19-22].
Figure 1.3 Block diagram of the experiments to verify the proposed hypothesis.

IR spectroscopy is a technique that can be used to study the electron and hole recombination and trapping, revealing a structureless IR absorption band from 3000 to 900 cm⁻¹ associated with photogenerated electrons. Addition of O₂ onto the TiO₂ surface causes a decay of the IR structureless absorbance with a half-life (i.e., the time required for the intensity of an IR band to drop to 50% of its initial value) of about 100 s at -133 °C [22]. Similar half-life times have evidenced for IR bands corresponding to intermediate species observed during the photocatalytic oxidation of alcohols and acetone on the TiO₂ surface [23-26]. The long half-lives of photogenerated electrons and
photocatalytic oxidation intermediates on the TiO$_2$ surface would allow the use of IR spectroscopy to simultaneously measure the changes in IR spectra of photogenerated electrons and adsorbed species, facilitating the elucidation of the reaction pathways.

The hypothesis proposed in this study is that the content of water on the surface of the TiO$_2$ photocatalyst reduces the rate of photocatalytic oxidation of ethanol. The use of an in situ infrared technique will allow the simultaneous monitoring of disappearance of reactants, formation of intermediate species, and generation of photogenerated electrons. The scope of this study will focus on the effect of water on the photocatalytic oxidation of ethanol on TiO$_2$ catalyst. Ethanol was selected as a model compound.

1.4 Outline

The structure of this dissertation is outlined in the following section. Chapter I provide a brief introduction to the electrochemical and photocatalytic oxidation of carbon and hydrocarbons, and present the hypothesis, objectives and scope of this work. Chapter II contains limited background information on the definitions of the fuel cell efficiency, current status of electrochemical oxidation of carbon and hydrocarbons, and photocatalytic oxidation. Chapter III presents the experimental apparatus and techniques used during the studies. Chapter IV presents a study of the effect of H$_2$O during photocatalytic oxidation of ethanol on TiO$_2$. Chapter V presents a study of the effect of methanol sacrificial reagents during the photocatalytic evolution of H$_2$ over a TiO$_2$ based catalyst. Chapter VI presents a study of the evaluation of the fuel cell energy efficiency during the electrochemical oxidation of coke on a Ni-YSZ anode solid oxide fuel cell. Chapter VII presents a study of the evaluation of the fuel cell energy efficiency during
the electrochemical oxidation of coke on a Cu/ Ni-YSZ anode solid oxide fuel cell.

Chapter VIII presents a study of the promoting effect of Ceria on the electrochemical oxidation of carbon. Chapter IX presents conclusions and future work.

Figure 1.4 Block diagram of the outline of this research work.
CHAPTER II
BACKGROUND

2.1 Fuel cell efficiency

The efficiency of a fuel cell can be defined in a number of ways by considering the different aspects affecting the conversion of the chemical energy into electricity. The most used definitions of fuel cell efficiency include the thermodynamic efficiency $\xi_T$, the electrochemical efficiency $\xi_v$, the Faradaic efficiency $\xi_F$, and the effective efficiency $\xi_{\text{eff}}$. The following section presents a brief discussion on the definitions of the fuel cell efficiency.

2.1.1 Thermodynamic efficiency $\xi_T$

The thermodynamic efficiency $\xi_T$ can be derived by considering the first and second law of thermodynamics. The fuel cell can be described, to a first approximation, by defining the operation of an ideal reversible cell in which the fuel and the air enter their respective compartments as non-mixed flows, the electrochemical reaction proceeds in a reversible manner at temperature T and pressure P, and the flue gas leaving the cell is
evacuated as a non-mixed flow. The energy associated with the reactants can be accounted for by the non-mixed reactants total enthalpy $\Sigma n_i H_i$ delivered to the reversible fuel cell, while the stream leaving the cell contributes the enthalpy term $\Sigma n_j H_j$. The cell can reversibly exchange heat $Q_{FC\text{rev}}$ with the surrounding environment, being a positive number if heat is transported to the fuel cell and negative number if the heat is transported from the cell to the environment. Additionally, reversible work $-W_{FC\text{rev}}$ can be delivered by the fuel cell. Figure 2.1 presents a schematic representation of the ideal reversible fuel cell.

![Schematic representation of a reversible fuel cell](image)

**Figure 2.1** Schematic representation of an ideal reversible SOFC operating at temperature $T$ and pressure $P$. The dotted line represents the boundaries between the ideal reversible fuel cell and the surrounding environment.

Applying the first law of thermodynamics to the system composed of the ideal reversible fuel cell exchanging heat and work with the surroundings we obtain:

$$Q_{FC\text{rev}} + W_{FC\text{rev}} = \sum_j n_j H_j - \sum_i n_i H_i = \Delta H_R \quad (2.1)$$
Considering the process to be ideal, the second law of thermodynamics gives

$$\int dS = 0 \quad (2.2)$$

The overall reaction taking place between the fuel and air (i.e. electrochemical oxidation) involves an entropy of reaction term \(\Delta S_R\), which must be compensated by the reversible exchange of heat to the environment \(Q_{FC\ rev}\) so that the net entropy change of the process is zero, as expressed by equation (2.2). Therefore the second law of thermodynamics may be rearranged as

$$\Delta S_R - \frac{Q_{FC\ rev}}{T} \quad (2.3)$$

Using equations (2.1) and (2.3) it is possible now to express the reversible work produced by the SOFC as

$$W_{FC\ rev} = \Delta H_R - T\Delta S_R \quad (2.4)$$

This equation shows the reversible work done by the fuel cell equals the Gibbs free energy of reaction \(\Delta G_R\)

$$W_{FC\ rev} = \Delta H_R - T \cdot \Delta S_R = \Delta G_R \quad (2.5)$$

This result shows that the maximum work that can be done by the fuel cell equals the Gibbs free energy of reaction \(\Delta G_R\). In this way, it is possible to define the thermodynamic efficiency of the fuel cell \(\xi_T\) as the ratio of the reversible work \(W_{FC\ rev}\), the and the enthalpy of reaction \(\Delta H_R\)

$$\xi_T = \left. \frac{W_{FC\ rev}}{\Delta H_R} \right| = \frac{\Delta G_R}{\Delta H_R} = \frac{\Delta H_R - T \cdot \Delta S_R}{\Delta H_R} \quad (2.6)$$

The thermodynamic efficiency \(\xi_T\) has been reported in the general literature for number of fuel cells, and selected examples are reproduced in table 2.1 for comparison purposes.
The thermodynamic efficiency described in the previous section considers an ideal fuel cell in which reactants and products resulted from the electrochemical reaction do not mix in the anode compartment. Unlike ideal reversible fuel cells, real systems generate reaction products (i.e., H₂O and CO₂) that inevitably mix with unreacted fuel in an irreversible process that generates entropy. Thus, the operation of the ideal fuel cell could only be possible as the limiting process when the fuel utilized tends to zero.

Table 2.1 Thermodynamic efficiencies for selected fuel cell examples under standard conditions at 25 °C.

<table>
<thead>
<tr>
<th>Fuel cell</th>
<th>Reaction</th>
<th>-ΔH° (kJ/mol)</th>
<th>-ΔG° (kJ/mol)</th>
<th>ξ_T (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>H₂ + 1/2O₂ → H₂O(ℓ)</td>
<td>286.0</td>
<td>237.3</td>
<td>83.0</td>
</tr>
<tr>
<td>CO</td>
<td>CO + 1/2O₂ → CO₂</td>
<td>283.1</td>
<td>257.2</td>
<td>90.9</td>
</tr>
<tr>
<td>Formic acid</td>
<td>HCOOH + 1/2O₂ → CO₂ + H₂O(ℓ)</td>
<td>270.3</td>
<td>285.5</td>
<td>105.6</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>CH₂O(ℓ) + O₂ → CO₂ + H₂O(ℓ)</td>
<td>561.3</td>
<td>522</td>
<td>93.0</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH + 3/2O₂ → CO₂ + 2H₂O(ℓ)</td>
<td>726.6</td>
<td>702.5</td>
<td>96.7</td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄ + 2O₂ → CO₂ + H₂O(ℓ)</td>
<td>890.8</td>
<td>818.4</td>
<td>91.9</td>
</tr>
<tr>
<td>Carbon</td>
<td>C + O₂ → CO₂</td>
<td>393.5</td>
<td>394.3</td>
<td>100.3</td>
</tr>
</tbody>
</table>

The mixing effects resulting from the evolution of products in the anode compartment of the fuel cell can be taken into account by considering the Gibbs free energy of reaction and the individual steps occurring inside the fuel cell. The individual steps occurring inside the fuel cell are presented in figure 2.2 for a solid oxide fuel cell operating in H₂.
It is important to note that the oxidation of hydrogen, irrespective of the process by which is being carried out, proceeds according to

\[ H_2 + \frac{1}{2} O_2 \rightarrow H_2O \]  

(2.7)

During the operation of the fuel cell hydrogen molecules are exposed to the anode electrocatalyst, adsorbing at the surface, forming hydrogen ions and releasing electrons to the external load where the electrical work is being used.

\[ H_2 \rightarrow 2H^+ + 2e^- \]  

(2.8)

Oxygen molecules present in air are simultaneously exposed to the cathode electrocatalyst, where they react with electrons drawn from the external load resulting in the formation of oxygen ions.

\[ \frac{1}{2}O_2 + 2e^- \rightarrow O^2^- \]  

(2.9)
The oxygen ions diffuse through the electrolyte to the anode, reacting with hydrogen and producing water.

\[ 2H^+ + O^{2-} \rightarrow H_2O \quad (2.10) \]

The dissociation of hydrogen at the anode, presented in equation 8, shows that the molar flow of electrons \( n \) in step 1 is two times the molar flow of the spent fuel \( N_{H_2} \).

\[ n = 2N_{H_2} \quad (2.11) \]

The electric current \( I \) produced on the SOFC depends linearly on the molar flow of electrons \( n \), and thus on the molar flow of the spend fuel.

\[ I = n \times (-e) \times N_A = -n \times F = -2N_{H_2} \times F \quad (2.12) \]

where \( e \), \( N_A \), and \( F \) represent the electron elementary charge, Avogadro’s number, and Faraday constant, respectively.

\[ e = 1.6021 \times 10^{-19} \, C \]

\[ N_A = 6.022 \times 10^{23} \]

\[ F = e \cdot N_A = 96485 \, C/mol \]

The matching of the thermodynamic and electrical quantities on the solid oxide fuel cell can be expressed by considering the power produced. The power can be defined as the rate at which reversible work is done by the cell as fuel is utilized. In the case of H\(_2\) we obtain

\[ P_{FC \, rev} = N_{H_2} \times W_{FC \, rev} \quad (2.13) \]

The power produced by the cell can also be expressed as the product of the current \( I \) and reversible voltage \( V_{FC \, rev} \).

\[ P_{FC \, rev} = V_{FC \, rev} \cdot I = N_{H_2} \cdot W_{FC \, rev} \quad (2.14) \]
Taking into consideration equation (2.5), the previous expression can be modified as

\[ V_{FC\ rev} \cdot I = N_{H_2} \cdot \Delta G_R \]  (2.15)

Equation (2.16) can be further rearranged using equation (2.12) in order to obtain the reversible voltage

\[ V_{FC\ rev} = \frac{-N_{H_2} \Delta G_R}{nF} \]  (2.16)

The mixing effects and their impact on the fuel cell voltage can be calculated by considering the change in partial pressure of species involved in the electrochemical oxidation. Expressing the Gibbs free energy of reaction in terms of the enthalpy of reaction and the entropy of reaction

\[ \Delta G_R(T, P) = \Delta H_R(T, P) - T \cdot \Delta S_R(T, P) \]  (2.17)

Assuming ideal behavior of gases with the purpose of simplifying the dependence on Temperature and pressure

\[ \Delta G_R(T, P) = \Delta H_R(T) - T \cdot \Delta S_R(T, P) \]  (2.18)

writing the entropy \( S_j \) of each component \( j \) using the thermodynamic relationship

\[ dS = \frac{(dH - \nu dP)}{T} \]  (2.19)

It is obtained

\[ S_j = S_j^\circ + \int_{T_0}^{T} \frac{C_{pj}}{T} dT - R \cdot \ln \left[ \frac{p_j}{p_0} \right] \]  (2.20)

where \( S_j^\circ \) represents the entropy of component \( j \) at the reference thermodynamic state, \( C_{pj} \) is the heat capacity of component \( j \), \( R \) is the universal gas constant, \( p_j \) is the partial pressure of component \( j \) and \( p_0 \) is the reference partial pressure, usually set as \( p_0=1 \) atm. Applying this expression to the entropy of reaction we obtain

\[ \Delta S_R(T, P) = \Delta S_R(T) - R\ln(K) \]  (2.21)
Where $K$ represents the reaction equilibrium constant.

$$K = \Pi_j \left[ \frac{P_j}{P_0} \right]^{\nu_j} \quad (2.22)$$

Introducing these equations for the enthalpy and entropy of reactions, the Gibbs free energy of reaction can be expressed as

$$\Delta G_R(T, P) = \Delta H_R(T) - T \cdot \Delta S_R(T) + T \cdot R \ln(K) \quad (2.23)$$

These ideal gas approximations allow writing the Nernst potential or the Nernst voltage $V_N$ as

$$V_N = -\frac{\Delta G_R(T)}{nF} - \frac{RT \ln(K)}{nF} \quad (2.24)$$

It is important to note that under no-current conditions the observed voltage of a fuel cell can be lower than the reversible Nernst potential $V_N$, indicating the presence of other parasitic processes.

2.1.2 Electrochemical efficiency $\xi_v$

The operation of a fuel cell under current flow conditions causes a deviation of the voltage from the open circuit voltage, resulting in cell overpotentials $\eta$.

Overpotentials can be associated to irreversible losses due to mass transport limitations and half reaction activation barriers occurring at the anode and cathode electrodes. In addition to cell overpotentials, the fuel cell is subject to further losses due to the ohmic resistances $R$ of the electrolyte, the electrodes, the interfaces between the electrodes and the electrolyte layer, and the interfaces between the electrodes and the current collectors. In general, the voltage observed when operating the fuel cell at a
specific current density $I$ can be expressed considering the electrode overpotentials and the ohmic resistances, as shown in equation (2.26).

$$V_{cell} = V_N - [\eta_a(I) + \eta_c(I) + R(I)] \quad (2.25)$$

The lowering of the useful voltage due to overpotentials and ohmic resistance of the cell can be accounted by defining the electrochemical efficiency $\xi_v$.

$$\xi_v = \frac{V_{cell}}{V_N} = 1 - \frac{[\eta_a(I)+\eta_c(I)+R(I)]}{V_N} \quad (2.26)$$

### 2.1.3 Faradaic efficiency $\xi_F$

The operation of the fuel cell under current flow conditions can be subject to parallel reactions occurring at the anode and cathode electrodes, limiting the electrical current from the maximum theoretically possible. Faradic efficiency is defined as the ratio of the electric current experimentally observed $I_{exp}$, and the maximum possible current $I_{max}$. Equation (2.28) presents the Faradaic efficiency $\xi_F$.

$$\xi_F = \frac{I_{exp}}{I_{max}} \quad (2.27)$$

### 2.1.4 Effective efficiency $\xi_{eff}$

The effective efficiency takes into account the loss of fuel utilized during the operation of the fuel cell. The effective efficiency or fuel utilization $\xi_{eff}$ is defined as the ratio of the fuel spent during the operation of the cell and the fuel supplied at the inlet.

$$\xi_{eff} = \frac{N_{F_0}-N_F}{N_{F_0}} \quad (2.28)$$
Where \( N_{F0} \) represents the fuel molar flow at the inlet of the SOFC, and \( N_F \) is the molar flow rate at the outlet of the anode compartment. A similar definition can be made using mass flow rates. The net efficiency of the fuel cell can be expressed considering the different efficiencies described in the previous sections, resulting in

\[
\xi = \xi_T \times \xi_V \times \xi_F \times \xi_{eff} \quad (2.29)
\]

2.2 Electrolyte for the carbon and hydrocarbon fuel cell

Park et al, have reported the use a copper–ceria composite anode electrode[27, 28] during the electrochemical oxidation of methane. Due to the low melting point of metallic copper and copper oxides, the fabrication of the anode electrode required the introduction of the metals into a Zirconium skeleton sintered to a dense YSZ electrolyte layer. Alternatively, electronic conducting ceramic materials (i.e., Perovskites) have been proposed as candidates for direct oxidation anodes. Perovskites responding to the general formula \( \text{ABO}_3 \), where A and B are two metals with total valence of 6, form a variety of solid solutions exhibiting different properties by partial substitution of either the A or B sites. Perovskites based on chromites have already been established as interconnect materials in SOFC technology due to their high electronic conductivity and stability within a broad range of oxygen partial pressures. Unfortunately, their electrocatalytic activity have proved to be low[29]. Primdahl et al[30] incorporated 3% vanadium on the chromium site of a lanthanum-strontium perovskite with the purpose of improving the anode electronic conductivity and activity, however, their experiments revealed the formation of secondary phases reactive towards YSZ forming insulating
SrZrO$_3$ layers. Recent studies have begun to explore the use of Ni alloys as active anode electrodes for the utilization of hydrocarbon fuels. Linic et al[31, 32] have studied the hydrocarbon steam reforming reactions on supported Sn/Ni alloys at experimental conditions that are consistent with typical SOFC operation. Results indicate the supported Sn/Ni alloys are more resistant to deactivation due to carbon deposition than supported monometallic Ni catalyst during the steam reforming of iso-octane at moderate steam to carbon ratios.
CHAPTER III
EXPERIMENTAL

3.1 Fuel cell fabrication

The following section contains a description of the experimental methods used for the fabrication and testing of the fuel cells in this study. The fuel cells contained 5 distinctive layers including: (i) a cathode conductive LSM layer, (ii) a cathode LSM-YSZ interlayer (50 wt % YSZ), (iii) an electrolyte (YSZ) layer, (iv) an anode (NiO-YSZ) interlayer (63 wt % NiO), and (v) an anode NiO-YSZ support layer (65 wt % NiO). The fabrication of the fuel cell involved the preparation of the above layers using ceramic engineering techniques such as tape casting, lamination, calcination, and screen printing. Tape casting was used for the preparation of an anode NiO-YSZ support tape, an anode NiO-YSZ interlayer tape, and an electrolyte YSZ tape. Lamination was used to integrate the above tapes into a planar multilayer structure. Two calcination cycles were used to remove organic species from the tapes, and densify the fuel cell. Screen printing was used for adhering the cathode LSM-YSZ interlayer and the cathode conductive LSM layer. The following sections describe the detailed sequence used for the fabrication of the fuel cells.
3.1.1 Tape casting of NiO-YSZ support

The Ni-YSZ support layer was made by mixing NiO (AEE Atlantic Equipment Engineers, Bergenfield, NJ), and YSZ (TZ-8Y Tosoh) powders with a carbon pore former (Avicel microcrystalline cellulose ph 301). The resulting powders were dispersed and ball milled for 24 h in a solution of polyester-polyamine copolymer (hypermer KD1, Uniqema) in absolute ethanol (Pharmco Aaper), acetone (Fisher Scientific), and n-amyl acetate (Alfa Aesar). The NiO-YSZ dispersion was further modified by adding a polyvinyl Butyral binder (B-76) and a benzyl n-butyl phthalate (S-160, 98% Alfa Aesar) plasticizer, generating a viscous slip. The slip was ball milled for 20 h, de-aired, casted on a silicon coated Mylar substrate using a 6 inch doctor blade (casting thickness = 3 mm), and allowed to dry at room temperature for 2 days. Table 3.1 presents a typical formulation of the anode supported slip.

Table 3.1 Composition of the anode support slip on the basis of 100 g NiO.

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (g)</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>100</td>
<td>35.4</td>
</tr>
<tr>
<td>YSZ</td>
<td>53.8</td>
<td>19</td>
</tr>
<tr>
<td>KD1</td>
<td>3.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Ethanol</td>
<td>40.9</td>
<td>14.5</td>
</tr>
<tr>
<td>Acetone</td>
<td>24.2</td>
<td>8.6</td>
</tr>
<tr>
<td>Amyl acetate</td>
<td>18.4</td>
<td>6.5</td>
</tr>
<tr>
<td>Ph301</td>
<td>16.9</td>
<td>6</td>
</tr>
<tr>
<td>B-76</td>
<td>13</td>
<td>4.6</td>
</tr>
<tr>
<td>S-160</td>
<td>11.6</td>
<td>4.1</td>
</tr>
</tbody>
</table>
3.1.2 Tape casting of Ni-YSZ interlayer

The Ni-YSZ anode interlayer was fabricated by mixing NiO and YSZ (50 % NiO). The particle size of the powders was decreased in a planetary ball mill, dispersing them in a solution polyester-polyamine copolymer (hypermer KD1, Uniquema) in isopropanol, and milling in a planetary ball mill (PM100 Restch GmbH) for 2 h at 400 rpm. The resulting dispersion was dried at 100 ºC to removing the solvent. The dried powders were (i) sieved with a 150 mesh, (ii) re-dispersed in a mixture of ethanol, methyl ethyl ketone (MEK), and hypermer KD1, and (iii) ball milled for 20 h. A mixture containing ethanol, MEK, benzyl n-butyl phthalate (S-160), polyalkylene glycol (PEG) and a polyvinyl Butyral binder (B-76) binder was prepared in a separate container and was incorporated to the dispersion containing the powders in order to generate a viscous slip. The resulting slip was ball milled for 20 hr, casted on Mylar substrates with a 6” doctor blade (casting thickness = 150 µm), and was allowed to dry for 1 day. Table 3.2 presents a typical formulation of the NiO-YSZ anode interlayer slip.

3.1.3 Tape casting of YSZ electrolyte layer

The thin electrolyte layer was fabricated according to the approach described in section 3.1.2, using polyethylene glycol (PEG-200, average molecular weight 200, Sigma Aldrich) plasticizer and hypermer KD1 polymeric dispersant. The resulting slip was ball milled for 20 h, casted on Mylar substrates with a 6” doctor blade (casting position= 115 µm), and allowed to dry for 1 day.
Table 3.2 Composition of the anode interlayer slip on the basis of 100 g NiO.

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (g)</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>100</td>
<td>29.5</td>
</tr>
<tr>
<td>YSZ</td>
<td>59</td>
<td>17.4</td>
</tr>
<tr>
<td>KD1</td>
<td>4.8</td>
<td>1.4</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>63.6</td>
<td>18.8</td>
</tr>
<tr>
<td>EtOH</td>
<td>35</td>
<td>10.3</td>
</tr>
<tr>
<td>MEK</td>
<td>52.3</td>
<td>15.4</td>
</tr>
<tr>
<td>S-160</td>
<td>4.9</td>
<td>1.4</td>
</tr>
<tr>
<td>PEG</td>
<td>7.3</td>
<td>2.2</td>
</tr>
<tr>
<td>B-76</td>
<td>12.2</td>
<td>3.6</td>
</tr>
</tbody>
</table>

3.1.4 Fuel cell lamination

The NiO-YSZ (70 wt % Ni) support layer and the NiO-YSZ (50 wt% Ni) anode interlayer were sprayed with a solution containing ethanol and turpineol (30 wt % ethanol) and were subsequently laminated using a bench top manual press (Carver 4128) operating at a temperature of 160 F. The resulting laminated was sprayed a second time and a thin YSZ electrolyte layer was laminated using the procedure described above. The resulting laminates were allowed to cool down to room temperature and were either punched with a 1 hole round arch punch, or cut with a laser cutter in order to generate 1.5” diameter green tape fuel cells.
3.1.5 Fuel cell calcination

The fuel cell discs obtained after hole-punching of the laminates were fired in a two stage process. In the first stage the discs were heated to 450 °C at a heating rate of 0.1 °C /min, and were kept at 450 °C for 4 h in order to remove the organic components. The resulting discs were heated to 1000 °C at a heating rate of 1 C/min, kept at 1000 °C for 4 h, and cooled to room temperature at a heating rate of 2 °C /min. In the second stage, the discs were heated to 1400 °C at a heating rate of 2 °C /min, and were kept at 1400 °C for 4 h in order to achieve disc densification.

3.1.6 Fuel cell screen printing

The LSM-YSZ (50 wt % LSM) cathode interlayer and the pure LSM cathode conductive layer were incorporated to the densified solid oxide fuel cell discs by the screen printing technique. The LSM-YSZ cathode interlayer was attached with the aid of a manual screen printing device by passing a 50 wt% LSM-YSZ paste (Heraeous CL 86-8706A) on the thin YSZ side of the discs, and firing the resulting layer at 1200 °C at a heating rate of 1.5 °C/min. Upon firing of the LSM-YSZ layer, the LSM cathode conductive layer was attached to the fuel cell by printing a pure LSM paste (Heraeous CL86-8706) on top of the LSM-YSZ cathode interlayer and firing the discs at 1100 °C following the same heating profiled used for the LSM-YSZ cathode interlayer.
3.2 Fuel cell testing apparatus

The experimental apparatus used for studying the electrochemical oxidation of carbon and hydrocarbons consisted of (i) a gas manifold, (ii) a high temperature furnace, and a (iii) a steel fuel cell reactor. Figure 3.1 presents a schematic representation of the fuel cell reactor for the electrochemical oxidation of carbon.

Figure 3.1 Fuel cell reactor for the electrochemical oxidation of carbon.
The gas manifold system consisted of Brooks mass flow controllers for regulating the flow rates of gases (i.e., He, H₂, CH₄). The gaseous reactants were fed to the fuel cell placed inside the high temperature furnace. The electrochemical oxidation of carbon was carried out by feeding solid samples using a feeding mechanism placed at the inlet of the fuel cell reactor. The performance of the fuel cell and impedance spectrum was recorded by a Solartron cell test system. The composition of gaseous products at the outlet of the fuel cell was quantified by a mass spectrometer (MS, Pfeiffer OmnistarTM) and a gas chromatograph (SRI 8610C) equipped with a Helium Ionization Detector (HID).

3.3 Experimental set up for photocatalytic oxidation studies

The following section presents a description of the experimental methods and techniques used during the photocatalytic oxidation studies. The experimental apparatus for the in situ IR studies consists of a Diffuse Reflectance Infrared Fourier Transform (DRIFT) cell (Harrick scientific HVC-DRP), a 350 W mercury lamp (Oriel 6286) with a light condenser (Oriel 77800), and a gas manifold for admission of O₂ and ethanol vapor into the DRIFT cell. Figure 5 presents a schematic representation of the experimental apparatus. Following the loading of the catalyst, the sample holder was enclosed by a stainless steel dome with two IR transparent ZnSe windows and a third CaF₂ window for UV illumination. Ethanol was introduced to the DRIFT cell by flowing a 15 cm³/min O₂ stream (Praxair, 99.999%) saturated with ethanol (10.3 % mol ethanol on O₂) for 10 min at a constant temperature of 298 K.
Figure 3.2 Experimental apparatus for the photocatalytic oxidation studies.

The ethanol photocatalytic oxidation reactions were carried out on the surface of the catalysts by operating the DRIFT cell in batch mode at 303 K and 1 atm for 120 minutes. The IR spectra were collected in the diffuse reflectance mode by a single beam FTIR spectrometer (DigiLab FTS 4000) with 20 co-added scan at a resolution of 4 cm\(^{-1}\). Three different types of single beam IR diffuse reflectance intensities (i.e., single beam IR spectra) were recorded during the experiments. First, the single beam IR spectrum of the catalyst was collected prior to exposure to ethanol and subsequent photocatalytic reactions (i.e., catalyst surface free from adsorbates). Second, the single beam IR spectra of the catalyst and adsorbed ethanol were recorded during exposure to flowing O\(_2\)/ethanol stream. Third, the single beam IR spectra of the catalyst, adsorbed ethanol, and oxidation
intermediate species were collected during UV illumination. The accurate representation of the concentration of adsorbed species on the surface of the catalyst was carried out using the absorbance intensity function, noted as “absorbance” by analogy with the absorbance = log (1/T) measured in transmission IR.
CHAPTER IV

INFRARED STUDY OF ETHANOL PHOTOCATALYTIC OXIDATION PATHWAY ON HIGH AND LOW H₂O CONTENT TiO₂

4.1 Abstract

This chapter contains the results of an in situ IR spectroscopy study of the effect of H₂O on the photocatalytic oxidation (PCO) of ethanol over a semiconductor TiO₂ catalyst. Ethanol was found to adsorb on high water H₂O content TiO₂ (1604 µmol H₂O/g catalyst) as molecularly adsorbed ethanol (CH₃CH₂OHₐd), which exhibit a lower initial C-H scission and CO₂ formation rate than ethoxy (CH₃CH₂Oₐd) produced from ethanol adsorbed low H₂O content TiO₂ (804 µmol H₂O/g catalyst) during PCO. The variation of the IR intensity of species showed CH₃CH₂OHₐd photooxidation produces formic acid (HCOOHₐd) and formate (HCOO⁻ₐd) species, whereas CH₃CH₂Oₐd reaction proceeds via formation of acetaldehyde (CH₃CHOₐd) and acetate (CH₃COO⁻ₐd). CH₃CHOₐd was found to react on TiO₂ via hydrogen abstraction of the α-Carbon producing CH₃COO⁻ₐd which can be further oxidized to HCOO⁻ₐd and CO₂. The photooxidation activity of CH₃CHOₐd on TiO₂ was found to decrease significantly in the presence of high contents of H₂O, suggesting that removal of H₂O from the surface
would increase the conversion of acetaldehyde, and thus, increase the overall rate of ethanol complete photooxidation. A reaction pathway consistent with the rates of formation and disappearance of IR observable intermediate is proposed for the photocatalytic oxidation of ethanol.

4.2 Introduction

TiO$_2$ is an active catalyst for the photocatalytic oxidation of organic pollutants present in air and wastewater. Photocatalytic oxidation reactions on TiO$_2$ are initiated by the generation of charge carriers (i.e., electron-hole pairs) upon absorption of light of appropriate wavelength, and their subsequent charge transfer reactions to species adsorbed on the surface of the catalyst [6, 17, 33, 34].

Research studies have shown H$_2$O can have either a promoting or an inhibiting effect during photocatalytic oxidation reactions of organic compounds on TiO$_2$ [35-37]. As a promoter, H$_2$O is believed to facilitate the formation of hydroxyl radicals (·OH), a highly active oxidizing species that participates in the photooxidation. The mechanisms reported in the literature for the formation of ·OH include the reaction of holes and adsorbed hydroxyl ions (OH$^-$), and the reaction of H$_2$O with oxygen ions (O$_2^-$) resulted from electron charge transfer reaction to adsorbed O$_2$. Water can also have an inhibiting effect due to its strong binding ability to TiO$_2$ surfaces compared with many organic compounds. TiO$_2$ binds water strongly, particularly in the dissociated form, and can displace those organic species bound to the catalyst surface by weak interactions (i.e., alkanes, alkenes and aromatics). Other species, such as carboxylic acids and alcohols,
have functional groups that form intense electrostatic interactions with surface cation sites, and tend to bind as strongly or more strongly to the TiO₂ surface compared to water.

The interactions between coadsorbed water and organic compounds will result in displacement of weakly bound species from the catalyst surface. Figure 4.1 presents a schematic representation of the opposing effects of H₂O during the photocatalytic oxidation of ethanol on TiO₂. The opposing effects of water during photocatalytic oxidation of organic compounds pose a barrier to understanding the overall rates and the mechanisms of photocatalytic oxidation, which in turn, could assist on the development of highly active catalysts. The objective of this study is to determine the effect of water on the photocatalytic oxidation of ethanol on TiO₂.

![Figure 4.1 Schematic representation of (a) the promoting and (b) inhibiting effect of H₂O during photocatalytic oxidation (PCO) reactions on TiO₂ catalysts.](image)

Figure 4.1 Schematic representation of (a) the promoting and (b) inhibiting effect of H₂O during photocatalytic oxidation (PCO) reactions on TiO₂ catalysts.
4.3 Experimental

TiO₂ powders (Degussa P25) were treated to increase the content of H₂O by: (i) dispersing 100 mg of TiO₂ in 30 mL of deionized water with an ultrasonicator, (ii) drying the resulting suspension in a vacuum oven for 20 hr at 333 K until obtaining a coarse powder, and (iii) grinding and sieving of the coarse powder. The water-treated and the as-received catalysts are designated as H₂O/TiO₂ and TiO₂, respectively. The content of H₂O on the catalysts was quantified using a thermogravimetric analyzer (TA instruments TGA 2950).

The apparatus for the in situ IR studies has been described in the Chapter III. Briefly, the experimental apparatus is composed of a Diffuse Reflectance Infrared Fourier Transform (DRIFT) cell (Harrick scientific HVC-DRP), a 350 W mercury lamp (Oriel 6286) with a light condenser (Oriel 77800), and a gas manifold for admission of gases. During each experiment, a thin 8-mg layer of the catalysts was placed on top of 80 mg of inert CaF₂ powder (325 mesh, Alfa Aesar) in the DRIFT cell’s sample holder. The use of a thin catalyst layer was adopted in consideration of the depth of optical penetration of the UV light into porous scattering TiO₂ powders, with the purpose of minimizing diffuse reflectance IR spectra showing bonds corresponding to dark fractions of the catalyst (i.e., not illuminated by UV light) [38, 39].

Ethanol vapors were introduced into the DRIFT cell by flowing a 15 cm³/min oxygen stream saturated with ethanol (i.e., flowing a dry O₂ stream into a glass-made liquid saturator containing 200 proof ethanol that produces a saturated stream containing 10.3 % mol ethanol). The amount of ethanol adsorbed on the catalyst was adjusted by changing the duration of the O₂/ethanol flow. The photocatalytic oxidation reactions
were initiated by UV illumination on the catalysts (25 mW/cm$^2$) while operating the DRIFT cell in batch mode at 303 K and 1 atm. The IR data were reported in three different types of single beam IR diffuse reflectance intensities of the catalysts: (i) prior to exposure to ethanol and UV light (i.e., catalyst surface free from adsorbates); (ii) after exposure to ethanol, and (iii) during UV illumination. The amount of CO$_2$ produced during the photocatalytic oxidation of ethanol was analyzed with a gas chromatographer (GC, SRI 8610C) equipped with a thermal conductivity detector (TCD).

4.4 Results and Discussion

Figure 4.2 presents the single beam IR spectra of the H$_2$O/TiO$_2$ and TiO$_2$ catalysts recorded prior to and during exposure to ethanol and UV illumination. The spectrum of the H$_2$O/TiO$_2$ catalyst displays a more broad and intense hydrogen bonding H$_2$O band at 2600 – 3700 cm$^{-1}$ than the TiO$_2$ catalyst. The intensity of the H$_2$O bands on the H$_2$O/TiO$_2$ and the TiO$_2$ catalysts corresponded to 840 and 1604 µmol of water per gram of catalysts, respectively. Exposure of the catalysts to ethanol before UV illumination (i.e., spectra at 0 min) produced the C-H stretching bands of adsorbed ethanol at 2870, 2931, and 2971 cm$^{-1}$ as well as a number of subtle bands in the 1100 – 1650 cm$^{-1}$ region. The intensity of these bands and their subsequent changes resulted from UV exposure can be clearly discerned in the IR absorbance spectra of figure 4.3, obtained by using the catalyst spectrum as background. The absorbance spectra magnify the intensity of each band by taking logarithmic ratio of single beam spectra. The positive (i.e, concave shape) and negative (i.e., convex shape) bands of the absorbance spectra indicate the formation and disappearance of species, respectively, on the surface of the catalysts.
Figure 4.2 IR single beam spectra collected before exposure to ethanol and during 120 min of photocatalytic oxidation of ethanol on (a) the H$_2$O/TiO$_2$ and (b) the TiO$_2$ catalysts.

The IR absorbance spectra at 0 min in figure 4.3 shows the positive bands for adsorbed ethanol and their band assignments [40-44] as well as the negative bands for isolated OH at 3692 and 3632 cm$^{-1}$, and a H$_2$O$_{ad}$ band at 3550 cm$^{-1}$.

Considering that the IR absorbance intensities are proportional to the amount of species present, the intensive negative H$_2$O$_{ad}$ band on the TiO$_2$ catalysts compared to that
of the H₂O/TiO₂ catalyst indicate that the former experienced displacement of larger amounts of water. The amount of ethanol adsorbed on the H₂O/TiO₂ and TiO₂ catalysts was determined to be 509 and 718 µmol per gram of catalysts according to the carbon balance between ethanol and the CO₂ product, with their IR intensities, and extinction coefficients.

Figure 4.3 IR absorbance spectra collected during 120 min of photocatalytic oxidation of ethanol on (a) the H₂O/TiO₂ and (b) the TiO₂ catalysts.

Figure 4.3 IR absorbance spectra collected during 120 min of photocatalytic oxidation of ethanol on (a) the H₂O/TiO₂ and (b) the TiO₂ catalysts.
Examination of figure 4.3 (b) revealed that adsorbed ethanol on TiO\textsubscript{2} give a lower intensity ratio of $\delta$(OH)/$\delta$(CH\textsubscript{3}) and a higher intensity of $\nu$(CO) band than those ethanol adsorbed on the H\textsubscript{2}O/TiO\textsubscript{2}. The lower $\delta$(OH)/$\delta$(CH\textsubscript{3}) intensity ratio and high intensity of CO band indicates that adsorbed ethanol has been converted to the ethoxy species (i.e., CH\textsubscript{3}CH\textsubscript{2}O\textsubscript{ad}) through breaking of the O-H bond [42]. In contrast to the formation of ethoxy species on TiO\textsubscript{2}, adsorbed ethanol is primarily present on H\textsubscript{2}O/TiO\textsubscript{2} in the form of molecularly adsorbed ethanol (i.e., CH\textsubscript{3}CH\textsubscript{2}OH\textsubscript{ad}), which exhibits the same $\delta$(OH)/$\delta$(CH\textsubscript{3}) and $\nu$(CO) intensities as those seen in pure liquid ethanol. Figure 4.3 also shows that UV illumination caused changes in the IR spectra. These changes can be magnified by the difference spectra in figure 4.4, which were obtained by subtracting the IR single beam spectrum recorded at 0 min from those collected during UV exposure.

The difference spectra of the TiO\textsubscript{2} catalysts show UV irradiation on the TiO\textsubscript{2} catalyst produced a noticeable increase in the base line of the spectra at wavenumbers below 2000 cm\textsuperscript{-1}. This baseline increase has been attributed to the infrared absorption of photogenerated electrons trapped in the conduction band [40, 45, 46]. The decrease in the intensity of the C-H stretching bands in ethanol appears to be related to the increase in the intensity of intermediates and gaseous CO\textsubscript{2} product for the H\textsubscript{2}O/TiO\textsubscript{2} and TiO\textsubscript{2} catalysts. The specific variations of the normalized IR intensities as a function of time are plotted in figure 4.5 for the C-H stretching band of the reactant ethanol, photooxidation intermediates, and CO\textsubscript{2} product.

Figure 4.5 shows the prominent contrast between the rapid decay of the C-H band in ethanol and the slow growth of gaseous CO\textsubscript{2}. The slopes of the curves for reactant
disappearance are greater than those of CO$_2$ product formation during the first 5 min of UV illumination.

Figure 4.4 IR difference spectra collected during 120 min of photocatalytic oxidation of ethanol on the H$_2$O/TiO$_2$ and TiO$_2$ catalysts.

These slopes reflect the rate of reaction, which is calculated in table 4.1 along with the coverage of H$_2$O and ethanol, and the initial intensity ratio of $\delta$(OH)/$\nu$(CO).

Comparison of the rates for the TiO$_2$ and H$_2$O/TiO$_2$ catalyst revealed increasing the
amount of H₂O from 840 to 1604 resulted in a 33 % decrease on the rate of C-H scission, and a 65 % reduction on the rate of CO₂ formation. The difference in the rates of C-H scission and CO₂ formation should be manifested on the rate of accumulation of adsorbed intermediates including acetaldehyde (CH₃CHOₐd), acetate (CH₃COO⁻ₐd), formic acid (HCOOHₐd), and formate (HCOO⁻ₐd). Due to the absence of extinction coefficients for these intermediate species, their rate of formation could not be calculated and their evolution can only be qualitatively displayed by their normalized IR absorbance intensity profiles.

The differences on the slopes of the normalized intensity profiles of CH₃CHOₐd, CH₃COO⁻ₐd, HCOOHₐd, and HCOO⁻ₐd reflect their rates of formation and disappearance, providing an insight into the reaction pathways for the photocatalytic oxidation of ethanol. The rates of formation of CH₃COO⁻ₐd, HCOOHₐd, and HCOO⁻ₐd increased sharply reaching a maximum during the first 5 min of reaction, in contrast to that of CH₃CHOₐd, which grew progressively during the 120 min of photooxidation. The higher initial rates of evolution of CH₃COO⁻ₐd, HCOOHₐd, and HCOO⁻ₐd suggest their formation preceded that of CH₃CHOₐd. Since formation of CH₃CHOₐd from CH₃COO⁻ₐd, HCOOHₐd, or HCOO⁻ₐd is unlikely to occur in an oxidation reaction scheme, the photooxidation of ethanol is proposed to proceed by at least two parallel pathways, one involving the formation of CH₃CHOₐd, and a second one producing CH₃COO⁻ₐd, HCOOHₐd, and HCOO⁻ₐd. Comparison of the normalized intensity profiles of intermediates on the H₂O/TiO₂ and TiO₂ catalysts indicate increasing the content of H₂O resulted in (i) an overlap on the rate of formation of CH₃CHOₐd, (ii) a decrease on the rate
of formation of CH$_3$COO$^-_{\text{ad}}$ and HCOO$^-_{\text{ad}}$ and (iii) a decrease on the rate of disappearance of HCOOH$^-_{\text{ad}}$.

Figure 4.5 Variation of the normalized IR intensities of the bands of reactant ethanol, intermediate species, and CO$_2$ product during 120 min of photocatalytic oxidation of ethanol on the H$_2$O/TiO$_2$ and the TiO$_2$ catalysts. Normalized intensity = $I(t) / I_{\text{max}}$, where $I(t)$: intensity of a species at time t; $I_{\text{max}}$: the maximum intensity of a species during the 120 min.
Table 4.1 Rate of change of IR intensities of the C-H in ethanol and formation of CO\(_2\) during the first minute of UV illumination on semiconductor TiO\(_2\) catalysts exposed to different ethanol and water coverage.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Experiment conditions</th>
<th>(H_2O_{ad}) content (µmol/g cat)</th>
<th>Ethanol coverage (µmol/g cat)</th>
<th>(\frac{\Delta \nu_{C-H}}{\Delta t})</th>
<th>(\frac{\Delta \nu_{CO_2}}{\Delta t})</th>
<th>CO(_2) rate (µmol/min)</th>
<th>(\delta(OH))</th>
<th>(\frac{\nu(CO)}{\nu(CO_2)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>Untreated TiO(_2) catalyst, exposed to ethanol for 10 min</td>
<td>840</td>
<td>718</td>
<td>4.58x10(^{-2})</td>
<td>5.74x10(^{-3})</td>
<td>1.38x10(^{-1})</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>H(_2)O/TiO(_2)</td>
<td>H(_2)O treated TiO(_2) catalyst, dried 20 hr, exposed to ethanol for 10 min</td>
<td>1604</td>
<td>509</td>
<td>1.49x10(^{-2})</td>
<td>6.20x10(^{-4})</td>
<td>8.93x10(^{-2})</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>Low ethanol-TiO(_2)</td>
<td>Untreated TiO(_2) catalyst, exposed to ethanol for 2 sec</td>
<td>945</td>
<td>341</td>
<td>4.63x10(^{-2})</td>
<td>1.93x10(^{-2})</td>
<td>3.71x10(^{-1})</td>
<td>0.61</td>
<td></td>
</tr>
</tbody>
</table>

Although the normalized intensity profiles of CH\(_3\)CHO\(_{ad}\) exhibited a gradual increase with reaction time that nearly overlapped on both catalysts, the magnitude of their IR absorbance intensities differed by more than 60 %, indicating that the photooxidation of ethanol to CH\(_3\)CHO\(_{ad}\) on the H\(_2\)O/TiO\(_2\) does not constitute a major reaction pathway. The photocatalytic oxidation of acetaldehyde was further investigated in the absence of the intermediate species, and it is discussed later in this document.

Interestingly, CH\(_3\)COO\(^-\)\(_{ad}\) and HCOO\(^-\)\(_{ad}\) showed a distinctly different trend, where the initial rate of CH\(_3\)COO\(^-\)\(_{ad}\) formation is higher than that of HCOO\(^-\)\(_{ad}\) on TiO\(_2\). The reverse trend for the higher initial formate formation on H\(_2\)O/TiO\(_2\) was observed. The differences on the rates of formation of CH\(_3\)COO\(^-\)\(_{ad}\) and HCOO\(^-\)\(_{ad}\) are clearly evidenced in
Figure 4.6, by expressing the ratio of the IR absorbance intensities of these species with respect to the IR absorbance intensity of all intermediates produced during ethanol PCO.

Figure 4.7 shows the IR absorbance spectra collected during acetaldehyde photocatalytic oxidation on the TiO$_2$ catalyst. Adsorption of acetaldehyde was carried out by the syringe injection of 5 cc of acetaldehyde vapor on the TiO$_2$ catalyst followed by 1 min purge in O$_2$ flow. Purging of acetaldehyde was limited to 1 min with the purpose of minimizing its conversion to crotonaldehyde prior to UV illumination [47].

Exposure to UV illumination caused a decrease in the intensity of the C-H stretching and the C=O bending bands of acetaldehyde, and the simultaneous increase of bands in the 1200-1800 cm$^{-1}$ range, indicating the photocatalytic oxidation of acetaldehyde and the formation of photooxidation products. The evolution of intermediates and CO$_2$ product during acetaldehyde photooxidation is highlighted in figure 4.8 by subtraction of the spectrum at 0 min.

![Figure 4.6 IR band intensity ratio as a function of time for major intermediates produced during ethanol PCO. IR band intensity ratio = $I(t)_A$ / $I(t)_{sum}$, where $I(t)_A$: intensity of species “A” at time t; $I(t)_{sum}$: sum of intensities for CH$_3$COO$_{ad}$, HCOOH$_{ad}$, HCOO$^-_{ad}$, and CH$_3$CHO$_{ad}$ at time t.](image)
The IR difference spectra of Figure 4.8 shows the rapid evolution of HCOO\textsuperscript{ad} and CH\textsubscript{3}COO\textsuperscript{ad} during the first two minutes of UV illumination, followed by the formation of CO\textsubscript{2} and a prominent broad band in the 3000-3500 cm\textsuperscript{-1} range associated to hydrogen bonding H\textsubscript{2}O. The specific variations of the normalized IR intensities as a function of time are plotted in Figure 4.9 for the C-H stretching band of the reactant acetaldehyde, intermediates, CO\textsubscript{2} and H\textsubscript{2}O. The decrease of the normalized intensity of the C-H bands during the first 5 min of UV illumination reflects the lower rate of photocatalytic oxidation of acetaldehyde compared to that observed for ethanol under similar conditions.

Figure 4.7 IR absorbance spectra collected during 120 min of photocatalytic oxidation of acetaldehyde on the TiO\textsubscript{2} catalyst.

Figure 4.7 IR absorbance spectra collected during 120 min of photocatalytic oxidation of acetaldehyde on the TiO\textsubscript{2} catalyst.
The slope of the normalized intensity profiles of CH$_3$COO$^-_{\text{ad}}$, HCOO$^-_{\text{ad}}$ and CO$_2$, revealed the formation of CH$_3$COO$^-_{\text{ad}}$ led that of HCOO$^-_{\text{ad}}$, suggesting that the major reaction pathway for acetaldehyde photo oxidation on the TiO$_2$ catalyst involves the formation of CH$_3$CHO$_{\text{ad}}$, and the subsequent conversion to HCOO$^-_{\text{ad}}$ and CO$_2$. The sudden increase on the normalized intensity profile of H$_2$O correlates with the decrease on the C-H band of acetaldehyde and formation of intermediates, indicating that H$_2$O has an adverse effect on the photooxidation of acetaldehyde.

Considering the suggested pathways for ethanol PCO along with our direct IR observations of the evolution of adsorbed species produced during the photooxidation of ethanol and acetaldehyde, a parallel/series reaction scheme is proposed in Figure 4.10 for the photooxidation of ethanol in the high and low H$_2$O content TiO$_2$. Exposure to ethanol (CH$_3$CH$_2$OH$_g$) on the high and low H$_2$O content TiO$_2$ produced molecularly adsorbed ethanol (CH$_3$CH$_2$OH$_{\text{ad}}$) and ethoxy (CH$_3$CH$_2$O$_{\text{ad}}$), respectively.

UV illumination caused the photooxidation of ethanol producing CH$_3$CHO$_{\text{ad}}$, as well as CH$_3$COO$^-_{\text{ad}}$ HCOOH$_{\text{ad}}$, HCOO$^-_{\text{ad}}$ and CO$_2$. In the absence of adsorbed ethoxy species, shown by the low intensity ratio of the $\delta$(OH)/$\nu$(CO), holes would be available for reaction with hydroxyl groups from H$_2$O adsorbed on the H$_2$O/TiO$_2$ catalyst, as well as with O$_2^-'$ produced from reaction of adsorbed oxygen and photo generated electrons. The higher rate of formation of HCOO$^-_{\text{ad}}$ with respect to CH$_3$COO$^-_{\text{ad}}$ on the H$_2$O/TiO$_2$ catalyst suggest ·OH species, produced from reaction of holes with dissociated water, abstracts hydrogen on the molecular ethanol, producing formate and acetate species. In contrast, the higher rate of formation of CH$_3$COO$^-_{\text{ad}}$ on the TiO$_2$ catalyst suggests the
reaction is initiated by photogenerated holes on the surface, which directly abstract hydrogen from CH$_3$CH$_2$O$_{ad}$ producing acetate species.

Figure 4.8 IR difference spectra recorded during 120 min of photocatalytic oxidation of acetaldehyde on the TiO$_2$ catalyst.
Figure 4.9 Variation of the normalized IR intensity of adsorbed acetaldehyde (CH$_3$CHO$_{ad}$), intermediate species, and CO$_2$ product during 120 min of photocatalytic oxidation of acetaldehyde on the TiO$_2$ catalysts.

Although we do not have direct evidence of formation of ·OH from water and hole, its formation has been well established. ·OH can further react with formate and acetate intermediates on H$_2$O/TiO$_2$ evidenced by their higher slope of decay in their normalized curve in Figure 4.5. The lower IR intensity of CH$_3$CHO$_{ad}$ on the H$_2$O/TiO$_2$ with respect to that observed on the TiO$_2$ catalyst indicates conversion of CH$_3$CH$_2$OH$_{ad}$ to CH$_3$CHO$_{ad}$ does not constitute a major photocatalytic oxidation pathway, whereas
CH$_3$CHO$_{ad}$ can be readily converted to CH$_3$CHO$_{ad}$. Results from acetaldehyde PCO indicate CH$_3$CHO$_{ad}$ is rapidly converted to CH$_3$COO$^{-}_{ad}$, which is further oxidized to HCOO$^{-}_{ad}$ and CO$_2$ on the TiO$_2$ catalyst. The presence of high contents of H$_2$O reduce the rate of photooxidation of CH$_3$CHO$_{ad}$, resulting the rate of formation of CO$_2$.

The slow rate of C-H scission on the H$_2$O/TiO$_2$ catalyst suggests the reaction of holes and H$_2$O would be slower than that of holes and ethoxy species, in agreement with recent studies [48]. The absence of significant changes in the IR intensity of OH groups during UV illumination, as shown in Figure 4.4, suggests holes in the surface of the H$_2$O/TiO$_2$ catalyst would be available for reaction with O$_2^-$, resulting in the formation of $^{1}$O$_2$ [49, 50] and explaining the absence of the increased base line of the spectra at wavenumbers below 2000 cm$^{-1}$. Previous studies have shown exposure to UV light on the TiO$_2$ surface involves a photo induced hydrophilicity, resulted from the dissociatively adsorption of water on oxygen vacancies present on the surface and subsequent formation of surface hydroxyl groups. The observation of minor changes of the IR intensity of OH groups during photocatalytic oxidation of ethanol on the H$_2$O/TiO$_2$ surface suggests UV illumination under high water coverage proceeds without photo induced hydrophilicity. A further study increasing the amount of water 840 to 945 µmol per gram of catalyst via controlling time of exposure to O$_2$/ethanol showed a minor change on the rate of C-H scission, accompanied by an improvement on the rate of CO$_2$ formation of nearly 2.7 times. Improvement on the rate of CO$_2$ formation may be attributed to the lower ethanol coverage, which would facilitate adsorption of O$_2$ on the surface of the catalyst, leading to the formation of O$_2^-$ species. The detailed analysis of this experiment will be subject of a future publication.
Figure 4.10 Major reaction pathways during ethanol PCO on H₂O/TiO₂ and TiO₂ catalysts.
CHAPTER V

DETERMINATION OF CONTRIBUTION OF METHANOL SACRIFICING REAGENT TO PHOTOCATALYTIC EVOLUTION OF HYDROGEN

5.1 Abstract

This chapter presents the results of a mass spectrometry (MS) and gas chromatography (GC) study of the contribution of CH₃OH on the photocatalytic evolution of H₂ from H₂O (i.e., water splitting) over semiconductor TiO₂ catalysts. The contribution of methanol (CH₃OH) sacrificing reagent to the photocatalytic evolution of H₂ from aqueous solutions was studied by tracing the reaction of D₂O over a Cu/S-TiO₂ catalyst under UV illumination. Use of D₂O/CH₃OH produced higher formation rates of HD and D₂ than that of H₂. The low H₂ formation rates indicate that the direct reaction of CH₃OH with photogenerated holes does not proceed to an appreciable extent in the presence of high concentrations of D₂O. The role of CH₃OH in accelerating hydrogen formation can be attributed to its ability to produce an electron donor, injecting its electrons to the conduction band.
5.2 Introduction

Production of H$_2$ and O$_2$ from H$_2$O by photocatalytic reactions on semiconductor materials such as TiO$_2$ has been extensively studied [3, 51-54]. Photocatalytic reactions are initiated on TiO$_2$ by absorption of light, which promotes electrons from the valence band (VB) to the conduction band (CB) and generates electron/hole pairs [17]. Photogenerated holes (h$^+$) can oxidize adsorbed H$_2$O molecules at the catalyst surface, producing protons (H$^+$) and O$_2$. The H$^+$ can further react with electrons (e$^-$) to form H$_2$, as shown in reactions (5.1 to 5.3).

\begin{align*}
\text{TiO}_2 + h\nu &\rightarrow e^- + h^+ \quad (5.1) \\
\text{H}_2\text{O}(l) + 2h^+ &\rightarrow \frac{1}{2} \text{O}_2(g) + 2\text{H}^+ \quad (5.2) \\
2\text{H}^+ + 2e^- &\rightarrow \text{H}_2(g) \quad (5.3)
\end{align*}

The evolution of stoichiometric amounts of H$_2$ and O$_2$ (i.e., water splitting) is characterized by rates of reaction that are two or three orders of magnitude smaller than conventional catalytic reactions [55]. The low formation rates of H$_2$ and O$_2$ could be due to rapid recombination of holes and electrons and large driving force for the backward reaction producing H$_2$O [56]. Addition of electron donor molecules that react irreversibly with holes (i.e., sacrificing reagents) has been shown to be an effective approach for enhancing the rate of H$_2$ formation. Common sacrificing reagents used in photocatalytic reactions include methanol (CH$_3$OH), ethanol (CH$_3$CH$_2$OH), ethylenediaminetetraacetic acid (EDTA), cyanide (CN$^-$), lactic acid (CH$_3$CHOHCOOH), and formaldehyde (HCHO) [57-61]. Table 5.1 presents the rates of H$_2$ formation over
various photocatalysts in the presence of CH$_3$OH sacrificing reagent, highlighting its prevalent use.

Table 5.1 Rates of H$_2$ formation over various photocatalysts in the presence of methanol (CH$_3$OH).

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Co-catalyst (wt%)</th>
<th>Light Source $^a$</th>
<th>Intensity (mW/cm$^2$)</th>
<th>CH$_3$OH (vol %)</th>
<th>H$_2$ Formation rate (µmol/hr g)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>Pt(0.1)</td>
<td>Hg-P</td>
<td>-</td>
<td>0</td>
<td>55</td>
<td>[62]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Pt (1.0)</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>30</td>
<td>[63]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Pt (1.0)</td>
<td>Hg-P</td>
<td>-</td>
<td>50</td>
<td>3000</td>
<td>[64]</td>
</tr>
<tr>
<td>TiO$_2$/SiO$_2$</td>
<td>Pt (0.5)</td>
<td>Xe-P</td>
<td>-</td>
<td>50</td>
<td>86</td>
<td>[65]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Cu (1.2)</td>
<td>-</td>
<td>-</td>
<td>41</td>
<td>2700</td>
<td>[66]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Ni (1.0)</td>
<td>Xe-P</td>
<td>-</td>
<td>10</td>
<td>24.7</td>
<td>[67]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Ni (1.0), Ta (2.0)</td>
<td>Xe-P</td>
<td>-</td>
<td>10</td>
<td>0.7</td>
<td>[67]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Ni (1.0), Nb (2.0)</td>
<td>Xe-P</td>
<td>-</td>
<td>10</td>
<td>1.0</td>
<td>[67]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>RuO$_2$ (10), Pt (5)</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>17334</td>
<td>[68]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Pd (10)</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>7334</td>
<td>[68]</td>
</tr>
<tr>
<td>N-TiO$_2$</td>
<td>Pt (0.5)</td>
<td>Xe-Q</td>
<td>340</td>
<td>-</td>
<td>60</td>
<td>[69]</td>
</tr>
<tr>
<td>S-TiO$_2$</td>
<td>Pt (0.5)</td>
<td>Xe-Q</td>
<td>340</td>
<td>-</td>
<td>100</td>
<td>[69]</td>
</tr>
<tr>
<td>TiO$_2$ (TNT)$^c$</td>
<td>Ni (4.7)</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>880</td>
<td>[70]</td>
</tr>
<tr>
<td>InVO$_4$</td>
<td>Ni(1.0)</td>
<td>Vis</td>
<td>-</td>
<td>0</td>
<td>691</td>
<td>[71]</td>
</tr>
<tr>
<td>S-TiO$_2$</td>
<td>Cu</td>
<td>Hg-Q</td>
<td>30</td>
<td>20</td>
<td>67.1</td>
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<tr>
<td>S-TiO$_2$</td>
<td>Cu</td>
<td>Hg-Q</td>
<td>30</td>
<td>25</td>
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</tr>
<tr>
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<td>30</td>
<td>100</td>
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</tr>
<tr>
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<td>Vis</td>
<td>-</td>
<td>20</td>
<td>11.5</td>
<td>this work</td>
</tr>
<tr>
<td>S-TiO$_2$</td>
<td>Cu</td>
<td>Hg-Q</td>
<td>30</td>
<td>0$^b$</td>
<td>4.28</td>
<td>this work</td>
</tr>
</tbody>
</table>

$^a$ Hg-Q: combination of a 350-500 W Hg lamp with a quartz cell, Hg-P: combination of a 250-500 W Hg lamp with a Pyrex cell, Xe-Q: combination of a 500 W Xe lamp with a Quartz cell, Xe-P: combination of a 300 W Xe lamp with a Pyrex cell. Vis: visible light.

$^b$ Reaction in H$_2$O solution containing 0.4 M Na$_2$S and Na$_2$SO$_3$

$^c$ TNT: Ni-intercalated titanate nanotube.
The need for replenishing of sacrificing reagents in order to maintain high rates of reaction precludes their use for continuous and large scale production of H₂. Instead, sacrificing reagents are used to determine the photocatalyst efficiency for reaction (5.3). A fundamental issue that needs to be addressed in the use of hydrogen-containing sacrificing reagents is whether these reagents simply serve as hole scavengers or contribute their hydrogen atoms to produce H₂ gas.

The objective of this study is to determine the contribution of CH₃OH sacrificing reagent on the overall rate of photocatalytic evolution of H₂ from dilute aqueous solutions. The reaction is investigated using H₂O/CH₃OH and D₂O/CH₃OH solutions over a Cu/S-TiO₂ catalyst, assuming that H₂O and D₂O molecules exhibit similar photocatalytic reactivity. The amounts of H₂, HD, and D₂ produced were determined with a mass spectrometer (MS) and gas chromatograph (GC). The Cu/S-TiO₂ catalyst was selected in consideration of the reported band gap narrowing due to sulfur doping of TiO₂ [72] and the enhanced absorption of visible light by Cu co-catalysts [73, 74].

5.3 Experimental

This section described the experimental methods and techniques used for preparing and characterizing the catalysts as well as for evaluating the effect of methanol sacrificial reagent during the photocatalytic evolution of H₂.
5.3.1 Preparation and characterization of Cu/S-TiO$_2$

The S-TiO$_2$ powder was synthesized by sol-gel method according to previously reported procedures [75]. Tetrabutyl titanate (13.6 g, 40 mmol, TCI America) was added dropwise to a mixture of thiourea (12.24 g, 160 mmol) and ethanol (200 ml, 3.42 mol) at 298 K under vigorous agitation, then acetic acid (14.4 g, 160 mmol, 96% Fisher Scientific) was added and allowed to react overnight. The resulted mixture was heated at 423 K for 2 h, dried under vacuum for 3 h, and calcined at 673 K for 3 h to produce S-TiO$_2$ powder. Cu was added to the S-TiO$_2$ powder by the electroless plating approach, which involved the reduction of Cu$^{+2}$ cations by formaldehyde (HCHO, Alfa Aesar). The S-TiO$_2$ powder was dispersed in a plating solution bath containing copper sulfate (0.04 M CuSO$_4$·5H$_2$O), ethylenediaminetetraacetic acid disodium salt (0.08 M EDTA·Na), formic acid (0.08 M HCHO), and 5 ppm pyridine as stabilizer. The temperature of the plating bath was kept constant at 343 K and the pH was adjusted to 12.5 under constant agitation. The Cu plated S-TiO$_2$ catalyst (Cu/S-TiO$_2$) was dried at 383 K for 24 h.

The crystalline structure of the Cu/S-TiO$_2$ catalyst was determined by X-Ray diffraction (XRD) using a Philips APD 3700 diffractometer equipped with Cu K$\alpha$ (wavelength 1.5406 Å). Diffuse reflectance ultraviolet-visible (UV-VIS) spectra of the catalyst were recorded by a HITACHI U-3010 spectrophotometer equipped with a diffuse reflectance accessory. The spectra were collected at room temperature by using the spectrum of pure barium sulfate (BaSO$_4$) as the reference spectrum.
5.3.2 Photocatalytic studies

The photocatalytic evolution of H$_2$ was carried out in a quartz square tubing reactor (100 cm$^3$), equipped with gas tight fittings for admission of gases and sampling of reaction products. During each experiment, a 30 cm$^3$ solution containing 0.1 g of the Cu/S-TiO$_2$ catalyst, CH$_3$OH, and H$_2$O or D$_2$O were dispersed and exposed to UV light with a 350 W mercury lamp (Oriel 2686) positioned at a fixed distance of 5 cm from the reactor. The reaction was also carried out in the presence of sodium sulfite (Na$_2$SO$_3$, 0.4 M) and sodium sulfide (Na$_2$S, 0.4 M) sacrificing reagents for comparison purposes. The amount of H$_2$ produced was determined by a Balzers QMG 112 mass spectrometer (MS) and a SRI 8610C gas chromatograph equipped with a Helium Ionization Detector (HID).

5.4 Results and Discussion

This section describes the results from the catalyst characterization and the photocatalytic evolution of H$_2$ in the presence of methanol sacrificial reagent.

5.4.1 Catalyst characterization

Fig. 5.1 shows the XRD patterns of the S-TiO$_2$ powder and the Cu/S-TiO$_2$ catalyst before and after the photocatalytic studies. The patterns reveal that the crystalline structure of TiO$_2$ corresponds to the anatase phase [76-80] and its bulk structure was not altered during the photocatalytic reaction.
Figure 5.1 XRD patterns of S-TiO₂ and Cu/S-TiO₂ before and after the photocatalytic reaction.

The absence of the rutile and brookite phases in the catalyst structure may be attributed to sulfur doping, which has been suggested to inhibit grain growth of the TiO₂ crystallites and limits phase transitions during calcinations [76, 77]. Cu is present in the form of CuO [81] with crystallite size of 15 nm calculated according to the Scherrer equation.

The diffuse reflectance UV-VIS spectra in Fig. 5.2 reveal that addition of Cu improved the light absorption of the S-TiO₂ powder in the visible range [69]. The band gap of the catalyst was estimated from the tangent lines in the plot of the square root of the Kubelka-Munk functions against the photon energy [69, 76, 82], as shown in the inset in Fig. 5.2. The band gap energies of the S-TiO₂ powder and Cu/S-TiO₂ catalyst were 2.39 and 1.54 eV, respectively. The spectrum of TiO₂ (p25, Degussa) was included for comparison purposes.
5.4.2 Formation of H$_2$ by photocatalytic reactions over Cu/S-TiO$_2$

Fig. 5.3 shows the evolution of hydrogen during UV and visible illumination of the Cu/S-TiO$_2$ catalyst dispersed in an aqueous solution containing Na$_2$SO$_3$ (0.4 M), and Na$_2$S (0.4 M) sacrificing reagents. The formation of H$_2$ increased with respect to time under UV illumination and remained relatively constant under visible light illumination. The low rate of H$_2$ formation during exposure to visible light could be due to (i) low potential of photogenerated electrons and (ii) lack of effectiveness of the sacrificing reagents for the hole scavenging reactions.
Fig. 5.3 Evolution of hydrogen during UV and visible light illumination of Cu/S-TiO\textsubscript{2} dispersed in a H\textsubscript{2}O solution containing Na\textsubscript{2}SO\textsubscript{3} (0.4 M), and Na\textsubscript{2}S (0.4 M).

Fig. 5.4 shows the amount of H\textsubscript{2} produced during UV illumination of the Cu/S-TiO\textsubscript{2} catalyst dispersed in CH\textsubscript{3}OH, H\textsubscript{2}O/CH\textsubscript{3}OH (9/1 molar ratio solution), D\textsubscript{2}O/CH\textsubscript{3}OH (11/1 molar ratio solution), and D\textsubscript{2}O. UV illumination of CH\textsubscript{3}OH resulted in the evolution of significantly more H\textsubscript{2} than that observed with the other solutions, and with the Na-based sacrificing reagents.

The evolution of H\textsubscript{2} from primary alcohols with \(\alpha\)-hydrogens such as CH\textsubscript{3}OH has been proposed to be initiated by the reaction with holes, producing protons (H\textsuperscript{+}) and a hydroxyalkyl radical intermediate (i.e., \(\cdot\text{CH}_2\text{OH}\)), as shown in reaction (6.4). The \(\cdot\text{CH}_2\text{OH}\) radical intermediate possesses sufficiently negative oxidation potential (i.e, -0.74 V) and could further react to produce H\textsuperscript{+} and electrons, as shown in reaction (5). These electrons can be injected into the conduction band (doubling current effect) [83].
\[
\text{CH}_3\text{OH} + h^+ \rightarrow \cdot\text{CH}_2\text{OH} + \text{H}^+ \quad (5.4)
\]
\[
\cdot\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}^+ + \text{e}^- \quad (5.5)
\]

The H\(^+\) produced from reaction (5.4) and (5.5) can also react with electrons to form H\(_2\) via reaction (5.3).

Figure 5.4 Evolution of Hydrogen during UV illumination of Cu/S-TiO\(_2\) dispersed in CH\(_3\)OH, D\(_2\)O, H\(_2\)O/CH\(_3\)OH (9/1 molar ratio solution), and D\(_2\)O/CH\(_3\)OH (11/1 molar ratio solution).

Transient spectroscopic studies have demonstrated that the reaction of CH\(_3\)OH and holes (reaction 5.4) occurs at a higher rate than that of holes and H\(_2\)O molecules [48]. Thus, decreasing the CH\(_3\)OH concentration by addition of H\(_2\)O should cause a decline in the rate of H\(_2\) evolution, which was observed in Fig. 5.4.

Since pure CH\(_3\)OH is more reactive than pure H\(_2\)O, the photocatalytic reaction of D\(_2\)O/CH\(_3\)OH solutions is expected to produce H\(_2\) at a higher rate than D\(_2\). MS analysis of
the gas products from the reaction of the D₂O/CH₃OH (11/1 molar ratio solution), shown in Fig. 5.5, revealed that the formation rates of H₂ were 1.7 times lower than those of HD and 7.1 times lower than those of D₂.

![Figure 5.5](image)

Figure 5.5 MS responses obtained after injecting 0.5 cm³ samples of the gas phase species produced during UV illumination over Cu/S-TiO₂ dispersed on D₂O/CH₃OH (11/1 molar ratio solution).

Fig. 5.6 shows the product distribution during the first 10 h of reaction determined by GC and factoring of the relative MS responses presented in Fig. 5.4. The amounts of D₂ and HD increased with time while that of H₂ level off after 7 h of reaction. The low formation rate of H₂ suggests that the reaction of hole with CH₃OH (reaction 6.4) did not occur to an appreciable extent. This observation can be explained by the low concentration of adsorbed CH₃OH on the TiO₂ surface. A recent IR study has shown that the high content of H₂O prevent alcohol to adsorb as alkoxy (i.e., RCH₂O) on the TiO₂
surface and allow photogenerated hole to initiate the reaction with H₂O as shown below [84]:

\[
\text{H}_2\text{O} + h^+ \rightarrow \cdot \text{OH} + \text{H}^+ \quad (5.6)
\]

\[
\cdot \text{OH} + \text{CH}_3\text{OH} \rightarrow \cdot \text{CH}_2\text{OH} + \text{H}_2\text{O} \quad (5.7)
\]

Thus, it is expected that the presence of H₂O or D₂O, would switch the CH₃OH reaction pathway from reacting with h⁺ to reacting with ·OH or ·OD, producing the hydroxyalkyl radical intermediate (·CH₂OH) of reaction (5.7).

Figure 5.6 Amount of H₂, HD, D₂, and CO₂ produced during UV illumination of Cu/S-TiO₂ dispersed on D₂O/CH₃OH (11/1 molar ratio solution). The evolution of gaseous products was determined via GC analysis, by factoring the relative MS response (i.e., areas under the profiles of H₂, HD and D₂ recorded after injection of 0.5 ml samples).
The \(-\text{CH}_3\text{OH}\) can be oxidized as described in reaction (5.5) providing electrons. These electrons then react with \(\text{H}^+\) and \(\text{D}^+\) to produce \(\text{H}_2\) and \(\text{HD}\). The observation of \(\text{H}_2\) and \(\text{HD}\) clearly confirm the occurrence of reactions (5.6) and (5.7), manifesting the function of \(\text{CH}_3\text{OH}\) as a sacrificing reagent. However, the role of sacrificing reagent is not through its direct reaction with \(\text{h}^+\) but with the involvement of \(-\text{OH}\). The possible role of \(\text{CH}_3\text{OH}\) for enhancing the rate of \(\text{H}_2\) formation includes inhibiting electron/hole recombination and the backward reaction to form \(\text{H}_2\text{O}\). Determination of the recombination reaction awaits further verification.
6.1 Abstract

This chapter presents the results of a study of the direct electrochemical oxidation of coke in a solid oxide fuel cell (SOFC) comprising a Ni-YSZ anode electrode. A sample of coke, obtained by pyrolyzing Ohio # 5 coal at 950 °C in inert environment, was fed to a SOFC operating at 800 °C and 1 atm. The fuel cell power generation characteristics and energy efficiency were determined by measuring the voltage vs current curves (i.e., V-I curves), and monitoring the composition of gaseous species at the outlet of the fuel cell. The Ni/YSZ anode was characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Results from the fuel cell material and energy balances in batch mode operation revealed the direct electrochemical oxidation of coke can result in energy efficiencies higher than those observed for H₂ (measured under similar conditions), reaching values close to 55 %. The results obtained during the electrochemical oxidation of coke on a Ni-YSZ anode will be used as reference for the evaluation of the performance of Cu-modified anode electrodes.
6.2 Introduction

The use of solid oxide fuel cells to carry out the electrochemical oxidation of carbonaceous materials is an attractive approach for converting the chemical energy of solid fuels (i.e., coal and coke) directly into electricity. The electrochemical oxidation of coke, a form of devolatized coal, could result in (i) higher energy efficiencies compared to conventional combustions processes, (ii) production of high purity CO\textsubscript{2} ready for sequestration, and (iii) minimization of NOx emissions. Accurate determination of the fuel cell energy efficiency requires the simultaneous quantification of gaseous products such as methane (CH\textsubscript{4}), carbon monoxide (CO) and carbon dioxide (CO\textsubscript{2}), and the electric power generated by the cell. The objective of this study is to determine experimentally the efficiency of a Ni-YSZ anode supported fuel cell during the electrochemical oxidation of coke. Ni-YSZ anode was selected because of its wide spread as a highly active anode electrode material, and compatibility with other fuel cell components.

6.3 Fuel cell efficiency

The efficiency of the SOFC during the electrochemical oxidation of coke was evaluated by considering the thermodynamic efficiency $\xi_T$, the electrochemical efficiency $\xi_V$, and the net efficiency $\xi_{net}$. The SOFC definitions have been discussed Chapter II and are only briefly discussed in the following section.
6.3.1 Thermodynamic efficiency $\xi_T$

The thermodynamic efficiency $\xi_T$ was estimated by measuring the electrical work performed by the cell, $W_e$, and the heat of combustion of the spent fuel, $\Delta H$. Equation 6.1 presents the definition of the thermodynamic efficiency.

$$\xi_T = \frac{W_e}{\Delta H} \quad (6.1)$$

The resulting thermodynamic efficiency was compared with the theoretical thermodynamic efficiency of the electrochemical oxidation of carbon, obtained from the enthalpy $\Delta H$, and the Gibbs energy change $\Delta G$ of the oxidation reaction, respectively [85, 86].

6.3.2 Electrochemical efficiency $\xi_v$

The electrochemical efficiency $\xi_v$ was determined by operating the fuel cell under load conditions, and at open circuit conditions. The operation of the fuel cell under load conditions resulted in deviations of the voltage from the ideal Nernst reversible potential, indicating electrode overpotentials $\eta_j$ and electrolyte resistance $R_e$. Overpotentials are associated to irreversible losses due to mass transport limitations and half-cell reaction activation barriers occurring at the anode and cathode electrodes. Overpotential losses allow the direct comparison of various fuels and cell configurations. Equation 6.2 presents the definition of the electrochemical efficiency.
\[
\xi_V = \frac{V_{cell}}{V_N} = 1 - \frac{\eta_a(t) - \eta_c(t) - R_e(t)}{V_N} 
\]  

(6.2)

\(V_N\) and \(V_{cell}\) represent the ideal Nernst potential and the fuel cell voltage under load conditions, respectively; \(\eta_a\), and \(\eta_c\), are the anode and cathode overpotentials, respectively; and \(Re\) is the electrolyte resistance.

6.3.3 Net efficiency \(\xi_{Net}\)

The net efficiency was evaluated by adopting the definition proposed by Cooper et al [85], considering the impact of the thermodynamic factor, the fuel utilization factor and the electrochemical factor. Equation 6.3 presents the definition of the net efficiency.

\[
\xi_{Net} = \left[ \frac{\Delta G_T}{\Delta H_{298 K}} \right] \times \frac{V(i)}{E^o} \times \mu 
\]  

(6.3)

Where \(V(i)\) and \(E^o\) represent the operating voltage at current \(i\) and the reversible potential respectively, and \(\mu\) represents the fuel utilization factor. The efficiency of the solid oxide fuel cell determined in this study was evaluated by computing the thermodynamic efficiency according to the definition presented in equation (6.1). In addition to the thermodynamic efficiency, the electrochemical efficiency and the net efficiency were evaluated (equations 6.2 and 6.3) with the purpose of comparing the coal-based fuel cell with other fuel cell systems and conventional technologies such as internal combustion engines.
6.4 Experimental

Anode supported fuel cells were fabricated by casting and laminating a 70 wt % NiO-YSZ green tape, a 50wt % Ni-YSZ tape and pure YSZ tape. During casting of the tapes, the starting NiO powders were weighted and mixed with YSZ powder, dispersant, pore former, binder, and plasticizers. The resulting mixtures were dissolved in ethanol, acetone and amyl acetate solvents and were ball milled for 20 hours at 20 rpm in order to produce homogenous slurries. The slurries were de-aired, casted on silicon coated Mylar films using a 6” doctor blade, and allowed to dry for 24 hr. The dry tapes were laminated, punched into 1.5” discs and fired at 1400 °C for 4 hr. The resulting anode supported cells were successively screen printed and fired with a 50 wt% LSM-YSZ cathode layer, and a pure LSM cathode current collector layer.

The anode supported fuel cells were tested in a steel batch reactor equipped with a gas inlet port, a coke feeding mechanism, and a gas exhaust outlet port connected to the MS and an off stream GC injection port. Prior to the each testing experiment, a thin layer of silver (Ag adhesive conductive paste, Alfa Aesar) was coated along the perimeter of the anode with the purpose of enhancing the electric contact between the fuel cell electrode and the steel reactor serving as fuel cell housing and current collector. After pasting the silver layer, the cells were attached to the reactors using an alumina based seal and were provided with a Ag strip connected to a Pd wire for current collection. Figure 6.1 presents a schematic representation of the current collection approach. Prior to the evaluation of the energy efficiency, the cell is conditioned in H₂ environment to reduce NiO to Ni. The microstructure of the fuel cell was characterized by scanning electron
microscopy (SEM, Quanta 200 FEI), and energy dispersive X-Ray spectroscopy (EDS, Edax).

The energy efficiency of the fuel cell was evaluated at 800 °C by introducing the fuel and simultaneously allowing the operation at 0.56 Volt for a specific period of time, recording the current produced, and monitoring the composition of the gas stream at the exhaust of the cell. In the case of hydrogen, the cells were operated under steady state conditions by flowing a stream composed of 84 cc/min of H\textsubscript{2} in 154 cc/min of He. In the case of coke, the cell was operated in batch mode by introducing 1.01 g of solid fuel in a continuous 154 cc/min He stream. The composition of the gases at the exhaust of the fuel cell was constantly monitored using mass spectrometer (MS, Pfeiffer Omnistar\textsuperscript{TM}) and a gas chromatograph (GC, SRI 8610C).

![Figure 6.1 Cathode current collector.](image)

6.5 Results and discussion

Figure 6.2 shows the microstructure of the Ni-YSZ/YSZ/LSM-YSZ/LSM fuel cell after exposure to H\textsubscript{2} at 800 °C for 10 h, characterized by scanning electron microscopy.
Evaluation of the grain sizes of Ni and YSZ on the anode support of the fuel cell revealed particle sizes of 1-5 and 0.5-1 µm, respectively. The observed particle sizes for Ni and YSZ are in agreement with those previously reported for fuel cell prepared by die pressing and tape casting methods [87]. The Ni-YSZ anode evidenced a homogeneous microstructure in which the Ni particles are surrounded by YSZ particles, preventing Ni sintering. The strong interaction between the Ni and YSZ phase at the anode of the fuel cell constitutes the key requirement for the development of anode electrodes exhibiting good mechanical properties and enhanced electrochemical activity.

Figure 6.2 Microstructure of the Ni-YSZ/YSZ/ LSM-YSZ/LSM fuel cell after exposure to H₂ flow for 10 h at 800 °C.

Prior to the evaluation of the efficiency of the fuel cell during the electrochemical oxidation of H₂ and coke, an initial experiment was carried out with the purpose of
evaluating the performance of the fuel cell in H\textsubscript{2}. For convenience, this experiment is designated as experiment I in the subsequent sections of this study. Figure 6.3 presents the performance of the fuel cell during experiment I, prior to the evaluation of the energy efficiency. Figure 6.3 show the cell produced an open circuit voltage of 0.833 volts and a maximum current density of 1.374 A/cm\textsuperscript{2}. The relatively low open circuit voltage exhibited by the fuel cell evidenced the presence of significant electrode overpotentials during the operation on H\textsubscript{2} fuel. The identification of the different processes responsible for the generation of the overpotentials at the anode and cathode of the fuel cell requires a detail impedance characterization of the cell, and will the subject of future studies.

![Figure 6.3 Performance of the fuel cell (V-I curve) operating in H\textsubscript{2} during experiment I, prior to the evaluation of the energy efficiency.](image)

Figure 6.3 Performance of the fuel cell (V-I curve) operating in H\textsubscript{2} during experiment I, prior to the evaluation of the energy efficiency.
6.5.1 Fuel cell efficiency during electrochemical oxidation of H$_2$

The efficiency of the fuel cell during the electrochemical oxidation of H$_2$, designated as experiment II, was evaluated by operating the cell at a constant load of 0.56 volt, recording the current produced by the fuel cell and monitoring the composition of the gases at the exhaust of the fuel cell reactor with the impedance spectrometer (IS), mass spectrometer (MS) and gas chromatograph (GC). Figure 6.4 presents the MS profile of H$_2$ (m/e=2) and the current produced by the cell during experiment II. The information presented in figure 6.4 was used to estimate the energy efficiency according to the definition discussed in the introduction. The following section presents a detailed description of the calculation of the fuel cell efficiency.

The thermodynamic efficiency $\xi_T$ was obtained by relating $w_e$, the electrical work performed by the fuel cell, and the enthalpy change of the oxidation reaction $\Delta H$. The electrical work $w_e$, was calculated based on the current produced by the cell at the operating voltage

\[ w_e = I \cdot A \cdot V \cdot t \]

where

- $I$ = average current density (A/cm$^2$)
- $A$ = Fuel cell active area (cm$^2$)
- $V$ = Fuel cell voltage (Volt)
- $t$ = time (s)
Figure 6.4 MS profiles and current produced by the fuel cell at 0.56 Volt during experiment II.

Resulting in

\[
I = 0.437 \, (A/cm^2)
\]
\[
A = 1 \, (cm^2)
\]
\[
V = 0.56 \, (V)
\]
\[
t = 4200 \, (s)
\]
\[
w_e = 1027.8 \, (J)
\]

The enthalpy change of reaction \( \Delta H \) was estimated considering the amount of \( H_2 \) consumed during the electrochemical oxidation reaction, the inlet \( H_2 \) flow rate, and the \( H_2 \) low heating value.
\[ \Delta H = LHV \cdot F_{H_2} \cdot U \cdot t \]

where

\[ LHV = \text{Lower heating value of } H_2 \ (J/mol) \]
\[ F_{H_2} = \text{inlet } H_2 \text{flowrate (mol/s)} \]
\[ U = \text{fuel utilized (\%)} \]
\[ t = \text{time (s)} \]

Using the fuel utilization was calculated from MS, which results in:

\[ LHV = 240 \ (kJ/mol) \]
\[ F_{H_2} = 3437 \ (\mu \text{mol/min}) \]
\[ U = 5.1 \% \]
\[ \Delta H = 2944 \ J \]

The thermodynamic efficiency \( \xi_T \) was then calculated as

\[ \xi_T = \frac{1027.8 \ J}{2944 \ J} = 34.3\% \]

In addition to the thermodynamic efficiency, the electrochemical efficiency was calculated according to equation 6.2 resulting in

\[ V_N = 0.978 \ (Volt) \]
\[ V = 0.56 \ (Volt) \]
\[ \xi_V = 0.57 \ (Volt) \]

The net efficiency \( \xi_{Net} \), representing the theoretical limiting efficiency of the fuel cell operating on \( H_2 \) at 0.56 Volt and 800 \( ^\circ C \) was calculated according to equation (6.3).

\[ \xi_{Net} = \left[ \frac{\Delta G_T}{\Delta H_{298 K}} \right] \times \frac{V(I)}{E^o} \times \mu = 0.7 \times \frac{0.56}{0.978} \times 1 = 40.0\% \]
6.5.2 Fuel cell efficiency during electrochemical oxidation of coke

The efficiency of the fuel cell operating in coke, designated as experiment III, was evaluated by injecting 1.01 g of Mansfield coke into the fuel cell reactor. Figure 6.5 and figure 6.6 presents the MS profiles at the exhaust of the reactor and current produced by the fuel cell during experiment III. The information presented in figure 6.5 and figure 6.6 was used to calculate the energy efficiency, as it is described in the following section.

The thermodynamic efficiency $\xi_T$ was obtained by relating $w_e$, the electrical work performed by the fuel cell, and the enthalpy change of the oxidation reaction $\Delta H$. The electrical work $w_e$ was calculated based on the current produced by the cell at the operating voltage

$$w_e = A \cdot V \cdot \int I(t) \cdot dt$$

where

$$A = \text{Fuel cell active area (cm}^2\text{)}$$

$$V = \text{Fuel cell voltage (Volt)}$$

$$I(t) = \text{instantaneous current density (A/cm}^2\text{)}$$

Resulting in

$$A = 1 \text{ (cm}^2\text{)}$$

$$V = 0.56 \text{ (Volt)}$$

$$\int I(t) \cdot dt = 183 \text{ (C/cm}^2\text{)}$$

$$w_e = 102.8 \text{ (J)}$$
Figure 6.5 MS profiles for gas phase species at the exhaust of the reactor and current produced by the fuel cell during experiment III.
Figure 6.6 MS profile for CO$_2$ (m/e=44) obtained during experiment III.

The enthalpy change of reaction $\Delta H$ was estimated considering the amount of CO$_2$ produced based on the GC results, and the coke lower heating value.

$$
\Delta H = LHV \cdot F_{CO_2} \cdot t \cdot U
$$

where

$LHV = \text{Lower heating value of carbon (J/mol)}$

$F_{CO_2} = \text{CO}_2 \text{ flowrate (mol/s)}$

$U = \text{fuel utilized (\%)}$

$t = \text{time (s)}$

With

$LHV = 355.2 \ (kJ/mol)$

$F_{CO_2} \cdot t = 575 \ \mu\text{mol}$

$U = 100\%$
The thermodynamic efficiency $\xi_T$ was calculated as

$$\xi_T = \frac{102.8 J}{204.2 J} = 50.3\%$$

In addition to the evaluation of the thermodynamic efficiency, the electrochemical efficiency was calculated according to equation (6.2) resulting in

$$V_N = 1.024\ (Volt)$$
$$V = 0.56\ (Volt)$$
$$\xi_V = 0.55\%$$

The net efficiency of the fuel cell operating on coke at 0.56 Volt and 800 °C was calculated according to equation (6.3)

$$\xi_{Net} = \left[ \frac{\Delta G_T}{\Delta H_{298 K}} \right] \times \frac{V(I)}{E^o} \times \mu = 1.003 \times \frac{0.56}{1.024} \times 1 = 54.8\%$$

The efficiency calculations presented during experiment II and experiment III were complemented by introducing the current collection efficiency of the fuel cell. The current collection efficiency $\xi_{collection}$ facilitates the evaluation of the effectiveness of various current collection approaches. The current collection efficiency is defined as the ratio of the charge experimentally measured by impedance spectroscopy and the charge produced by the electrochemical oxidation of the consumed fuel (equation 6.4)
\[ \xi_{\text{collection}} = \frac{I \cdot A}{\left[ \frac{\dot{w}}{M} \right] n \cdot F} \] (6.7)

Where

\[ \xi_{\text{collection}} = \text{current collection efficiency} \]

\[ I = \text{current drawn from the fuel cell} \ (A/cm^2) \]

\[ A = \text{Fuel cell active area} \ (cm^2) \]

\[ \dot{w} = \text{mass flowrate of spent fuel} \ (g/s) \]

\[ M = \text{fuel molecular weight} \ (g/mol) \]

\[ n = \text{number of electrons transfer in oxidation} \]

\[ F = \text{Faraday's constant} = 96500 \ (C/mol) \]

The current collection efficiency of the fuel cell was calculated for the operation on H\(_2\) fuel (experiment II), resulting in

\[ I = 0.437 \ (A/cm^2) \]

\[ A = 1 \ (cm^2) \]

\[ \left[ \frac{\dot{w}}{M} \right] = 172 \ (\mu\text{mol/min}) \]

\[ n = 2 \]

\[ \xi_{\text{collection}} = 78.9\% \]

Similarly, the current collection efficiency was calculated for experiment III, resulting in

\[ \xi_{\text{collection}} = \frac{A \cdot \int l(t) \cdot dt}{\left[ \frac{\dot{w}}{M} \right] \cdot n \cdot F} \]
Where

\[ A = 1 \text{ (cm}^2) \]

\[ \int I(t) \cdot dt = 183 \text{ (C/cm}^2) \]

\[ \frac{w}{M} = 775 \text{ (\mu mol)} \]

\[ n = 4 \]

\[ \eta = 61.2\% \]

The above result was further confirmed by analyzing the amount of CO\textsubscript{2} produced during the experiment by GC. The amount of CO\textsubscript{2} produced during the electrochemical oxidation of coke according to GC was 575 \mu mol resulting in an efficiency \( \xi_{collection} = 82.7\% \). The experimental results suggest the current collection efficiency of the fuel cell can be further improved in order to achieve higher power densities this, enhancing the overall fuel cell efficiency.
CHAPTER VII
DETERMINATION OF THE ENERGY EFFICIENCY OF A Cu/Ni-YSZ SOLID
OXIDE FUEL CELL DURING THE ELECTROCHEMICAL OXIDATION OF
COKE

7.1 Abstract

This chapter presents the results of a study of the direct electrochemical oxidation
of coke in a solid oxide fuel (SOFC) comprising a Cu/Ni-YSZ anode electrode. A
sample of coke, obtained by pyrolyzing Ohio # 5 coal at 950 °C in inert environment,
was fed to the SOFC operating at 800 °C and 1 atm. The fuel cell power generation
characteristics and energy efficiency were determined by measuring the voltage vs
current curves (i.e., V-I curves), and monitoring the composition of the gaseous species at
the outlet of the fuel cell. The Cu/Ni anode was characterized by Scanning Electron
Microscopy (SEM) and Energy Dispersive Spectroscopy EDS). Results from the fuel
cell material and energy balances in batch mode operation revealed the direct
electrochemical oxidation of coke can result in energy efficiencies higher than those
observed with \( \text{H}_2 \), reaching values close to 54.8%. The results obtained during the fuel
cell batch operation will be used to design a series of experiments for the continuous
electrochemical oxidation of coke.

7.2 Introduction

The direct electrochemical oxidation of carbonaceous materials (i.e., coal and
coke) in a SOFC constitutes an attractive approach for the conversion of chemical energy
to electricity, owing to its higher efficiency and low emission of pollutants.
Hydrocarbons and sulfur containing species present in the coal and coke can poison the
anode catalyst of the fuel cell. Therefore, the key issue of developing a carbon fuel cell
(i.e., a solid oxide fuel cell with a direct feed of coal or coke) lies in enhancing the
electrochemical oxidation activity and improving the resistance to deactivation of the
anode.

The majority of the SOFC use a Ni-YSZ anode which has been designed for the
electrochemical oxidation of H$_2$, and is susceptible to deactivation due to formation of
carbon deposits (i.e., coking) [88-91]. Formation of carbon deposits can have a severe
impact on the long term durability of the fuel cell, causing anode electrocatalyst
deactivation and even mechanical failure. Previous studies have shown the direct
electrochemical oxidation of hydrocarbons such as CH$_4$ at 700-800 °C can be carried out
using Cu-based anodes without observing deactivation due to coking.[92]. The
resistance to deactivation of Cu-based anodes has been attributed to its low activity for C-
C bond formation, which is a reaction step leading to coking. The formation of carbon
deposits can be avoided, to a certain extent, by considering the thermodynamic equilibrium of the species present at the high operation temperature of the fuel cell. Figure 7.1 presents a thermodynamic analysis of the deposition of carbon and electrochemical oxidation of CH$_4$ at 750 °C. The thermodynamic calculations have been carried out according by the method proposed by Koh et al [93].

![Equilibrium diagram of carbon and gas species as a function of current density for a feed mixture of dry methane (10 sccm) in nitrogen (150 sccm) at 750 °C.](image)

Figure 7.1 Equilibrium diagram of carbon and gas species as a function of current density for a feed mixture of dry methane (10 sccm) in nitrogen (150 sccm) at 750 °C.

Figure 7.1 shows the formation of carbon can be alleviated by operating the fuel cell at 750 °C and high current densities. Other approaches for reducing or completely eliminate carbon formation on the fuel cell have been investigated, namely (i) selection of
anode materials based on perovskites and oxide materials having oxygen vacancies [94-99], impregnation of metal dopants into the Ni-YSZ anode [100-103], and (iii) use of ceramic-metal anodes such as Cu-CeO$_2$ [104]. The poor catalytic activity of Cu to catalyze the C-C bond formation makes it an ideal candidate for preventing the formation of carbon deposits by blocking the Ni sites. Traditional methods to incorporate metals in a support include impregnation, deposition precipitation, and grafting. These methods result in the incorporation of metal particles onto a support, with uneven metal distribution, and in various oxidation states. Addition of reduced Cu in the Ni-YSZ anode is needed in order to prevent formation of C-C bonding and increasing the electronic conductivity of the anode electrode. In the present study, a Cu/Ni-YSZ anode system has been investigated for the electrochemical oxidation of coke, by adding a Cu(NO$_3$)$_2$ solution into a Ni-YSZ fuel cell (Ni reduced in previous step). Microstructure analysis of the Cu/Ni-YSZ has been performed by scanning electron microscopy (SEM, Quantas 200, FEI) and energy dispersive X-ray diffraction (EDS, EDAX).

7.3 Experimental

Anode supported fuel cells were fabricated according to the procedures described in Chapter III and further discussed in Chapter VI. Briefly, a NiO-YSZ (70 wt % Ni) anode supports, a NiO-YSZ (50 wt % Ni) and YSZ layer were produced by the tape casting and lamination procedure. The resulting multilayer materials were fired at 1400 °C for 4 hours. A LSM-YSZ (50 wt % LSM) layer and a pure LSM layer were successively screen printed and fired at 1100 °C. The Ni-YSZ anode was modified by
addition of aqueous Cu nitrate (15 wt% Cu) solution. Upon addition of Cu solution, the reactor was heated to 110 °C and was kept at that temperature for 10 h with the purpose of removing the majority of water from the Cu solution. The fuel cell was subsequently heated to 800 °C in H₂ and was reduced overnight prior to the electrochemical testing.

The anode supported fuel cells were tested in a steel batch reactor equipped with a gas inlet port, a coke feeding mechanism, and a gas exhaust outlet port connected to the MS and an off stream GC injection port. Prior to each testing experiment, a thin layer of silver (Ag adhesive conductive paste, Alfa Aesar) was coated along the perimeter of the anode with the purpose of enhancing the electric contact between the fuel cell electrode and the steel reactor serving as fuel cell housing and current collector. After pasting the silver layer, the cells were attached to the reactors using an alumina based seal and were provided with a Ag strip connected to a Pd wire for current collection.

7.4 Results and discussion

Prior to the energy efficiency evaluation, the open circuit voltage of the fuel cell was monitored during the initial heating and pretreatment step with the purpose of identifying potential deactivation phenomena. Figure 7.2 presents the MS profiles and the open circuit voltage of the fuel cell during the initial heating procedure. Figure 7.2 shows the fuel cell developed an open circuit voltage of 0.92 volt, which is lower than the reversible voltage at 800 °C, suggesting the presence of small overpotentials during the operation. The nature of the overpotentials presented during the initial heating step can be attributed to the rapid reduction of the Cu/Ni-YSZ anode.
Figure 7.2 MS profiles of gaseous effluents of the fuel cell reactor and open circuit voltage during initial heating of the Cu/Ni-YSZ fuel cell.

**Figure 7.3** presents the performance of the Cu/Ni-YSZ SOFC at 800 °C. Following the initial performance testing, the fuel cell was allowed to operate at 0.65 volts for 12 h (overnight) before initiating the complete testing in H₂ and coke. **Figure 7.4** presents the performance of the fuel cell collected after the 12 h operation at 0.65 volts. Comparison of figures 7.3 and 7.4 reveals a small decay of the maximum current and power densities exhibited by the fuel cell after the operation at 0.65 V for 12 h.
Figure 7.3 Performance of the Cu/Ni-YSZ fuel cell (V-I curve) operating at 800 °C in H₂

Figure 7.4 Performance of the Cu/Ni-YSZ fuel cell (V-I curve) after 12 h of operation at 0.65 V and 800 °C in H₂.
Prior to the evaluation of the energy efficiency, a short experiment, designated as experiment I, was carried out with the purpose of evaluating the optimum H\textsubscript{2} flow rate resulting in the highest possible performance of the fuel cell. The evaluation of the optimum H\textsubscript{2} flow rate could result in an improvement of the fuel cell energy efficiency. During the experiment the cell was allowed to operate at a constant voltage of 0.56 volts while changing the concentration of H\textsubscript{2} in the feed stream. The fuel cell power density was monitored by the Impedance spectrometer, and GC and MS respectively. Table 1 summarizes the highest current density at 0.56 V for various concentration of H\textsubscript{2}.

Table 7.1 H\textsubscript{2} flow rates during experiment I.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>H\textsubscript{2} (cc/min)</th>
<th>He (cc/min)</th>
<th>H\textsubscript{2} (%)</th>
<th>I @ 0.56V (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>23</td>
<td>207</td>
<td>10</td>
<td>268</td>
</tr>
<tr>
<td>B</td>
<td>46</td>
<td>184</td>
<td>20</td>
<td>271</td>
</tr>
<tr>
<td>C</td>
<td>69</td>
<td>161</td>
<td>30</td>
<td>302</td>
</tr>
<tr>
<td>D</td>
<td>92</td>
<td>138</td>
<td>40</td>
<td>324</td>
</tr>
<tr>
<td>E</td>
<td>184</td>
<td>46</td>
<td>80</td>
<td>329</td>
</tr>
</tbody>
</table>

The maximum current density increases with the increase in H\textsubscript{2} concentration from 10 % to 40 % but no change in maximum current density was observed after 40 %. This result suggests that the fuel cell reaches a performance limit and unavailability of the active sites for H\textsubscript{2} electrochemical oxidation causes the stagnant cell performance. The results obtained during experiment I will be used in future studies with the purpose of
evaluating the fuel cell energy efficiency under different flow conditions, and their relation to the development of electrode overpotentials.

Prior to the determination of the energy efficiency the performance of the fuel cell was re-evaluated in order to investigate additional cell overpotentials developed at any of the different operation conditions used in experiment I. Figure 7.5 presents the performance of the cell after the experiment I.

Figure 7.5 Performance of the Ni-Cu fuel cell (V-I curve) operating at 800 °C in H₂ after experiment I.

Figure 7.5 shows the fuel cell did not develop additional overpotentials due to experiment I. However, it is interesting to note the difference in the performance of the Cu/Ni-YSZ fuel cell compared to the Ni fuel cell discussed in Chapter VI. Comparison of the current density of the Cu/Ni-YSZ fuel cell and the Ni-YSZ fuel cell (Chapter VI)
during operation at 0.56 V and 800 °C show a decrease of 25.8% from 0.437 to 0.324 A/cm². The decreased performance of the Cu/Ni-YSZ fuel cell can be attributed to (i) development of overpotentials in the anode due to slower rate of desorption of water from the active sites, (ii) a lower rate of activity of Cu/Ni-YSZ catalyst for H₂ activation comparing to Ni in the earlier case.

The energy efficiency of the fuel cell operating in coke, which has been designated as experiment II, was evaluated by injecting 11.82 g of coke into the fuel cell reactor. During injection, coke was introduced to the purging section of the fuel cell reactor and a 100 cc/min of He stream was flown to remove gas phase O₂ present in the solid fuel. Following the purging step, the hydrogen supply into the fuel cell was suspended, replacing it with a 150 cc/min inert He stream. The solid fuel was subsequently introduced into the anode compartment of the fuel cell reactor and the cell was operated at 0.56 volts while recording the current produced, and the composition of the gas phase species at the outlet of the reactor. The current produced by the fuel cell was monitored using the impedance spectrometer and the composition of the gas phase species at the outlet of the reactor was analyzed using GC and MS. Figure 7.6 presents the MS profiles of major species, and current produced during experiment II. The point label as A, in figure 7.6, correspond to the time when a 100 cc/min He stream was suddenly introduced to the reactor with the purpose of disturbing the coke (i.e., facilitating removal of reacted coke and contact between fresh fuel and the anode electrode).
The energy efficiency of the fuel cell during the electrochemical oxidation of coke was estimated by relating the amount of CO$_2$ produced during the experiment, and the electricity produced by the cell as measured by the impedance spectrometer. The amount of CO$_2$ produced during the injection of coke was estimated by monitoring the composition of the gases at the exhaust of the fuel cell. An initial calculation was carried out using the composition information obtained using MS, and a second calculation was carried out using the composition information obtained with GC.

Figure 7.6 MS profiles for gas phase species at the exhaust of the reactor and current produced by the Cu/Ni-YSZ fuel cell during experiment II.
Figure 7.7 shows the evolution of the MS intensity of CO$_2$ at the outlet of the fuel cell (m/e=44) during experiment II.

![MS Profile](image)

Figure 7.7 MS profile for CO$_2$ (m/e=44) obtained during experiment II on the Cu/Ni-YSZ fuel cell.

Figure 7.8 shows the volumetric flow rate of CO$_2$ at the exhaust of the fuel cell during addition of the coke sample. The volumetric flow rate of CO$_2$ at exhaust of the fuel cell was calculated by converting the mass spectrometry (MS) intensities for the CO$_2$ mass over charge (i.e., m/e = 44) into concentration with the aid of a previously prepared calibration curve. The amount of CO$_2$ produced during the direct electrochemical...
oxidation of the coke sample in the fuel cell according to the mass spectrometry results was 1473 µmol (area under figure 7.7).

Figure 7.8 Volumetric flowrate of CO\textsubscript{2} at the exhaust of the fuel cell reactor during experiment II. CO\textsubscript{2} flow rate was calculated from MS intensity profile with the aid of calibration gas and calibration curve.

The power produced by the cell during the operation on coke was calculated from the following equation, integrating the data from figure 7.6.
\[ w_e = A \cdot V \cdot \int I(t) \cdot dt \]

where

\[ A = 1 (cm^2) \]
\[ V = 0.56 (Volt) \]
\[ \int I(t) \cdot dt = 407.1 (C/cm^2) \]
\[ w_e = 227.9 (J) \]

The enthalpy of the spent fuel was calculated according to the following equation

\[ \Delta H = LHV \cdot F_{CO_2} \cdot t \cdot U \]

where

\[ LHV = lower \ heating \ value \ of \ coke \]
\[ F_{CO_2} \cdot t = Amount \ of \ CO_2 \ produced \]
\[ \Delta H = enthalpy \ of \ spent \ fuel \]
\[ U = fuel \ utilization \ (%) \]

Resulting in

\[ LHV = 292.6 \ (kJ/mol) \quad * \]
\[ F_{CO_2} \cdot t = 1473 \ \mu mol \]
\[ U = 100 \% \]
\[ \Delta H = 430.9 \ J \]

*: Calculated by bomb calorimeter
The thermodynamic efficiency $\xi_T$ was calculated as

$$\xi_T = \frac{w_e}{\Delta H} = \frac{227.9}{430.9} = 52.9\%$$

The amount of CO$_2$ produced by the electrochemical oxidation of coke determined by GC was 1302 µmol leading to an efficiency of 59.8 %.

In addition to the thermodynamic efficiency $\xi_T$, the net efficiency was calculated using the heat of combustion obtained of coke, according to equation (6.3)

$$\xi_{Net} = \left[ \frac{\Delta G_T}{\Delta H_{298 \, K}} \right] \times \frac{V(I)}{E^o} \times \mu = \frac{395.5}{292.6} \times 0.56 \times 1 = 73.9\%$$

The current collection efficiency of the coal fuel cell was calculated according to

$$\xi_{collection} = \frac{A \cdot \int I(t) \cdot dt}{\frac{w}{M} \cdot n \cdot F}$$

$$\int I(t) dt = 407.1 \, (C/cm^2)$$

$A = 1\, (cm^2)$

$\left[ \frac{w}{M} \right] = 1473 \, (\mu mol)$

$n = 4$

$F = 96500 \, (C/mol)$

$\xi_{collection} = 71.5\%$
The current collection efficiency for the amount of CO$_2$ determined by GC is 81.2%.

The current collection efficiency for coke is similar to the observation in the cases previously reported.
CHAPTER VIII
PROMOTING EFFECT OF CERIA ON A SILVER-SAMARIUM STRONTIUM COBALT OXIDE (Ag/SSC) ANODE FOR THE COAL ELECTROCHEMICAL OXIDATION

This chapter presents the results of a study of the promoting effect of Ceria on the activity of a Ag/SSC anode for the electrochemical oxidation of coal. A sample of Ohio # 5 coal was fed into an electrolyte supported solid oxide fuel cell (SOFC) comprising an Samarium doped Ceria (SDC) electrolyte and a Ag/SSC anode. The fuel cell power generation characteristics were determined by measuring the voltage vs current curves (i.e., V-I curves). The Ag/SSC and Ceria-modified Ag/SSC anodes were characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Results from the batch electrochemical oxidation of coal revealed addition of Ce to the Ag/SSC anode improved the activity of the anode catalyst for the electrochemical oxidation of coal. These results will be used for the design of a highly active anode electrode for the continuous electrochemical oxidation of coal.
8.1 Introduction

Direct electrochemical oxidation of carbon in a solid oxide fuel cell (i.e., carbon SOFC) constitutes an attractive approach for the generation of electric power. Electrochemical oxidation of carbon involves the formation of CO\(_2\) by reaction with oxygen ion species (O\(_2^-\)) produced at the cathode electrode of the fuel cell, according to reaction 8.1

\[
C + O_2^- \rightarrow CO_2 \quad (8.1)
\]

Utilization of solid carbon fuel directly inside the SOFC presents challenges due to the difficulty to make physical contact between fuel particles and the anode electrochemical oxidation sites, which results in large resistances and reduced power outputs. One approach to alleviate these high resistances is to increase the operation temperature above 900 °C. Operating the SOFC at elevated temperatures facilitates the formation of carbon monoxide (CO) from carbon. Although the SOFC can oxidize CO, the overall thermodynamic efficiency decreases because of the difference in the number of electron transferred per mol of reactant (i.e., 2 electrons per mol of CO, and 4 electrons per mol in carbon).

Alternatively, the development of novel anode electrodes that possess high oxidation activity could result in reduced charge transfer resistance and increased fuel cell power output. Ceria is a highly active oxidation catalyst employed in a number of applications including three way catalysts. Incorporation of Ceria into the anode electrode of the SOFC could improve the oxidation activity, enhancing the fuel cell performance. In the present study, a Ceria modified anode system has been investigated.
for the electrochemical oxidation of carbon from coal, by adding a Ce nitrate into a Ag/SSC/SDC/SSC fuel cell. Samarium strontium cobalt oxide (SSC) and Samarium doped Ceria (SDC) materials have been selected due to their compatibility with Ceria catalyst.

8.2 Experimental

Electrolyte supported fuel cells comprising a 30 µm thick Ag/SSC-SDC anode, a 350 µm SDC electrolyte, and a 30 µm SSC-SDC cathode were prepared by dry-pressing and screen printing SDC and SSC powders (NexTech Materials). The fabrication of the fuel cells involved: (i) generating a binder-containing SDC powder and an SSC-SDC screen printing paste (70 wt % SSC), (ii) uniaxially pressing the binder-containing SDC at a pressure of 120 MPa in a steel die with the shape of a disc (20 mm diameter), (iii) sintering the pressed discs at 1500 °C for 4 hr, (iv) screen printing the SSC-SDC paste onto the anode and cathode side of the sintered discs and (v) firing at 900 °C for 4 hr.

The binder-containing SDC powders were prepared by ball milling a slurry containing SDC, menhaden fish oil dispersant, polyvinyl butyral (Butvar, PVB B-79) binder, and 2-propanol solvent. The slurry was dried at 90 °C, grinded with a ceramic mortar, and screened with a 100 mesh sieve until obtaining a fine powder. The SSC-SDC paste was prepared by mixing SSC and SDC powders (70 wt % SSC) with polyethylene glycol (Sigma Aldrich, PEG wt 550) until forming a viscous paste.
Ag was added to the fired SSC-SDC anode by infiltrating a solution of ethanol and silver nitrate (0.03 M AgNO₃, 150 µg Ag per cm²) and firing the resulted electrode at 800 °C for 2 hr. Current collectors were attached to the cells by adhering Pt paste and Pt paste (Engelhard, A3788A). The cells were sealed to alumina tubes with the aid of ceramic cements (i.e., Ceramabond 571). Figure 8.1 presents a schematic representation of the coal fuel cell housing and testing approach.

![Figure 8.1](image_url)

Figure 8.1 Experimental apparatus for the Ag/SCC-SDC fuel cell.

Ceria was infiltrated into the Ag/SSC-SDC anode after testing the cell in H₂ fuel. An ethanol/cerium nitrate solution (0.06 M Ce(NO₃)₃, 6 ml) was added into the anode compartment, and the cell was subsequently heated to 70 °C overnight to remove the alcohol. The fuel cells were placed inside a furnace and were heated to 600 °C at heating rate of 1°C/min in flowing 20 sccm of hydrogen. The current vs voltage and current vs power curves of the fuel cells (i.e., V-I and P-I curves) were recorded at 600, 700 and 750
°C using a LabVIEW software. The testing of the coal fuel cells was carried out by loading a 1.0 g coal sample (Ohio #5 coal) in to the anode compartment, heating the cell in flowing H₂ and He flow, and suspending the H₂ flow before recording the (I-V and I-P) curves. The microstructure of the cells was characterized with by scanning electron micrographs (SEM, Quanta 200 FEI), and energy dispersive X-Ray spectroscopy (EDS, Edax). The crystalline structure of the Ag/SSC-SDC electrode was invesigated by X-Ray Diffraction (XRD, Phillips APD 3700).

8.3 Results and Discussion

Figure 8.2 shows the XRD patterns of the SSC-SDC and Ag/SSC-SDC anode, exhibiting the characteristic peaks of the SSC perovskite and the SDC fluorite structure [105-107] without the formation of additional phases during the fabrication procedure.

Figure 8.2 X-ray diffraction patterns of the SSC-SDC and Ag/SSC-SDC anode electrode.
The presence of Ag on the Ag/SSC-SDC anode was not detected in the diffraction pattern due to the low relative intensity of the Ag metal peaks for concentrations lower than 1 wt% [108], and their proximity to those peaks of the perovskite structure.

Figure 8.3 presents the SEM micrograph and EDS elemental mapping of the cross-section of the fuel cell prior to the \( \text{H}_2 \) and coal testing, revealing the grain morphology and microstructure of the Ag/SSC-SDC anode. The good attachment of the anode and electrolyte layers, achieved by the densification of SDC on both layers, produced interconnected structures that can be observed from the Ce and Sm mapping profiles. These interconnected structures can lead to the formation of highly conductive ionic paths. The mapping profiles reveal the formation of Ag particles with an average grain size of 9 µm estimated from the image analysis.

![Figure 8.3: Microstructure and element distribution of cross-section of the cell prior to testing in \( \text{H}_2 \): (left) SEM micrograph of Ag/SSC-SDC anode electrode, and (right) corresponding EDS elemental mapping.](image)

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Figure 8.4 (a) shows the performance of the fuel cell (i.e., $I-V$ and $I-P$ curves) at 600, 700, and 750 °C with H$_2$ as fuel. Increasing the temperature from 600 to 700 °C caused a 2.8 times increase on the fuel cell maximum current density, accompanied by a slight improvement on the open circuit voltage.

![Graph showing cell voltage and power density as functions of current density for fuel cells operating with Ag/SSC and Ce-Ag/SSC anode electrodes.](image)

Figure 8.4 Cell voltages and power densities as a function of current density for the fuel cells operating with (a) a Ag/SSC anode electrode and (b) a Ceria promoted Ce-Ag/SSC anode electrode.
Further increasing the temperature to 750 °C decreased the fuel cell open circuit voltage and $I_{\text{max}}$, suggesting the development of electronic conductivity of the SDC electrolyte by reduction of Ceria. The marked convex up curvature of the $I$-$V$ curve at 750 °C, a characteristic attributed to the mixed ionic-electronic conducting properties of ceria [109], further indicates the reduction of Ceria upon exposure to H$_2$ gas at 750 °C.

Figure 8.4 (b) reveals addition of Ceria to the Ag/SSC-SDC anode significantly improved the fuel cell performance in H$_2$ fuel, reaching a maximum current density $I_{\text{max}}$ of 270 mA/cm$^2$ at 750 °C. The area-specific resistances (ASR) of the cell was calculated from the $I$-$V$ curves, as shown in Table 1.

Table 8.1 Area-specific resistances (ASR) of the cell.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>H$_2$</th>
<th>Coal</th>
<th>H$_2$</th>
<th>Coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>13.8</td>
<td>-</td>
<td>-</td>
<td>21.8</td>
</tr>
<tr>
<td>700</td>
<td>3.8</td>
<td>-</td>
<td>1.08</td>
<td>3.9</td>
</tr>
<tr>
<td>750</td>
<td>4.0</td>
<td>-</td>
<td>0.79</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Figure 8.5 shows the performance of the fuel cell modified by addition of Ceria operating in coal as fuel at 700 and 750 °C. The fuel cell produced an OCV of 0.75 and maximum current density of 91 mA/cm$^2$ at 700 °C. Increasing the temperature to 750 °C increased the fuel cell $I_{\text{max}}$ and OCV to 156 mA/cm$^2$ and 0.83 V, respectively. The performance of the fuel cell decayed after 2 h of operation, suggesting the consumption
of coal due to the semi batch operation. Attempts to measure the performance of the coal fuel cell without the addition of Ceria proved futile, and only a small OCV could be detected.

Figure 8.5 Cell voltages and power densities as a function of current density for the fuel cells with Ag/SSC anode electrode.
CHAPTER IX

CONCLUSIONS

9.1 Photocatalytic oxidation

The reaction pathway for the photocatalytic oxidation of ethanol and acetaldehyde was found to be dependent on the content of H₂O on the TiO₂ catalyst. In situ IR studies showed that ethanol photooxidation on low H₂O content TiO₂ proceeded via a parallel/series reaction pathway involving formation of CH₃COO⁻_ad and CH₃CHO_ad intermediates, and their subsequent conversion to CO₂. Separate experiments showed the evolution of CO₂ from CH₃CHO_ad photooxidation was preceded by the formation of either CH₃COO⁻_ad or HCOO⁻_ad, being the second species more rapidly converted to CO₂. The increasing of the content of H₂O on TiO₂ causes a sharp decrease on the rates of formation of ethanol to CH₃COO⁻_ad, and CH₃COO⁻_ad, as well as on the subsequent CH₃CHO_ad-photooxidation. As a result, the overall rate of CO₂ is reduced and CH₃CHO_ad is accumulated on the surface of the catalyst. The hypothesis that the content of H₂O on the TiO₂ photocatalyst reduced the rate of ethanol photocatalytic oxidation was verified.
9.2 Effect of CH$_3$OH sacrificial reagent over the photocatalytic evolution of H$_2$O

Addition of CH$_3$OH sacrificial reagent enhanced the rate of H$_2$ formation from aqueous solutions under UV illumination and contributed a small amount of its hydrogen atoms to the overall rate of H$_2$ formation. The low rate of H$_2$ formation from D$_2$O/CH$_3$OH solutions indicate that the hole scavenging reaction of CH$_3$OH does not proceed to an appreciable extent under diluted CH$_3$OH concentrations. Instead, the scavenging process would result from reaction with H$_2$O molecules producing free hydroxyl radical (·OH) and injecting electrons to the conduction band, increasing the potential for the evolution of H$_2$.

9.3 Electrochemical oxidation of carbon and hydrocarbons

The activity of the Ni/YSZ anode for the electrochemical oxidation of coke and hydrocarbons was investigated. The performance of the Ni-YSZ fuel cell was evaluated during the continuous operation in H$_2$, and the batch operation in coke, resulting in fuel cell energy efficiencies of 40 and 55 %, respectively. Evaluation of the current collector efficiency $\xi_{c\text{-collection}}$ indicates the fuel cell has not reached its full potential and further improvements on the current collection approach are needed. Future studies will include the development of alternative approaches for current collection focusing on enhancing the current collection efficiency, and reducing current collector cost. Current collectors for the anode and cathode electrodes will be characterized by microscopy techniques and impedance spectroscopy.
The incorporation of Cu on Ni/YSZ anode by impregnation of Cu(NO$_3$)$_2$ is an effective technique to improve activity of the Ni-YSZ anode catalyst for towards the direct electrochemical oxidation of hydrocarbons and carbon in the solid oxide fuel cell. Impregnation of Cu(NO$_3$)$_2$ into the Ni-YSZ anode allows the copper species to deposit on the surface of the Ni substrate, providing good contact with the fuel cell anode, as evidenced by the SEM study of the Cu/Ni-YSZ anode. The addition of Cu to the Ni-YSZ anode increased the activity for the electrochemical oxidation of carbon and hydrocarbons, resulting in fuel cell energy efficiencies as high as 73.9 %, as measured during the operating of the fuel cell at 800 °C and 1 atm, in flowing an inert Argon stream. The hypothesis that addition of Cu to the Ni-YSZ anode could facilitate the operation of the fuel cell in carbon and hydrocarbon fuels, resulting in higher energy efficiencies was verified.

Studies carried out on electrolyte supported SDC fuel cells revealed addition of ceria to a Ag/SSC anode electrode promotes the electrochemical oxidation of coal, resulting in higher power outputs. Characterization of the fuel cell microstructure of the fuel cell indicated addition of Ceria into the Ag/SSC anode electrode did not caused structural damages (i.e., microcracks) due to differences in thermal expansion coefficients. Future studies will be carried out to determine the long term durability of the Ce-Ag/SSC anode electrode.


[55] H.S. Fogler, Elements of chemical reaction engineering. Prentice-Hall PTR,
1535-1538.


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APPENDICES
APPENDIX A

DETERMINATION OF THE HEAT OF COMBUSTION OF OHIO #5 COAL
AND COKE

A.1 Introduction

The heat of combustion of the Ohio #5 coal and coke was experimentally determined using an adiabatic oxygen bomb calorimeter with the purpose of improving the accuracy of the energy efficiency calculation for the coal-based fuel cell.

A.2 Experimental

The heat of combustion of coke and coal was evaluated using a 1241 adiabatic oxygen bomb calorimeter operating with a 1108 oxygen combustion bomb (Parr Instrument Company, Moline, Illinois). The coal and coke particles were grinded in a pestle and mortar until obtaining a fine powder. The resulting powders were subsequently shaped in the form of a pellet (dia=1 cm) by introducing them in a steel die and applying a pressure of 5000 lb/inch$^2$ using an isobaric press. In the case of coke, a
combustion aid (Benzoic acid, combustion standard, Parr) was mixed with the powder in order to facilitate ignition.

A.3 Results

Figure A.1 presents a sequence of images describing the experimental procedure for the operation of the adiabatic oxygen bomb calorimeter during heat of combustion measurement. The heat of combustion of the coke and coal samples was calculated according to the procedures described in the following section.

A.3.1 Assembly of the data for coal

\[ t_a = \text{Temperature at time of firing, corrected for thermometer scale error as read from the correction chart supplied with the Parr calorimetric thermometer. (} t_a = 24.579 \degree \text{C}). \]

\[ t_f = \text{Temperature at time of firing, corrected for thermometer scale error as read from the correction chart supplied with the Parr calorimetric thermometer (} t_f = 27.647 \degree \text{C}). \]

\[ c_1 = \text{Milliliters of standard alkali solution used in acid titration (} c_1 = 24.2 \text{ ml)}. \]

\[ c_2 = \text{Percentage of sulfur in sample (} c_2 = 1.04\% \) \]

\[ c_3 = \text{Centimeters of fused wore consumed in firing (} c_3 = 7.4 \text{ cm)} \]

\[ W = \text{Energy equivalent of calorimeter in calories per degree Celsius (} W = 2403.2 \text{ cal/}\degree \text{C)} \]

\[ m = \text{Mass of sample in grams (} m = 1.0016 \text{g)} \]

\[ t = \text{Temperature rise during the experiment (} t = t_f - t_a \text{ (} t = 3.068 \degree \text{C)} \]

\[ e_1 = \text{Correction in calories for heat of formation of nitric acid (HNO}_3\text{) (} e_1 = 24.2 \text{ cal)} \]

\[ e_2 = \text{Correction in calories for heat of formation of sulfuric acid (} e_2 = 14*1.04*1.0016 = 14.58 \text{ cal)} \]
e_3 = Correction in calories for heat of combustion of fuse wire (e_3=2.3*7.40 = 17 cal)

Gross Heat of combustion

Heat of combustion is calculated according to equation A1.1

\[
H_g = tW - e_1 - e_2 - e_3
\]

\[
H_g = \frac{(3.068 \times 2403.2 - 24.2 - 14.58 - 17)}{1.0016}
\]

\[
H_g = 73,055 \text{ cal/g}
\]

\[
H_g = 13,140 \text{ Btu/lb}
\]

A.3.2 Assembly of the data for coke

Sample composition:
Coke = 51.643 wt%
Benzoic acid = 48.357 wt%
Heat of combustion Benzoic acid = 6318 cal/g

\(t_a\) = Temperature at time of firing, corrected for thermometer scale error as read from the correction chart supplied with the Parr calorimetric thermometer. \(t_a=21.943^\circ C\).

\(t_f\) = Temperature at time of firing, corrected for thermometer scale error as read from the correction chart supplied with the Parr calorimetric thermometer \(t_f=22.965^\circ C\).

\(c_1\) = Milliliters of standard alkali solution used in acid titration \((c_1=24.2 \text{ ml})\).

\(c_2\) = Percentage of sulfur in sample \((c_2 =1.04\% )\)

\(c_3\) = Centimeters of fused wore consumed in firing \((c_3 =7.4 \text{ cm})\)

\(W\) = Energy equivalent of calorimeter in calories per degree Celsius \((W=2403.2 \text{ cal/}^\circ C)\)
m = Mass of sample in grams (m=0.3977g)

t = Temperature rise during the experiment t= t_f - t_a (t= 1.022 °C)

e_1 =Correction in calories for heat of formation of nitric acid (HNO_3) (e_1=24.2 cal)

e_2 =Correction in calories for heat of formation of sulfuric acid

(e_2=14*1.04*0.51643*0.3977 = 2.99 cal)

e_3 =Correction in calories for heat of combustión of fuse wire (e_3=2.3*7.40 = 17 cal)

e_4 =Correction in calories for heat of combustión of combustion aid

(e_4=6318*0.48357*0.3977=1215.05)

Gross Heat of combustión

Heat of combustión is calculated according to equation A1.1

\[ H_g = \frac{tW - e_1 - e_2 - e_3}{m} \]

\[ H_g = \frac{(1.022 \times 2403.2 - 24.2 - 2.99 - 17 - 1215.05)}{0.51643 \times 0.3977} \]

\[ H_g = 5,827.3 \text{ cal/g} \]

\[ H_g = 10,489 \text{ Btu/lb} \]

The heat of combustion obtained by bomb calorimeter is 13,149 Btu/lb for coal and 10,489 Btu/lb for coke.
Figure A.1 Experimental procedure for the operation of the calorimeter. (a) cold pressed coke pellet sample, (b) sample mounted on the bomb head (c) detail of the fuse wire (45C10 Parr Nickel alloy wire) in contact with the sample, (d) oxygen bomb assembled, (e) charged oxygen bomb, 30 atm O₂, (f) oxygen bomb loaded in calorimeter bucket (g) empty bomb head after the experiment.
B.1 Introduction

Photocatalytic oxidation of organics on TiO$_2$ has long been shown to occur via generation of light-induced charge carriers (i.e., electron/hole pairs), and charge transfer reactions of electrons and holes to species adsorbed on the surface. Transient spectroscopic studies have demonstrated that charge carrier generation and charge transfer reactions occur in time scales of femtoseconds and nanoseconds, whereas the overall conversion of organics to CO$_2$ and H$_2$O occur in a time scale of min to hours. The factors governing the slow conversion of reactants and the rate-determining steps in photocatalytic reactions have seldom been studied. We have determined the rate-determining step in the photocatalytic oxidation of ethanol by an in situ infrared (IR) spectroscopy coupled with mass spectrometric method. Ethanol was selected as a model molecule for tracing the reaction pathways because it produces IR–observable adsorbed species and possesses the ability to displace adsorbed H$_2$O, slowing down electron and hole recombination.
B.2 Experimental

The reaction steps involving O₂ and IR-observable species were studied by illuminating adsorbed ethanol on TiO₂ (p25, Degussa) with UV light (25 mW/cm²) and dosing small amounts of O₂ (i.e., pulsing 10-500 µl of O₂) into a 15 cm³/min He stream flowing through the DRIFT cell. The experimental apparatus for the photocatalytic oxidation of ethanol consisted of (i) a DRIFT cell (Harrick scientific HVC-DRP) enclosed by a dome with two IR transparent ZnSe windows and a CaF₂ window for UV illumination, (ii) a 350 W mercury lamp (Oriel 6286) with a light condenser (Oriel 77800), (iii) a gas manifold connected to an ethanol saturator for admission of He and ethanol vapors, and (iv) a gas tight septum for addition of 10-500 µl ultra-high purity O₂ (Praxair, 99.999%) pulses. A thin 15-mg layer of TiO₂ (p25, Degussa) was placed on top of 60 mg of inert CaF₂ powder in the DRIFT cell’s sample holder. The thin catalyst layer was used to minimize the changes in IR intensity due to species adsorbed on dark fractions of the catalyst (i.e., not illuminated). The intensity of the UV light was measured with a thermopile detector (818P-001-12, Newport), connected to a hand-held optical meter (1918-C, Newport). Single beam IR spectra were recorded by an FTIR spectrometer (DigiLab FTS 4000), co-adding 20 scan at a resolution of 4 cm⁻¹. The spectra were obtained in the form of absorbance, log(I/I₀), using an appropriate single beam reference sample for I₀. The amount of CO₂ evolved during the photooxidation experiments was quantified by a gas chromatograph (GC, SRI 8610C) equipped with a Helium Ionization Detector (HID), and was correlated with the IR intensity of the band at 2350 cm⁻¹.
B.3 Results and discussion

Ethanol was adsorbed on the TiO$_2$ by flowing a 15 cm$^3$/min ethanol/He stream (10.3 mol % mol ethanol) through the DRIFT cell for 10 min, followed by purging of gaseous ethanol with He (15 cm$^3$/min) for 20 min. Figure B1 shows the IR spectra recorded during adsorption of ethanol on the TiO$_2$.

![IR spectra recorded during adsorption of ethanol on TiO$_2$ at 30 °C.](image)

Figure B.1 IR spectra recorded during adsorption of ethanol on TiO$_2$ at 30 °C.

The top spectrum in Figure B2 (a) (i.e., spectrum at 0 min) shows ethanol adsorbed as ethoxy (CH$_3$CH$_2$Oad) and molecularly adsorbed ethanol (CH$_3$CH$_2$OH$_{ad}$), giving the increased (i.e., positive) C-H bands at 2971, 2931, and 2870 cm$^{-1}$. The
formation of CH$_3$CH$_2$O$_{ad}$ can be distinguished by the intense $\nu$(C-O) band at 1147 cm$^{-1}$ and the low intensity ratio of $\delta$(OH)/$\delta$(CH$_3$). The appearance of the ethanol bands was accompanied by the decreased (i.e., negative) OH stretching band at 3632 cm$^{-1}$ and the HOH bending at 1625 cm$^{-1}$, indicating that adsorption of ethanol displaced H$_2$O and consumed the OH groups on the TiO$_2$. The initial surface coverage was determined to be 820 µmol/g TiO$_2$ for adsorbed ethanol/ethoxy, and 980 µmol/g TiO$_2$ for H$_2$O$_{ad}$. 

Figure B.2 IR spectra recorded during photocatalytic oxidation of ethanol. (a) Ethanol adsorbed on the TiO$_2$ prior to and during UV illumination and O$_2$ pulses. (b) Variation of the IR intensity at 2000 cm$^{-1}$, MS profile of O$_2$ concentration, and volume of O$_2$ pulsed and adsorbed; the latter shown in µl in parenthesis.
The spectrum at 0.6 min in Figure B2 (a) shows that UV illumination caused the decrease of the ethanol C-H bands and the rise of an IR structure-less background absorbance in the 3000–1000 cm\(^{-1}\) range (i.e., background shift), attributed to photogenerated electrons accumulating on the conduction band. The absence of variation in the IR intensity of the H2O and OH bands during this period indicates that the decrease of the C-H bands was the result of the reaction of CH\(_3\)CH\(_2\)O\(_{\text{ad}}\)/CH\(_3\)CH\(_2\)OH\(_{\text{ad}}\) with h\(_+\) (i.e., holes), allowing accumulation of the photogenerated electrons giving the intense background shift. The changes on the intensity of the background shift were followed by plotting the IR intensity at 2000 cm\(^{-1}\) (I\(_{2000}\)). Figures B3 and B4 presents the IR spectra recorded during the first 5 min of UV illumination, and addition of 50 µl of O\(_2\), respectively.

Figure B.3 IR spectra recorded during the first 5 min of UV illumination of ethanol on TiO\(_2\), showing the increase of the background shift.
Pulsing O$_2$ on ethanol adsorbed on the TiO$_2$ caused a decrease in the extent of the background shift intensity, as shown by the spectrum at 30 min in Figure B2 (a), indicating that O$_2$ directly reacted with photogenerated electrons. Subsequent O$_2$ pulses (e.g. spectrum at 76 min) produced similar changes on the background shift intensity accompanied by the formation of adsorbed acetate (CH$_3$COO$^-_{ad}$) at 1542 and 1441 cm$^{-1}$, adsorbed H$_2$O and CO$_2$. The reaction process for producing these IR-observable species can be described by the following proposed scheme.

\[
\begin{align*}
\text{CH}_3\text{CHO}^+_\text{ad} & \rightleftharpoons \text{CH}_3\text{CO}^-\text{ad} \\
\text{CH}_3\text{CH}_2\text{O}^+_\text{ad} & \rightleftharpoons \text{CH}_3\text{CHO}^-\text{ad} \\
\text{O}_2^-\text{ad} & \rightarrow \text{O}_2^+\text{ad} \\
\text{O}_2^+\text{ad} & \rightarrow \text{H}_2\text{O}^+\text{OH}^{-}
\end{align*}
\]
The oxygen adsorption step and its interaction with photogenerated electrons 
\((\text{O}_{2\text{ad}} + e^- \rightarrow \text{O}_2^-)\) can be further examined by comparing the intensity of the background shift, measured as the IR absorbance intensity at 2000 cm\(^{-1}\) \((I_{2000})\) and the \(O_2\) concentration profile, as presented in Figure B2 (b). Expanding the initial IR intensities versus time in the inset of Figure B2 (b) shows the rapid rise in \(I_{2000}\), accompanied by the gradual decay of the C-H intensity, highlighting the fact that the process of electron and hole generation is significantly faster than the hole-abstracting reaction \((\text{CH}_3\text{CH}_2\text{O}_{\text{ad}} + h_+ \rightarrow I_{\text{CH}_3\text{CHO}_{\text{ad}}})\). \(I_{\text{CH}_3\text{CHO}_{\text{ad}}}\) would be a common intermediate for the formation of \(\text{CH}_3\text{COO}^-_{\text{ad}}, \text{CH}_3\text{CHO}_{\text{ad}},\) and \(\text{CH}_3\text{CO}_{\text{ad}}\). The presence of such intermediate can be inferred from the observation of the evolution of \(\text{CH}_3\text{COO}^-_{\text{ad}}\) at 1542 and 1441 cm\(^{-1}\), which preceded that of \(\text{CH}_3\text{CHO}_{\text{ad}}\) at 1718 cm\(^{-1}\), and \(\text{CH}_3\text{CO}_{\text{ad}}\) at 1650 cm\(^{-1}\), as shown in Figure B5.

Each \(O_2\) pulse caused the adsorption of \(O_2\) and the sudden decrease in \(I_{2000}\) followed by a gradual recovery to nearly its initial intensity. Since the \(\text{TiO}_2\) temperature and the irradiation intensity is constant, the rate of photoelectron and hole generation is expected to be constant. Thus, the decrease in the extent of the \(I_{2000}\) recovery can be attributed to (i) the reaction of \(O_2\) and electrons \((O_2 + e^- \rightarrow O_2^-)\), and (ii) an increase in the rate of electron and hole recombination. The \(O_2^-\) produced can react with OH groups or \(H_2O\) on the \(\text{TiO}_2\) surface to form oxygen reactive intermediates (\(O^*_{\text{int}}\)) such as hydroxyl radicals (\(\cdot\text{OH}\)). Although we do not have direct evidence of the formation of these oxygen intermediates, their formation has been well established. The \(O^*_{\text{int}}\) can further react with \(I_{\text{CH}_3\text{CHO}_{\text{ad}}}\) or \(\text{CH}_3\text{CO}_{\text{ad}}\) to produce \(\text{CH}_3\text{COO}^-_{\text{ad}}\) \((\text{CH}_3\text{CO}_{\text{ad}} + O^*_{\text{int}} \rightarrow \text{CH}_3\text{COO}^-_{\text{ad}})\) and ultimately \(\text{CO}_2\), through the Koble reaction.
Figure B.5 Evolution of intermediates during the photocatalytic oxidation of ethanol. (a) Difference IR spectra of adsorbed species and CO$_2$. (b) Variation of the coverage of adsorbed species as a function of UV illumination time. The dotted line represents the cumulative coverage of O$_{2\text{ad}}$ and the continuous black line the resulting IR intensity at 2000 cm$^{-1}$ ($I_{2000}$) after each O$_2$ addition.
The formation of CH$_3$COO$^-_{\text{ad}}$ and CH$_3$CO$^-_{\text{ad}}$ can be unambiguously determined by the difference IR spectra in Figure B5 (a), which were obtained by subtracting spectra exhibiting the same I$_{2000}$ intensity. The IR intensities of CH$_3$COO$^-_{\text{ad}}$, the major intermediate of the reaction, were further calibrated with those of adsorbed ethanol and CO$_2$ to convert them to the quantities shown in Figure B5 (b).

Figure B5(b) shows formation of CH$_3$COO$^-_{\text{ad}}$ preceded that of CH$_3$CHO$_{\text{ad}}$, suggesting the abundance of $h^+$ and O$^*_{\text{int}}$ for reacting with I$_{\text{CH$_3$CHO}}$. In turn, CH$_3$CHO$_{\text{ad}}$ can only be formed when O$_2$ adsorption is limited, as shown in pulse 9. The O$_2$$_{\text{ad}}$ from the first three pulses, which corresponds to 494 µmol/g TiO$_2$, caused a 5.3% decrease of I$_{2000}$ with the formation of negligible CO$_2$/H$_2$O and 31% of the final acetate coverage. The subsequent 3 pulses reduced 9.3% of I$_{2000}$ and produced additional 17.6% of the final acetate coverage. This observation indicates that (i) the initial O$_2$$_{\text{ad}}$ fills those TiO$_2$ surface sites which do not have a significant influence on the electron and hole recombination rate and (ii) sufficient coverage of O$_2^-$ is needed to increase the rate of electron and hole recombination and initiate formation of CH$_3$COO$^-_{\text{ad}}$ and H$_2$O. Further O$_2$ additions did not increase the O$_2$$_{\text{ad}}$ coverage, but resulted in a significant increase in the formation of CH$_3$COad, CO$_2$ and H$_2$O with a slight decrease in I$_{2000}$. As the coverage of O$_2$$_{\text{ad}}$ approached 640 µmol/g TiO$_2$ and the accumulation of acetate reached 300 µmol/g TiO$_2$, the addition of a large O$_2$ pulse at 90 min produced little changes in O$_2$$_{\text{ad}}$ and formation of CH$_3$COO$^-_{\text{ad}}$ and CO$_2$, indicating that the oxygen adsorption step is a rate-limiting step. In conclusion, IR coupled with MS method showed that oxygen adsorption step controls the overall reaction process; this step is further slowed down by the presence of the stable acetate on the TiO$_2$ surface. The effective removal of carboxylate
species from the catalyst holds the key to accelerate the rate of photocatalytic oxidation of organics. This study bridges the gap between the results of nanosecond and millisecond time transfer adsorption studies and that of min scale photocatalytic oxidation studies.