INVESTIGATION OF ACTIVE SITES AND REACTION NETWORKS IN CATALYTIC HYDROGEN PRODUCTION: STEAM REFORMING OF LOWER ALKANES AND THE WATER-GAS SHIFT REACTION

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

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* * * * *

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Steam reforming (SR) of hydrocarbons and water-gas shift (WGS) are of importance in hydrogen generation technologies due to recent attention focusing on fuel cells. Current research efforts have focused on catalyst development to improve activity, selectivity, and stability under a realistic range of operating conditions. Although coke formation is a major concern for Ni-based catalysts when used for hydrocarbon steam reforming, their low cost and long-proven performance warrants further investigation. Moreover, hydrogen and fuel cell technologies will greatly benefit from innovative high-temperature shift (HTS) catalyst formulations that can overcome some serious drawbacks (i.e., low activity at low temperatures, sintering of magnetite (Fe₃O₄), a pyrophoric nature, and the harmful effects of Cr⁶⁺ on human health).

In this Ph.D. study, lanthanide-promoted Ni/Al₂O₃ catalysts and Fe-based catalysts promoted with first row transition metals were synthesized by a modified sol-gel technique and a coprecipitation method, respectively. The effect of synthesis variables on the catalyst properties (i.e., BET surface area, reducibility, crystallite size, crystal structure, oxidation states, adsorption/desorption behavior, and surface intermediates during the reaction) and, in turn, on the catalytic performance in SR of lower alkanes and
the WGS reaction has been investigated. Catalysts were characterized by BET surface area and pore size distribution measurements, temperature-programmed desorption/reduction/oxidation (TPD/TPR/TPO), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), static chemisorption, transmission electron microscopy (TEM), thermogravimetric analysis (TGA).

The introduction of small amounts (2 wt%) of Ce and Yb in sol-gel Ni/Al₂O₃ catalysts improves SR activity significantly by enhancing Ni surface area, reducibility of Ni species, and Ni sintering resistance. In addition, the incorporation of Ce in Ni/Al₂O₃ catalysts results in the reduction of carbon dissolution/diffusion through nickel crystallites, thus preventing catalyst deactivation by coke formation. Formulations of highly active and Cr-free HTS catalysts can be achieved by adding both Al and Cu. The activity of Fe-based catalysts is strongly related to catalyst reducibility, magnetite crystallite size, and redox characteristics. More detailed characterization has provided additional insights into phase transformations, surface intermediates, and reaction/deactivation mechanisms, giving further evidence of the modification of the properties and performance of catalysts through optimized synthesis.
Dedicated to my mother, Wannaporn Natesakhawat
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CHAPTER 1

INTRODUCTION

Hydrogen is the ultimate clean energy carrier. When it is combusted, heat and water are the only products. The use of hydrogen as a fuel for fuel cell-powered vehicles can greatly reduce greenhouse gas emissions from internal combustion engines. Moreover, development of affordable hydrogen fuel cells will help reduce our nation’s dependence on foreign oil, leading to an increased national energy security. Thus, hydrogen offers a potentially non-polluting, inexhaustible, efficient, and cost attractive fuel for today’s rising energy demands [1]. Currently, steam reforming of natural gas, which is composed mainly of methane, is used to produce most of hydrogen in the U.S. and about half of the world’s hydrogen supply. Naphtha fractions with a final boiling point of less than 220 °C are also considered as suitable feedstocks [2]. However, supported Ni catalysts suffer from catalyst deactivation by coke formation more severely when higher hydrocarbons are reformed at low steam/carbon ratios. Although supported precious metals such Pd, Pt, and Rh have been reported to be active and stable for steam reforming of hydrocarbons, cost of the precious metals is still a major issue. The low-cost and long-proven performance of Ni-based catalysts, therefore, warrant the efforts to optimize these catalysts for more demanding steam reforming applications. On-board
steam reforming of hydrocarbons for proton exchange membrane (PEM) fuel cell-powered vehicles has attracted much attention. Widespread applications of fuel cells in transportation will depend on the development of an effective and efficient fuel processing technology from existing liquid fuels such as gasoline and diesel especially during transition to hydrogen economy. Therefore, development of novel Ni-based catalysts with superior performance and stability for the steam reforming process is essential.

A potential alternative that makes use of our nation’s most abundant fossil fuel resource, coal, to produce hydrogen is an attractive prospect. In fact, coal gasification may be one of the best ways to produce clean-burning hydrogen for tomorrow’s automobiles and power-generating fuel cells [www.fossil.energy.gov]. It is a process that converts coal from a solid to a gaseous fuel through partial oxidation [3]. Depending on operating conditions, processes, and coal rank, the raw coal gas from a gasifier consists primarily of CO, H₂, CO₂, CH₄, H₂O, H₂S, COS, and nitrogen compounds. The gas is further purified to remove impurities for the final use.

The Department of Energy (DOE) has demonstrated Integrated Gasification Combined-Cycle (IGCC) operation to produce power, fuels, and chemicals from coal. This advanced technology is proposed to be one of the most efficient and cleanest available technologies for coal-based power generation, with emissions comparable to those of natural gas-based power production as indicated in the U.S. DOE Topical Report# 21 [4]. At present, IGCC processes are aimed at direct combustion of synthesis gas after particulate and H₂S removal. Production of chemicals such as methanol and diesel-grade hydrocarbons from syngas is also an important market worldwide [5].
However, wide applications of the IGCC technique will require significant advances in some of the steps that follow gasification. Especially developing efficient processes for hydrogen production from syngas will bridge the gap between coal utilization and fuel cell technology.

In hydrogen production, the WGS reaction remains as a technology that would benefit from innovative approaches such as development of highly active, sulfur-tolerant, and Cr-free catalytic systems. Additionally, DOE’s Clean Coal Technology (CCT) program highlights the need for advanced water-gas shift reactors using sulfur-tolerant catalysts to produce hydrogen from synthesis gas at lower cost. [www.fe.doe.gov]. Figure 1.1 demonstrates a conceptual process where gasified coal is converted to hydrogen rather than being directly combusted. The sulfur in the gasified stream is in the form of H$_2$S, which is much easier to separate by scrubbing than SO$_2$. The sensible heat of the effluent gas from the gasifier can also be used through a heat exchanger to heat steam or the effluent from the scrubber. If the activity of WGS catalysts is high enough, high CO conversion levels can be achieved at lower temperatures. If hydrogen production is desired for PEM fuel cell operation, further purification or separation of hydrogen would be needed. However, if it is targeted for Solid Oxide Fuel Cells (SOFC), hydrogen can be used without any further purification. For stationary power generation, solid oxide fuel cell applications are much more relevant.
Figure 1.1: WGS integrated in the IGCC system for H₂ Production
Generally, the steam reforming process involves the reaction of hydrocarbons with steam (Reactions 1 and 2) on supported Ni catalysts at 500-950 °C. It is accompanied by the water-gas shift (WGS, Reaction 3) and methanation reactions (Reaction 4) as follows:

\[
C_nH_{2n+2} + nH_2O \rightleftharpoons nCO + (2n+1)H_2 \quad (1)
\]

\[
C_nH_{2n+2} + 2nH_2O \rightleftharpoons nCO_2 + (3n+1)H_2 \quad (2)
\]

\[
CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (3), \quad \Delta H (298 K) = -41.2 \text{ kJ/mol}
\]

\[
CO + 3H_2 \rightleftharpoons CH_4 + H_2O \quad (4), \quad \Delta H (298 K) = -206.2 \text{ kJ/mol}
\]

Both WGS and methanation reactions are exothermic and become significant at lower temperatures. In general, the overall reaction enthalpy of alkane steam reforming is still positive and heat needs to be supplied. The equilibrium composition of gaseous products depends on temperature, pressure, and the molar ratio of water to alkane. In practice, steam reforming of hydrocarbons is performed at high temperature and low pressure. However, the high temperature required may also favor several routes to carbon products (Reactions 5-8) such as the Boudouard reaction and methane/hydrocarbon decomposition.

\[
2CO \rightleftharpoons C + CO_2 \quad (5)
\]

\[
CH_4 \rightleftharpoons C + 2H_2 \quad (6)
\]

\[
CO + H_2 \rightleftharpoons C + H_2O \quad (7)
\]

\[
C_nH_{2n+2} \rightleftharpoons nC + (n+1)H_2 \quad (8)
\]

Further comprehensive reviews on thermodynamics of alkane steam reforming can be found in the literature [2, 6-8]. The equilibrium composition of the products can
be calculated at different ratios of steam to carbon and operating conditions using published thermodynamic data in the literature [6, 8]. For example, Figure 1.2 shows the equilibrium compositions of propane steam reforming at \( \text{H}_2\text{O}/\text{C}_3\text{H}_8 = 4 \) where significant carbon formation is below 700 °C. The main products of propane steam reforming at higher temperatures are \( \text{H}_2 \) and CO with small amounts of \( \text{CO}_2 \). On the other hand, methane-rich gases are produced at lower temperatures. It should be noted that, however, these calculations only predict the equilibrium concentrations and do not provide any information about the kinetic rates of various reaction steps involved in the network.

In practice, it is the kinetics rates that determine the concentration of various reaction products. As a result, coking is encountered at higher steam-to-carbon conditions than what thermodynamics predicts. In addition, carbon observed under actual reaction conditions may be in various forms of gas-phase and surface-grown with properties quite different than those of graphite [9]. Therefore, thermodynamic data can only give an initial starting point and kinetics of the many constituents representing different molecular weights and aromaticity present in liquid fuels must be considered in the experimental determination of coking characteristics. Generally, excess steam/carbon ratios of 3.5-4.5 are used to prevent coke formation but minimal water input needs to be considered to provide a higher \( \text{H}_2 \) concentration.
Figure 1.2: Equilibrium compositions in steam reforming of propane at $T = 400-1000\,^\circ C$ and $H_2O/C_3H_8 = 4$. 
The WGS reaction (Reaction 3) is an important step in the production of H₂, where CO, which is produced from steam reforming or coal gasification, is reacted with water to give H₂ and CO₂. The water-gas shift reaction is exothermic and thermodynamically limited at high temperatures. The thermodynamic equilibrium constant, Kₚ, as defined by $K_p = \frac{P_{\text{H}_2} P_{\text{CO}_2}}{P_{\text{CO}} P_{\text{H}_2} \text{O}}$. The exothermic nature of the reaction makes the activity of the catalyst at lower temperatures very important since at higher temperatures conversion is limited by thermodynamic equilibrium, as seen in Figure 1.3, which is constructed for three different ratios of CO and H₂O in the feed mixture. The equilibrium conversion is independent of pressure for this reaction. In addition to their activity, another consideration for WGS catalysts is their selectivity, since methanation (Reaction 4) is a competing reaction that can lower the selectivity.

Key challenges for development of novel catalytic systems include carbonaceous deposit formation particularly at lower steam/carbon ratios, short lifetimes due to loss of active surface area and metal agglomeration under steam reforming and WGS conditions, sulfur tolerance, and resistance to other poisons found in the feed stream. Current research focuses on synthesis, formulations, and characterization of catalysts designed to meet these challenges. Solving the hydrogen generation problems will ultimately help drive advancements in fuel cell technology, which brings a hydrogen energy future much closer to reality.
Figure 1.3: CO conversion as a function of T and H₂O/CO molar ratio in the WGS reaction.
CHAPTER 2

LITERATURE REVIEW

2.1 Steam reforming of hydrocarbons

Hydrocarbon steam reforming has been a process of major importance for production of hydrogen, synthesis gas, and town gas for several decades. Classical steam reforming is the process by which methane, and other hydrocarbons in natural gas, is converted into hydrogen and carbon monoxide by reaction with steam over a nickel catalyst on a ceramic support. The hydrogen and carbon monoxide are used as feedstock for many other industrial processes. Generally, Ni-based catalysts are industrially used in hydrocarbon steam reforming due to their fast turnover rates, long-term stability, and low cost [2, 8]. However, in practice, the process industry of steam reforming faces many challenges. The major concern is catalyst deactivation by coke formation and, to a lesser extent, thermal sintering at high operating temperatures. Supports and promoters play an important role on the prevention of coke formation. Alkalis such as K₂O and CaO are introduced into Ni-based catalysts to enhance carbon gasification and suppress olefin adsorption, which leads to carbon deposition. Basic supports such as MgAl₂O₄, CaAl₂O₄, BaAl₂O₄, and Al₂O₃ containing lanthanide elements have gained wide interest since they were reported to be successful in steam reforming of C₂-C₄ [7, 8]. The introduction of
certain additives such as lanthanides (i.e., uranium, lanthanum, and cerium) into nickel catalysts has also shown an improvement in resistance to coking. Therefore, innovative approaches to catalyst promotion, which can minimize catalyst coking but maintain their activity, are of great importance.

This chapter provides an overview of catalytic hydrogen production from steam reforming of hydrocarbons and the water-gas shift reaction. Catalyst deactivation by coke formation during steam reforming, different approaches to control coking, and the role of promoters or supports on coke minimization are also discussed. Further detailed reviews on steam reforming of hydrocarbons and the WGS reaction can be found elsewhere [1, 2, 7, 8, 10-19].

2.1.1 Methane Steam Reforming

**Thermodynamics**

The reversible steam reforming reaction of methane ($\Delta H^\circ_{298} = 206$ kJ/mol) is highly endothermic. The forward reaction is favored at high temperature and low pressure. On the other hand, the WGS reaction ($\Delta H^\circ_{298} = -41.2$ kJ/mol) is exothermic and becomes significant at lower temperature. In general, the overall reaction enthalpy of methane steam reforming is still positive and heat needs to be supplied. The main products of the steam reforming reaction at higher temperatures are CO and H$_2$. In contrast, methane-rich gases are produced at lower temperatures. The equilibrium composition of gaseous products depends on temperature, pressure, and the molar ratio of
water to methane. Further comprehensive reviews on thermodynamics of methane steam reforming can be found in the literature [2, 6-8].

**Kinetics**

The kinetics of methane steam reforming on nickel catalysts has been extensively studied [2, 8, 20-22]. It is widely accepted that the reaction is first order with respect to methane concentration. However, the values of the activation energies were reported to be in a wide range of 20-160 kJ/mol, depending on the influence of pore diffusion and heat transfer limitations.

Bodrov et al. [20] studied the kinetics of methane steam reforming on nickel foil at 800-900 °C and atmospheric pressure using a circulation-flow reactor. The rate of methane decomposition was found as follows:

\[ r = kP_{CH_4}/[1+a(P_{H_2O}/P_{H_2}) + bP_{CO}] \]

At 800 °C, a and b were 0.5 and 2.0 atm\(^{-1}\) and at 900 °C, a and b were 0.2 and 0 atm\(^{-1}\), respectively. The activation energy of the reaction was 130 kJ/mol. It was concluded that the reaction of methane with steam was much faster than the decomposition of methane to carbon on the nickel surface, which was the rate-determining step. Al-Ubaid et al. [21] investigated the kinetics of catalytic steam reforming of methane over nickel on supports with different acidities at 450-550 °C. The order of decreasing acidity of supports is Y-zeolite > Ni aluminate > (Ni, Ca) aluminate. The positive “effective” order of methane steam reforming with respect to steam was observed for the most acidic support (Y-zeolite). A dual-site mechanism, in which steam and methane were adsorbed on different active sites, was suggested. On the other hand,
negative “effective” reaction order with respect to steam was found for the less acidic support. It was suggested that steam and methane were competitively adsorbed on the same active sites (single-site mechanism), thus giving a non-monotonic dependence of the rate of reaction on reactant concentration.

Luna and Becerra [22] studied the kinetics of methane steam reforming on a commercial Ni on alumina-titania catalyst at 500-600 °C. A Hougen-Watson kinetic model was proposed and was in good agreement with the experimental rates. In addition, the results supported the mechanism of methane steam reforming proposed by Rostrup-Nielsen [8], that is, steam simultaneously adsorbs on both the nickel surface and the support and oxygen subsequently spills over to the nickel.

**Catalysts**

As mentioned earlier, supported nickel catalysts are preferred for most commercial steam reforming applications. However, other catalysts such as ZrO$_2$-supported metals and supported Pd, Pt, and Rh catalysts have also been reported to be active and stable for methane steam reforming and are discussed in the following section.

**Supported Nickel Catalysts**

The introduction of certain additives such as potassium and oxides of rare earth metals (i.e., uranium, lanthanum, and cerium) into nickel catalysts has shown an improvement on their resistance to coking. Although potassium-promoted catalysts, widely used in industry, can prevent catalyst coking, their activity decreases during steam reforming. Borowiecki and Golebiowski [23] investigated the influence of molybdenum
and tungsten additives on the properties of nickel steam reforming catalysts. A Ni/Al₂O₃ catalyst containing 0.5 wt% WO₃ or MoO₃ was found to retain its catalytic activity in methane steam reforming as opposed to the potassium-promoted nickel catalyst. However, the beneficial effect of the molybdenum addition is still unclear since Ni/Al₂O₃ catalyst (3 wt% MoO₃) was also reported to increase the rate of carbon deposition in CO methanation by one order of magnitude. Moreover, it is known that the morphology and mechanism of the formation of carbon deposits in steam reforming of hydrocarbons and CO methanation are quite similar [24].

Borowiecki et al. [25] further investigated the effects of small MoO₃ additions on the properties of nickel catalysts for steam reforming of hydrocarbons. It is interesting that an introduction of small amounts of molybdenum compounds (≤0.1 wt% MoO₃) considerably reduced the rate of carbon deposition but increased the activity of methane steam reforming. Furthermore, with higher amounts of MoO₃, the activity decreased more slowly than the reduction of the coking rate. The authors also stated that the activity of Ni-Mo/Al₂O₃ catalysts depended on the ratio of hydrogen to steam in the reaction mixture; the maximum in activity moved towards higher H₂ contents when the amounts of molybdenum increased.

Zhuang et al. [26] investigated the effect of cerium oxide as a promoter in supported nickel catalysts for methane steam reforming. It showed a positive effect by decreasing the rate of carbon deposition, thus maintaining the catalytic activity during the induction period and in the constant carbon deposition region. Su and Guo [27] also reported a significant improvement in the stability and the high temperature steam resistance of Ni/Al₂O₃ catalysts doped with rare earth oxides. The growth of Ni particle,
the oxidation of active component Ni, and the formation of NiAl₂O₄ were suppressed by the addition of rare earth oxides, thus significantly reducing the catalyst deactivation. Also, the heavy rare earth oxides had a more distinct effect than the light ones.

The advantages of magnesia as a support for nickel steam reforming catalysts were examined [28]. Compared to nickel supported on alumina, nickel-magnesia catalysts showed similar initial specific activities but considerably minimized coke formation. It is believed that magnesia enhances coke gasification on the catalyst surface, thereby preserving the active sites for steam reforming.

The deactivation of Ni/Al₂O₃ catalysts by sintering during methane steam reforming at 500 and 800 °C was studied [29]. High temperature, the presence of steam, and nature of solid phases upon sintering of nickel crystallites were found to be the important parameters. The authors concluded that the combined action of steam and high temperature enhanced the rate of sintering of small nickel crystallites, particularly for narrow initial crystallite size distributions and high initial dispersions. The beneficial effect of lanthanum as a promoter is suggested to be inhibiting the metal crystallite growth under reduction and reaction conditions. The effect of hydrogen on catalyst deactivation by sintering was also reported [30]. An introduction of 2 vol% H₂ in the feed gas mixture at 589 °C had a negative impact on the activity of a Ni/Al₂O₃ catalyst due to continuous and irreversible deactivation by sintering of Ni particles. At 744 °C, a decrease in activity was still observed but was stabilized over 130 h and then recovered by stopping the H₂ addition.

The coupled methane oxidative conversion and steam reforming (CMOCSR) process was performed over a NiO-CaO catalyst to develop the methane-to-syngas
The catalyst was chosen due to its high activity, selectivity, and productivity in the oxidative conversion of methane to CO and H₂. The benefit of this process was that little or no external energy is needed since the process is mildly exothermic. However, the effect of process variables on oxygen conversion and CO selectivity is quite complex. Choudhary et al. [32] further investigated simultaneous steam and CO₂ reforming of methane to syngas over supported NiO/MgO in the presence and absence of oxygen. This study emphasized the importance of the afore-mentioned CMOCSR process in that it can be efficient and safe by manipulating the reaction temperature and/or the concentration of O₂ in the feed. Furthermore, methane can be converted to syngas with desirable H₂/CO ratio (close to 2.0) by controlling the relative concentrations of steam and CO₂ in the feed.

To produce CO-free hydrogen for fuel cells and other processes that are sensitive to CO poisoning, stepwise methane steam reforming has been developed. The two-step process, which involves the catalytic decomposition of methane to produce CO-free hydrogen (step I) followed by the steam gasification of the surface carbon on Ni/zirconia catalysts (step II), has been proposed [33]. It was concluded that no CO was observed in the products from step II and that this process, which was operated in cycles, could provide an excellent source of hydrogen. Subsequently, Choudhary and Goodman [34] continued their work by optimizing the reaction conditions of this process such as temperature and carbon coverage. High temperatures were found to have a detrimental effect on step II while an increase in the coverage of surface carbon had a negative impact on its removal. As a result, the optimum temperatures and carbon surface
coverage were found to be of 375-400 °C and of 0.10-0.20 monolayer equivalents (MLEs), respectively.

Other Catalysts

Although nickel catalysts have many advantages as mentioned earlier, they are not resistant to carbon formation, causing a major drawback in their industrial use. Therefore, it is essential to develop alternative catalysts, which are active but more coke-resistant. York et al. [35] developed molybdenum and tungsten carbides as catalysts for methane steam reforming using stoichiometric feedstocks at slightly elevated pressures. Surprisingly, the catalysts were extremely active and stable for more than 72 h. Furthermore, no carbon deposition was observed.

In addition, zirconia-supported catalysts have been reported to be effective in many processes such as CO₂ reforming of methane, partial oxidation of methane, and combined steam and CO₂ reforming. Catalysts containing 1 wt% of Co, Cu, Fe, Ni, Pd, and Pt supported on zirconia were tested for methane steam reforming at 400-800 °C [36]. The Pt, Pd, and Ni catalysts showed highest activity but only the Pt catalyst remained stable at 800 °C due to higher resistance to carbon deposition. The Pt/ZrO₂ catalyst was also found to be active and stable for both CO₂ reforming and partial oxidation of methane.

Porous metal/ceramic catalysts based on powdered aluminum and lanthanum nickelate mixture were also reported to be active and stable. Tikhov et al. [37] studied the impact on the specific catalytic activity of pore structure formation of porous composite materials based on Al/Al₂O₃. The phase composition of the active component
precursor was found to be the most important parameter for high activity; the catalysts containing ceramic perovskite as a precursor showed much higher activity and CO selectivity than those prepared by a plasma thermolysis technique.

2.1.2 Steam reforming of higher hydrocarbons

Thermodynamics

The overall steam reforming of hydrocarbons is generally endothermic since Eq. (1) is strongly endothermic (\(\Delta H^{\circ}_{298} = 1,108 \text{ kJ/mol} \) for n-heptane). Like methane steam reforming, it is desirable to perform steam reforming of hydrocarbons at a high temperature and low pressure. As a result, the water-gas shift reaction is inhibited by high temperature but largely unaffected by pressure [2]. The equilibrium composition of the products can be calculated at different ratios of steam to carbon and operating conditions using published thermodynamic data in the literature [7, 8].

It is known that energy requirements for steam reforming of higher hydrocarbons is very flexible depending on the reaction conditions [16]. By manipulating temperature and molar ratios of steam to hydrocarbon, the overall reaction enthalpy may be positive or negative. For example, the overall process is exothermic (\(\Delta H^{\circ}_{298} = -47.9 \text{ kJ/mol} \) at a relatively low temperature of 450 °C and a steam/naphtha ratio of 2.0. On the other hand, the process becomes endothermic (\(\Delta H^{\circ}_{298} = 102.9 \text{ kJ/mol} \) at higher temperatures and higher steam/naphtha ratios (i.e., 800 °C and 3.0, respectively).

However, carbon formation is of greater concern in steam reforming of hydrocarbons. In practice, excess steam/carbon ratios of 3.5-4.5 are used to favor the
reforming reaction. Furthermore, methanation begins to dominate at low steam/carbon ratios and the overall reaction can be exothermic under certain process conditions of temperature and pressure [2].

**Kinetics**

Rostrup-Nielsen [38] studied the kinetics of ethane steam reforming at atmospheric pressure and 500 °C over various catalysts. A difference in the kinetics of the reaction was influenced by steam partial pressure, which was related to the catalyst composition. Magnesia-supported and alkali-promoted catalysts were found to enhance steam adsorption. For a Ni/MgO catalyst, the following rate expression was obtained:

\[
r = 20p_{C2H6}\left[1 + 30p_{C2H6}p_{H2}/p_{H2O} + 1.26 \times 10^{-2} p_{H2O}/ p_{H2}\right]^2
\]

where \( r \) [\( \text{mol/m}^2 \text{(Ni) h} \)] and \( p \) [\( \text{Mpa} \)].

In addition, a mechanism for steam reforming of hydrocarbons was proposed in the same study. It was assumed that hydrocarbon was adsorbed on a dual active site, followed by successive \( \alpha \)-scission of the C-C bonds. The resulting C\(_1\) species subsequently reacted with adsorbed steam to yield CO and H\(_2\).

Tottrup [39] investigated the macrokinetics of steam reforming of n-heptane on a commercial Ni/MgO catalyst at 450-550 °C and 5-30 bar. The rate of reaction was strongly influenced by internal diffusion and was found to be:

\[
r = k_a \left(p_{C7H16}\right)^{0.6}\left(p_{H2O}\right)^{-0.1}\left(p_{H2}\right)^{0.2}
\]

where \( k_a \) was the apparent rate constant and the apparent activation energy was 38.3 kJ/mol.
Phillips et al. [40] investigated the kinetics and mechanism of steam reforming of n-hexane and n-heptane over a nickel-alumina catalyst at 360-450 °C and 200 psig. The reaction rate was found to be proportional to \((\text{pC}_{6}\text{H}_{14} \text{ or pC}_{7}\text{H}_{16})^{0.3}\) and the activation energy for the reaction was \(21\pm1\) kcal/mol. A Langmuir model was applied to the kinetic data and the relative reaction rates were strongly influenced by the relative adsorption coefficients of the reactants. Muraki and Fujitani [41] studied the kinetics of steam reforming of n-heptane over a Rh/MgAl\(_2\)O\(_4\) catalyst at 400-500 °C. The observed initial reaction rate was best expressed by a Langmuir-type equation with the adsorption equilibrium constant for n-heptane and water of 111 and 0.712 atm\(^{-1}\), respectively. Furthermore, the reaction between n-heptane adsorbed on rhodium metal and adsorbed steam on the spinel surface was found to be the rate-determining step. CO was a primary product whereas both CO\(_2\) and CH\(_4\) were secondary products. More kinetic studies for steam reforming of hydrocarbons can be found elsewhere [7, 8].

**Catalysts**

*Supported Nickel Catalysts*

The introduction of MgO to Al\(_2\)O\(_3\) in Ni catalysts has been known to improve the catalytic properties such as activity, stability, and resistance to coking. However, the role of MgO on enhancement in reaction performance is unknown. Borowiecki [42] investigated the effects of calcination and reduction conditions on the phase composition and the resistance to coking of the Ni/MgO-NiO-Al\(_2\)O\(_3\) catalysts for steam reforming of n-butane. Calcination and reduction temperatures were found to strongly affect the nickel crystallite sizes and the phase composition of the catalysts. A phase of solid
solution rich in NiO was observed with a rise in calcination temperatures but a fall in the degree of NiO reduction. In addition, higher reduction temperatures were found to increase the degree of NiO reduction. It was concluded that the optimum calcination and reduction temperatures were 400 and 500 °C, respectively. Furthermore, a phase of solid solution MgO-NiO (rich in MgO) and a MgO phase suppressed the rate of carbon deposition of the catalyst while that of solid solution NiO/MgO (rich in NiO) enhanced coking.

Borowiecki [43] further examined direct and indirect factors affecting the coking rate. Nickel dispersion and phase composition of the support were found to have the direct effect on the coking rate. On the other hand, other variables connected with preparation procedures such as catalyst composition and preparation conditions indirectly affected the catalyst coking. The structure of carbon deposits on Ni/Al₂O₃ and Ni/MgO catalysts during steam reforming of n-butane at 400-680 °C was subsequently studied [44]. The similar carbon structures, which were true filaments, tubes, and shells, were observed on both catalysts. The dependence of temperature on the created forms and their degree of graphitization was also observed. Moreover, the arrangement of the carbon layers in the deposits was strongly affected by the shape of the nickel particles. It was suggested that rate of catalyst coking did not affect the morphology of carbon deposits formed.

The introduction of small amounts of molybdenum (≤ 1.0 wt%) into the Ni-Mo catalysts has shown the increase in their resistance to coking [45-47]. This was likely due to lower rates of carbon deposit formation caused by the addition of molybdenum as a promoter [45]. In addition, the gasification of carbonaceous deposits on the catalyst
surface was found to depend on the composition of the reaction mixture. The presence of N₂ in steam showed highest rate of the deposit removal whereas the lowest rate was obtained with further addition of H₂ (H₂O: H₂ = 1:1). However, the rate of gasification was unaffected by the presence of molybdenum in the H₂ + N₂ mixture.

Kepinski et al. [47] investigated carbon deposition on Ni/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts during steam reforming of n-butane. Ni-Mo/Al₂O₃ catalyst showed a remarkable reduction in coke deposition with much lower numbers of Ni particles observed in the carbon filaments growth. Furthermore, the morphology of carbon was found to be similar on both catalysts.

A beneficial effect of small amounts of molybdenum in the Ni catalysts was examined during steam reforming of n-heptane [46]. The mechanism of improved coking resistance of catalysts promoted with molybdenum was proposed as follows: Mo⁺ⁿ on the nickel surface was initially oxidized to Mo⁺(n+2), which then reacted with adsorbed Ni-C or Ni-CHₓ yielding CO and H₂, and was finally reduced back to Mo⁺ⁿ. It was believed that only a few atoms of Mo⁺ⁿ could significantly increase the oxidation of adsorbed Ni-C or Ni-CHₓ, thus preventing the accumulation of carbon on the nickel surface.

As mentioned earlier, magnesia as a support has been known to reduce catalyst coking via the enhancement of gasification by steam. The benefits of magnesia for nickel steam reforming of ethane and propane were established by O. Sidjabat and D.L. Trimm [28]. Ni/MgO catalysts were found to deactivate much slower than Ni/Al₂O₃ catalysts and performed even better with the presence of H₂. Also, the preparation method for magnesia did not strongly affect the catalytic activity and coking rate.
Hydrogen generation for PEM fuel cell-powered vehicles from heavy and more complex hydrocarbon fuels such as gasoline and diesel has gained much attention. Coke formation and sulfur poisoning over Ni-based catalysts become even more serious when heavy hydrocarbons are steam reformed. Moon et al. [48] investigated POX reforming (or autothermal reforming, ATR) of iso-octane with/without 100 ppm sulfur and of reformulated naphtha over a commercial ICI naphtha reforming catalyst (NRC). The NRC catalyst did not show coke deposition at 700 °C, $\text{H}_2\text{O}/\text{C} = 3$, and $\text{O}/\text{C} = 1$ over 24 h. However, the NRC catalyst deactivated from sulfur poisoning when 100 ppm sulfur (thiophene) was introduced into the iso-octane feed. The authors concluded that a preferential partial oxidation (PROX) reactor for CO conversion and highly coke- and sulfur-resistant catalysts are needed to successfully develop a gasoline fuel processor.

Hydrogen production by partial oxidation and steam reforming (POSR) of n-octane over alumina-supported Ni catalysts has been reported [49, 50]. n-Octane conversion and $\text{H}_2$ selectivity were strongly affected by Ni loading and reaction parameters such as reaction temperature and $\text{O}_2/\text{C}_8\text{H}_{18}$ ratio [50]. An increase in these parameters resulted in an increase in n-octane conversion and $\text{H}_2$ selectivity at $\text{H}_2\text{O}/\text{C} = 3.0$. However, 5 wt% Ni/\gamma-Al$_2$O$_3$ catalysts deactivated rapidly at 750 °C mainly due to carbon deposition. The presence of Pd in the Ni-based catalysts significantly improved the catalytic performance and stability. However, SEM and TGA results did not show any differences between the fresh and deactivated catalysts.

While scarce literature exists on the use of catalyst systems for hydrogen production from gasoline and diesel fuels, additional insight into the performance of Ni-based catalysts for heavy feedstocks can be obtained from examining the literature related
to the steam reforming of oils. Wang et al. [51, 52] investigated the production of H₂ from biomass by catalytic steam reforming of fast pyrolysis oils over commercial Ni-based catalysts. Hydrogen yields as high as 85% of the stoichiometric value were achieved from steam reforming of poplar oil aqueous fraction at 750 °C. Furthermore, the catalysts were easily regenerated by steam or CO₂ gasification of carbonaceous deposits at 800 °C for 12 h. A variety of research and commercial Ni-based catalysts were tested in the catalytic steam reforming of bio-oils derived from pyrolysis of biomass [53]. It appeared that Ni-Co and Ni-Cr catalysts supported on MgO-La₂O₃-Al₂O₃ were the best performing catalysts. The addition of Co or Cr was believed to modify the existing nickel metal sites by forming alloys that led to smaller crystallite size. Marquevich et al. [54-56] studied steam reforming of sunflower oil for hydrogen production over a commercial Ni-based catalyst. Although the catalyst showed some deactivation, the activity was restored after gasification of the carbon deposits.

Other Catalysts

It has been known that rhodium and ruthenium catalysts are more active than nickel catalysts for steam reforming of ethane and n-heptane. Thus, in many studies, they are used at higher space velocities. Kikuchi et al. [57] investigated the effect of the rhodium dispersion on catalytic activity of rhodium supported on γ-alumina for steam reforming of n-heptane. The specific activity was found to strongly depend on the dispersion of rhodium, that is, the activity decreased when the dispersion of rhodium increased. It was suggested that the proportion of active face atoms, as opposed to corner and edge atoms, decreased with an increase in the rhodium dispersion.
Barbier and Duprez [58] studied steam reforming of propane with and without oxygen over Pt-Rh catalysts supported on CeO$_2$/Al$_2$O$_3$. The Pt (1 wt%)-Rh (0.2 wt%) catalyst was found to be the most active. The catalyst was initially active and deactivated completely after 12 h time-on-stream. The authors concluded that platinum, which was intrinsically inactive, significantly increased the activity of rhodium in the bimetallics, hence showing a synergistic effect. Moreover, CeO$_2$/Al$_2$O$_3$-supported catalysts showed much higher activity than those supported only on ceria. In addition, the catalysts were more stable during the reforming reaction with the presence of oxygen in the reactant mixture. Maillet et al. [59] further investigated oxy-steam reforming of propane on a Pd/Al$_2$O$_3$ catalyst. Pd was found to be more thermally resistant than Pt and Rh. It was suggested that the addition of steam in propane oxidation was not necessary due to its inhibition effect. However, steam protected an active PdO$_x$ species from reduction into a less active phase, Pd$^{0}$, below 400 °C.

### 2.1.3 Catalyst Deactivation by Coke Formation

Due to high operating temperatures during alkane steam reforming, catalyst deactivation by coke formation cannot be avoided. As a result, understanding the mechanism of coke formation and exploring any measures to control coking are considerably significant. Studies of coke formation on supported nickel catalysts have been of interest for the last two decades [23-28, 42-47, 60-69].

Although more studies have reported on the positive effect of promoters or supports on coke minimization, still more studies need to be conducted. The following
section reviews the important aspects of carbon and coke formation (i.e., mechanism, carbon morphology, thermodynamics, kinetics) and discusses different approaches to control coking and the role of promoters or supports on coke minimization.

**Carbon and Coke Formation**

*Mechanism and Morphology*

Carbon is described as a product of CO disproportionation or the Boudouard reaction [reaction (5)] while coke is produced by decomposition or condensation of hydrocarbons on metals [24]. At high temperatures, coke formation via reactions (6) and (7) become insignificant whereas reactions (5) and (8) are favored. Also, the rate of carbon formation depends on the nature of the feed. Furthermore, the different routes to carbon formation affect the morphology of the carbon and how easily it may be gasified. The most common types of carbon observed in steam reforming are whisker-like, encapsulating, and pyrolytic [8]. Whisker-like carbon is formed at temperatures approximately greater than 450 °C. Basically, its formation is involved with the diffusion of carbon through Ni crystals and the nucleation and whisker growth with Ni crystals at the top. However, whisker carbon does not deactivate the catalyst but it will eventually break the catalyst surface down and increase the pressure drop. Unlike whisker-like carbon, encapsulating carbon films are formed by slow polymerization of C\textsubscript{n}H\textsubscript{m} radicals on Ni surface at temperatures below 500 °C. The catalyst is then deactivated continuously. Pyrolytic carbon originates from thermal cracking of hydrocarbons. It subsequently deposits on the catalyst surface and encapsulates the catalyst particles. Not surprisingly, its effects are catalyst deactivation and an increase in pressure drop.
Moreover, carbon deposits via CO decomposition can be further divided into five forms, depending on their reactivity and temperature of formation: adsorbed atomic carbon (\(C_\alpha\)), amorphous carbon (\(C_\beta\)), vermicular carbon (\(C_v\)), bulk Ni carbide (\(C_\gamma\)), and crystalline, graphitic carbon (\(C_\gamma\)) [24].

*Thermodynamics*

Calculations based on thermodynamic data can be used to estimate the amount of carbon formed in equilibrium with gaseous products at any specific values of O/H ratio, temperature, and pressure. Nonetheless, any deviations from the calculation at equilibrium can occur. For example, although the equilibrium composition is predicted to form no carbon, it may be formed due to poor activity or selectivity of the catalyst under steady-state condition [24]. Likewise, based on the bulk gas temperature, no carbon formation is predicted when the temperature of the catalyst surface is higher than that of the bulk gas.

In addition, the effects of temperature, pressure, composition, and carbon type on equilibrium carbon deposition isotherms were investigated [24]. It was found that carbon fraction had the most impact on the carbon-forming boundary. The tendency to form carbon decreased when water or hydrogen was added. At moderate temperatures and high pressures, amorphous carbon could be produced from H\(_2\)/CO mixtures. On the other hand, H\(_2\)O/CH\(_4\) mixtures could form graphitic carbon at low pressures and very high temperatures.

It is noted that thermodynamics of carbon formation is independent of catalyst composition, promoters, and supports whereas its kinetics is strongly influenced by these
factors. Furthermore, since graphitic carbon is mainly formed in steam reforming at the typical operating conditions, thermodynamic data for graphite are more applicable to this process over the catalysts containing relatively large metal particles. However, any deviation needs to be considered when amount of carbon is predicted from the thermodynamic data for small crystallite catalyst systems.

Kinetics

Although carbon is largely deposited by CO disproportionation, little information on its kinetics is known. More detail on two comprehensive kinetic studies can be found in [24]. In general, the forward reaction is favored at temperatures below 700 °C. The catalytic activity of carbon formation depends on metals in the following order: Fe > Co > Ni. Also, the temperature-dependent rate of carbon formation was found to be zero to first order in the concentration of CO.

Adsorbed atomic carbon ($C_\alpha$) is so highly reactive that most can be further gasified to reduce coking with a suitable ratio of steam/carbon in the feedstock. However, some of $C_\alpha$ can be converted to less active amorphous carbon ($C_\beta$) via polymerization and rearrangement of $C_\alpha$. Subsequently, $C_\beta$ may be gasified or converted to different carbon forms by encapsulation of the catalyst surface and dissolution into the nickel crystallite. Therefore, understanding of the kinetics of the various reactions of $C_\alpha$ and $C_\beta$ is of significance since it can be used to predict the extent of coking.
Coke Minimization

Different Approaches to Control Coking

Two different approaches to control coking have been proposed and explained in terms of the mechanism of coke formation: the ensemble size control and the prevention of carbide formation [66, 67].

The concept of the ensemble size control is to minimize coking by controlling the number of surface sites required for coke formation. It is known that coke formation is involved with a carbonaceous intermediate, which is produced from reactions (5)-(8). Therefore, coke minimization could be accomplished by controlling the selectivity of the reaction that favors steam reforming rather than coke formation [67]. Furthermore, it is suggested that coke formation demands more surface sites than steam reforming. The benefit of this approach has been emphasized by adding traces of sulfur in the feed to create correct size ensembles. When suitable amounts of sulfur are adsorbed on the catalyst surface, coke formation could be prevented at the expense of catalytic activity. Consequently, careful control of sulfur levels in the feed is of great concern to avoid poisoning the catalyst surface.

On the other hand, the prevention of carbide formation could also suppress coke formation since carbide was suggested to be an essential intermediate in carbon dissolution and precipitation. Doping with small amounts of metals to form an alloy on the catalyst surface could possibly reduce carbide formation, thus significantly reducing coke formation. However, although surface segregation may occur, formation of the
alloy with a dopant does not necessarily follow [67]. Moreover, the impact of nickel carbide formation on coke formation is still unknown.

It is known that a catalyst may lose its activity to some extent when alkali or alkali-earth elements are added as promoters to suppress carbon deposition [8]. However, cerium oxide-containing nickel catalysts were found to suppress the rate of carbon deposition but maintain their activity during the induction period and in the constant carbon deposition region [26]. The promoting effect of cerium oxide was suggested to occur via a redox mechanism. Cerium oxide may dissociatively adsorb water and enhance the reaction of steam with adsorbed species on the nickel surface to quickly yield the products. A significant improvement in the stability and high temperature steam resistance of rare earth oxide-promoted Ni/α-Al2O3 catalysts were confirmed by the work of Su and Gao [27]. It was found that the presence of rare earth oxides retarded the growth of Ni particle size and the transformation of active components to unreducible NiO and NiAl2O4, thus suppressing the catalyst deactivation.

Trimm [67] further explored the kinetics of steam reforming and carbon formation over supported nickel catalysts doped with various amounts of tin. It was concluded that small amounts of tin (less than 1.75 wt% Sn) had a minor effect on steam reforming while coke formation was greatly reduced even with 0.5 wt% of tin addition. Also, the supported nickel catalyst with 1.75 wt% Sn was the best performing catalyst showing the highest rate of steam reforming compared to that of coke formation among various metal-doped catalysts examined.
2.2 The water-gas shift (WGS) reaction

There has been renewed interest in the WGS reaction in recent years because of its necessity in conjunction with fuel cell power generation. The high-temperature shift (HTS) reaction is performed at 320-450 °C using Fe-Cr oxides catalysts, while the low-temperature shift (LTS) reaction is conducted at 200-250 °C. The LTS catalysts commonly used are Cu/ZnO/Al₂O₃ and precious metal-based catalysts. The WGS reactor currently represents the largest volume of any catalyst in a fuel processor due to slow kinetics at temperatures where the equilibrium is favorable [70]. In the absence of a catalyst, the reaction is very slow at accessible industrial temperatures [71]. Two main categories of WGS catalytic systems, which have been studied in recent years, can be summarized as follows:

2.2.1 Precious metal catalysts

Ceria-supported precious metals have gained much interest as potential candidates for low-temperature water-gas shift catalysts in the past years. Their enhanced activity is attributed to higher oxygen storage capacity and improved reducibility. Gorte and coworkers [72-74] have proposed that the mechanism of the WGS reaction over ceria-supported precious metals involves a redox process, with reduced ceria being oxidized by water and then transferring oxygen to the precious metal to react with adsorbed CO. Interestingly, ceria-supported Pd, Pt, and Rh catalysts were found to show similar WGS activity and they were even more active than alumina-supported catalysts. Work
performed at NexTech Materials on the development of Pt/ceria catalysts showed that hydrothermal synthesis methods for dispersed suspension of nanoscale ceria and ceria-zirconia gave more active WGS catalysts compared to a commercial Süd-Chemie Cu-based catalyst at 300–400 °C [75]. Johnson Matthey has also developed new WGS catalysts including non-pyrophoric platinum group metals (PGM) formulations with improved durability and no methanation activity at 200-500 °C [76]. However, the deactivation mechanisms of Pt/ceria and Pd/ceria catalysts for the water-gas shift reaction are still under debate. Wang et al. [77] have suggested that the deactivation of these catalysts is due to the growth of metal particles in the presence of CO based on accelerated aging tests. On the other hand, Zalc et al. [78] have claimed that Pt/ceria catalysts deactivate rapidly with the presence of H₂ in the feed due to the irreversible over-reduction of ceria. The authors further implied that these ceria-supported precious metals could not be practical for automotive fuel processing. Therefore, better understanding of deactivation mechanisms of these catalysts for the WGS reaction will definitely play a crucial role on the success of their transportation applications.

Gold-containing catalysts are known for high activity at low temperatures for CO oxidation and methane oxidation. As a result, they have been increasingly studied for low-temperature water-gas shift reaction in recent years. An increase in catalytic activity of gold-containing catalysts could be due to synergism between the gold and metal oxide supports, which strongly depends on catalyst preparation conditions. Andreev et al. [79] reported that a Au/α-Fe₂O₃ catalyst prepared by deposition-precipitation (DP) method showed much higher catalytic WGS activity and stability than a co-precipitated (CP) sample at 120-200 °C. It was found that highly dispersed gold particles (avg. 2 nm) and
more uniform gold particle size distribution on $\alpha$-Fe$_2$O$_3$ were detected on the DP sample. Later, the authors concluded that the catalytic activity of gold catalysts supported on metal oxides depended not only on the dispersion of gold particles but also on the nature and structure of the supports [80]. Gold catalysts on well-crystallized supports such as Fe$_2$O$_3$ and ZrO$_2$ were more active and stable than those on amorphous supports (i.e., ZnO, ZrO$_2$, Fe$_2$O$_3$-ZnO, and Fe$_2$O$_3$-ZrO$_2$). As mentioned earlier, ceria can promote Pd, Pt, and Rh for the water-gas shift reaction. Fu et al. [81] and Andreeva et al. [82] investigated the role of ceria as a support on the catalytic behavior of gold catalysts. Their enhanced activity has been related to much improved Ce reducibility, that is, the surface oxygen of ceria was substantially weakened by the presence of gold particles. In addition, the catalytic behavior of gold catalysts supported on titania has been investigated [83, 84]. Sakurai et al. [83] presented that TiO$_2$-supported gold catalysts prepared by a deposition-precipitation method exhibited very high WGS activity, comparable with that of a conventional Cu/ZnO/Al$_2$O$_3$ catalyst for forward and reverse WGS reactions. The activity was found to increase with increasing gold loading (3.4-10 at% Au).

2.2.2 Non-precious metal catalysts

The development of low-cost non-precious metal catalysts is of great significance for WGS reaction for fuel cell applications. However, this still poses major challenges since non-precious metal catalysts possess lower WGS catalytic activity at low temperatures compared to PGM or gold catalysts. Li et al. [85] reported that Cu or Ni (2
wt% supported on Ce (La)O₃ prepared by a urea precipitation-gelation method gave high WGS activity at high space velocities. Hydrogen addition (40% in the feed) did not suppress the reaction over the Cu-containing sample. The enhanced activity was related to improved ceria reducibility with the addition of Cu or Ni. Saito et al. [86] investigated the effect of ZnO on the specific activity of Cu-based catalysts supported on Al₂O₃, ZrO₂, or SiO₂ for various reactions including the water-gas shift reaction. The specific activity was defined as the reaction rate per unit of Cu surface area of the spent catalyst. Interestingly, the addition of ZnO did not improve the specific activity of the supported Cu-based catalysts for methanol steam reforming and the WGS reaction but for methanol synthesis and the reverse WGS reaction. Therefore, the development of high-performance Cu-based catalysts can be achieved by increasing Cu surface area. The authors also found that catalyst preparation methods play a major role on Cu surface area of Cu-based catalysts. A co-precipitated Cu/ZnO catalyst displayed much larger Cu surface area than an impregnated Cu/ZnO catalyst. Not only the presence of ZnO in Cu-based catalysts can improve activity and selectivity in the WGS reaction, but it enhances the catalyst life by adsorbing sulfur poisons as discussed by Spencer [87].

Tanaka et al. [88] studied the WGS reaction over various Cu-based mixed oxides under severe conditions including a large amount of H₂O (25% vol.) in the reformed fuels. It was found that CuMn₂O₄ showed similar WGS activity over 300 °C compared to Cu/ZnO/Al₂O₃. CuFe₂O₄ and CuAl₂O₄ also showed a moderate activity. The effect of reduction treatment on the WGS activity was also investigated. The catalytic activity after reduction in 10% H₂/N₂ at 225 °C decreased as follows:

CuMn₂O₄ > CuFe₂O₄ > CuY₂O₅ > CuAl₂O₄ > CuLa₂O₄ > CuCr₂O₄
Furthermore, without reduction, CuMn$_2$O$_4$ became even more active at 200-350 °C. It was concluded that excessive reduction led to the sintering of Cu particles, thus resulting in a decrease in WGS activity.

Additionally, superior tolerance to contaminants in the feed such as H$_2$S and chlorine must be considered for non-precious metal WGS formulations used for fuel processing. It is reported that alkali promoters can increase sulfur tolerance of Co-Mo/Al$_2$O$_3$ catalysts in the WGS reaction. However, little is known for the effect of alkali promotion on the structure of Co-Mo/Al$_2$O$_3$ catalysts. Xie et al. [89] examined the influence of potassium on the structure of Co-Mo/Al$_2$O$_3$ catalysts. The presence of potassium was found to enhance not only the reducibility but also the sulfidation ability of the catalysts. XRD and XPS results indicated that potassium was well dispersed on the surface in both oxidic and sulfided states. The authors further concluded that the WGS activity of K-promoted Co-Mo/Al$_2$O$_3$ was affected by the potassium content. Mellor et al. [90] investigated the influence of sulfur present in coal-derived process gas on the performance of novel cobalt-based WGS catalysts. Both Co-MnO and CoCr$_2$O$_4$ catalysts were found to be active under the feed containing sulfur up to 220 ppm. However, they suffered from sulfur poisoning in the WGS reaction of coal-derived process gas containing 0.25-0.3 mol% sulfur. Interestingly, the activity and stability of the CoCr$_2$O$_4$ catalyst were improved when it was pre-sulfided in a gas mixture of H$_2$S, H$_2$, and N$_2$ before use. The sulfided CoCr$_2$O$_4$ catalyst exhibited the highest activity in a sulfur-rich feed (0.91 mol% sulfur) at 400 °C.

Andreev et al. [79] studied the active components in non-promoted and K-promoted NiMo-sulfided catalysts for the WGS reaction. Water vapor in the feed caused
hydrolysis of the sulfide phase to yield an oxysulfide phase which also showed catalytic activity. An increase in the Mo\(^{4+}\) content was also observed in the more active K-promoted samples. Laniecki et al. [91] studied the influence of three different oxide supports (\(\gamma\)-Al\(_2\)O\(_3\), TiO\(_2\), ZrO\(_2\)) on NiMo-sulfided catalysts on the catalytic activity in the WGS reaction with sulfided feed. The best performing catalyst was 3 wt% Ni-6 wt% Mo/TiO\(_2\) [precursor = Mo(CO)\(_6\)]. High activity of TiO\(_2\)-supported catalysts was due to better homogeneity in the coordination of Mo species on titania than on alumina and zirconia. Moreover, the authors have currently investigated the effect of different surface properties of alumina and zirconia modified with different ions (i.e., SO\(_4^{2-}\), PO\(_4^{3-}\), F\(^-\), or Na\(^+\)) on the WGS activity. However, literature on the active forms of sulfided WGS catalysts is very limited. Mo carbide catalysts are known for good tolerance to sulfur poisons for many catalytic reactions. Patt et al. [92] reported that, with the absence of methanation, high surface area Mo\(_2\)C was more active than a commercial Cu-Zn-Al catalyst in the WGS reaction of a synthetic steam reformer exhaust at 220-295 °C.

It is known that the activation process can play an important role on the activity and stability of catalysts. Rethwisch et al. [93] investigated the effect of reducing agents (CO/CO\(_2\) and H\(_2\)/H\(_2\)O gas mixtures) on WGS activity at 390 °C over a 16.8 wt% Fe\(_3\)O\(_4\) supported on graphite. It was found that the pre-reduction of the catalyst in CO/CO\(_2\) at 390 °C increased the catalytic activity. In contrast, reducing in H\(_2\)/H\(_2\)O caused the growth of magnetite particles, leading to a decrease in the catalytic activity. Gonzalez et al. [94] studied the influence of thermal treatments and reduction process on HTS activity of Fe-Cr catalysts. The active phase, Fe\(_3\)O\(_4\), can be obtained from partial reduction of Fe\(_2\)O\(_3\). However, over-reduction to form metallic Fe should be avoided. Moreover,
metallic Fe is believed to enhance methanation and carbon formation reactions. It was found that the surface area of Fe-Cr catalysts decreased with increasing calcination temperature from 360 to 500 °C under both N₂ and N₂/H₂O. The presence of steam led to an even more pronounced decrease in the surface area. The effect of reducing agents on the catalyst reduction was further examined. The reducing agents tested were N₂/H₂, CO/N₂, and N₂/H₂/H₂O. TPR results indicated that, compared to the sample reduced under N₂/H₂, the reduction peak maxima shifted toward higher temperatures when steam was added in the reducing mixture. On the other hand, CO/N₂ enhanced the reducibility significantly, which may lead to the formation of inactive metallic Fe. The authors concluded that reduction under either N₂/H₂ or CO/N₂/H₂/H₂O at temperatures below 500 °C should be performed to obtain higher activity without over-reduction of Fe₂O₃.

Tsagaroyannis et al. [95] investigated the effect of preparation conditions (i.e., Gd/Fe atomic ratio, atmosphere, and firing temperature) on catalytic behavior of gadolinium-iron ferrites in the WGS reaction. All the catalysts were prepared by a co-precipitation method followed by thermal treatment in air or Ar. The optimum catalyst preparation variables giving the best reaction performance were as follows: at% Gd:Fe = 3:5, firing temperature = 800 °C in air. An improved catalytic activity of ferrite catalysts over pure Fe₃O₄ was attributed to the presence of punctual defects in their crystal lattice associated with their n- or p- semiconductivity. However, all ferrite catalysts showed lower activity than a commercial catalyst.

Hakkarainen et al. [96] studied the WGS activity of a commercial Co-Mo oxide catalyst with transient respond experiments in a gradientless spinning basket reactor at 350-400 °C. The Co-Mo oxide catalyst exhibited WGS activity above 350 °C. The
reaction mechanism was further proposed based on transient response experiments and chemisorption studies. It involved water adsorption and decomposition to form hydroxyl groups. The surface hydroxyl groups subsequently reacted with CO producing H₂ and CO₂. In addition, hydrogen formation was found to be faster than that of CO₂. It was suggested that surface reaction and CO₂ desorption were rate-determining steps. Rhodes et al. [97] discussed the mechanism of the WGS reaction for both Cu/ZnO/Al₂O₃ and Fe₃O₄/Cr₂O₃ catalysts. The mechanism of the WGS reaction over Cu/ZnO/Al₂O₃ catalysts is still under debate due to lack of data under reaction conditions. Two possible mechanisms over Cu/ZnO/Al₂O₃ catalysts have been proposed: associative and regenerative. The associative mechanism involves CO and H₂O adsorption on the catalyst surface forming an unknown intermediate that decomposes later to CO₂ and H₂; formate species could be the possible reaction intermediate. On the other hand, the regenerative (redox) mechanism involves cyclic reduction-oxidation reactions on the catalyst surface.

For Fe₃O₄/Cr₂O₃ catalysts, there is strong evidence supporting the WGS reaction proceeds via the regenerative mechanism. The dissociative adsorption of H₂O leads to the oxidation of Fe²⁺ to Fe³⁺ and production of H₂. The Fe³⁺ ion could be further reduced by CO, thus making CO₂. Interestingly, the authors also suggested that the presence of Cu could modify the electronic properties of Fe₃O₄/Cr₂O₃ catalysts, which results in an improvement in catalytic activity. Hu et al. [98] examined the reductive behavior of iron-based shift catalysts promoted by cerium oxide to explain high activity, selectivity, and stability under the WGS reaction conditions. It was confirmed that the mechanism of the WGS reaction on ceria-promoted Fe-Cr catalysts occurs through a redox process. H₂O
can adsorb dissociatively to produce H\textsubscript{2} and adsorbed hydroxyl groups. Subsequently, CO reacts with hydroxyl groups to form H\textsubscript{2} and CO\textsubscript{2} simultaneously. TPR results showed that there were two reduction peaks observed around 250 and 400 °C on the ceria-promoted Fe-Cr catalyst. A low-temperature peak was assigned to the reduction of surface oxygen species whereas a high-temperature peak was due to the bulk reduction of Fe\textsubscript{2}O\textsubscript{3}. It appeared that the presence of ceria enhanced the catalyst reducibility. The optimum reduction of ceria-promoted Fe-Cr catalyst should be 200-450 °C to avoid over-reduction of Fe\textsubscript{2}O\textsubscript{3}.

Development of Fe-Cr catalysts to improve their activity and stability has been pursued in the last two decades. Andreev et al. [99] studied the effect of the addition of CuO, CoO, and ZnO (5 wt%) on the activity of Fe-Cr catalysts. The unpromoted sample showed lower WGS activity than the promoted samples; the Cu-promoted sample was the most active at 380 °C. Although Fe-Cr oxide catalysts have been widely used in high-temperature WGS reaction, the role of the Cr\textsubscript{2}O\textsubscript{3} addition on the stabilization of the catalyst structure is still unclear. Edwards et al. [100] reported a detailed microstructural comparison of Fe\textsubscript{3}O\textsubscript{4}/Cr\textsubscript{2}O\textsubscript{3} and Cu-promoted Fe\textsubscript{3}O\textsubscript{4}/Cr\textsubscript{2}O\textsubscript{3} co-precipitated catalysts to identify the location and distribution of the chromia structural stabilizer and the Cu promoter. The authors suggested that a model for a high stabilizing effect of chromium is proposed whereby a shell of chromium enriched material is formed on each catalyst grain, which stabilizes the catalysts. They also concluded that Cu seemed to preferentially segregate toward the surface layers of the spinel structure, but the mechanism by which promotion occurs is still uncertain. Kappen et al. [101] studied the state of Cu promoter (0.17-1.5 wt%) in Fe-Cr catalysts by in situ fluorescence XAFS combined with on-line
gas analysis. It was found that Cu was in a metallic phase under the WGS reaction conditions. However, it reoxidized easily when exposed to the atmosphere. The reduction of Cu (II) to Cu (I), occurred at 120-150 °C, was not much affected by Cu concentration. On the other hand, further reduction of Cu (I) to metallic Cu was significantly enhanced at low Cu concentrations. Rhodes et al. [102] examined the promotion of Fe$_3$O$_4$/Cr$_2$O$_3$ high-temperature water-gas shift catalysts with 2 wt% B, Cu, Ba, Pb, Hg, and Ag. It was found that the WGS activity at 350-440 °C decreased in the following order:

$$\text{Hg} > \text{Ag, Ba} > \text{Cu} > \text{Pb} > \text{unpromoted} > \text{B}$$

A beneficial effect of adding Hg, Ag, or Ba could be due to their different ionic sizes compared to that of Fe$^{2+}$, influencing the electronic structure of the active Fe$^{3+}$ center. Despite its best WGS activity, it is unlikely that toxic Hg-promoted catalysts will be considered as a commercial HTS catalyst.

Even though chromium oxide has been used as a stabilizer in industrial HTS catalysts, development of non-toxic catalytic systems is needed due to environmental concerns related to chromium. Araujo and Rangel [103] investigated the catalytic performance of aluminum-doped iron-based catalyst with small amounts of copper (%wt Cu ≈ 3) in the HTS reaction. The aluminum and copper-doped catalyst showed similar catalytic activity compared to a commercial Fe-Cr catalyst even at more severe conditions (H$_2$O/CO = 0.4, 350 °C). However, there was no information about the stability of the aluminum and copper-doped catalyst under industrial conditions. Costa et al.[104] subsequently examined the use of thorium instead of chromium in iron- and copper-based catalysts for the HTS reaction. It was found that the thorium and copper-
doped catalyst was more active than a commercial Fe-Cr catalyst at H₂O/CO = 0.6 and 370 °C. Its high activity was attributed to an increase in surface area by thorium. The authors concluded that a non-toxic thorium and copper-doped catalyst is a promising HTS catalyst. A review of the state of the art makes it clear that alternatives to Fe-Cr catalysts that can overcome the drawbacks such as low activity at low temperatures, sintering, poisoning by sulfur and chlorine, pyrophoric nature, fragmentation with water and harmful effects of Cr⁶⁺ would have an impact in many processes that target hydrogen production.
3.1 Catalysts synthesis

3.1.1 Ni-based catalysts for steam reforming of lower alkanes

Catalysts were prepared using a modified sol-gel technique. Nickel and lanthanide precursors (Aldrich) used were in nitrate form. For the aluminum precursor, aluminum tri-sec-butoxide (ATB; Aldrich) was used. Ethanol (Alfa Aesar; 130 cm$^3$) was used as the solvent. The following sol-gel variables were controlled during the synthesis: nickel content = 20 wt%, lanthanide content = 2-5 wt%, H$_2$O/ATB molar ratio = 3.6, and pH of the resulting gels = 4.8. Initially, ATB was placed in ethanol and stirred to form a white suspension. The aqueous solutions with the desired amounts of nickel and lanthanide were added dropwise into the suspension using a syringe pump at the flow rate of 0.5 cm$^3$/min. It is noted that the aqueous lanthanide nitrate solution was added first followed by that of nickel. The pH of the resulting green gels was measured and adjusted by adding HNO$_3$ (Fisher) or NH$_4$OH (Fisher). The gels were stirred for an additional 15 min. and were kept at room temperature for 30 min. The samples were then dried overnight in the oven at 110 °C to remove the remaining water and ethanol. The dry
samples were ground to a fine powder and were calcined under O₂ at 450-600 °C (ramp rate = 10 °C/min) for 4 h. For simplicity, all the catalysts prepared were denoted to indicate compositions and calcination temperature: for example, 20Ni2CeAl(450) represents 20%Ni-2%Ce/Al₂O₃ catalyst calcined at 450 °C.

3.1.2 Fe-based catalysts for the HTS reaction

Catalysts were prepared using a coprecipitation method. All metal precursors (Aldrich) used were in nitrate form. Ammonium hydroxide (29.63 vol%, Fisher Scientific) was used as the precipitating agent. Initially, 0.5 M aqueous solutions of metal nitrates were prepared and mixed in a beaker in appropriate proportion to yield the desired Fe/promoter molar ratio. NH₄OH was subsequently added drop-wise to the mixed solution until the desired pH was reached. The resulting dark brown solution was stirred vigorously for an additional 30 min. The precipitate was washed with demineralized distilled water and filtered several times to remove ammonium ions. The remaining solid was then dried overnight in an oven at 110 °C. The dry samples were ground to a fine powder and were calcined under air at 350-500 °C (ramp rate = 2.5°C/min) for 4 h. For catalysts promoted with first-row transition metals (Cu, Co, Zn), they were synthesized by a coprecipitation-impregnation method. Before drying, the precipitate obtained after washing was further impregnated with a calculated amount of 0.5 M aqueous solution of the first row transition metal and stirred for 30 min.
3.2 Catalyst characterization

Various characterization techniques were incorporated into this research to determine the physical, chemical, and structural properties of the catalysts and the role of different preparation variables. Among the techniques which will be regularly used for catalyst characterization are BET surface area measurements, pore size distribution measurements, temperature-programmed desorption/reduction/oxidation (TPD/TPR/TPO), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), H₂ chemisorption, transmission electron microscopy (TEM), and thermogravimetric analysis (TGA). Important catalytic properties of the synthesized catalysts are the catalyst composition, the BET surface area and pore size distribution, metal dispersion, reducibility, crystal structure, surface morphology, and oxidation state of the metals. For Ni-based catalysts, metallic Ni is generally known as an active site for steam reforming of hydrocarbons. The activity is, therefore, correlated to the nickel surface area, which increases with Ni content. However, the Ni dispersion decreases with increasing Ni content. Furthermore, the ease of reduction of to metallic Ni is also expected to influence the Ni surface area. For example, nickel aluminate (NiAl₂O₄) formation may result in inactive nickel species which require higher reduction temperatures to obtain similar catalytic activity. For Fe-based catalysts, magnetite (Fe₃O₄), which is produced by the partial reduction of hematite (Fe₂O₃), is reported to be the active phase for high-temperature water-gas shift reaction in Fe-based catalysts. Over-reduction of Fe₂O₃ to form either inactive FeO or metallic Fe needs to be avoided to prevent sintering. Calcination/reduction temperatures and reducing agents therefore strongly affect the catalytic activity, selectivity, and stability of
these catalysts. BET surface areas of catalysts were measured to investigate the surface change upon the promotion. As mentioned earlier, the addition of lanthanide elements in Ni-based catalysts has been reported to inhibit nickel crystallite growth under reduction and reaction conditions. On the other hand, the presence of Al or Cr in HTS Fe-based catalysts can prevent the growth of magnetite crystallites. TPR helped elucidate the nature of active sites and interaction of active and promoter/support species and examine the catalyst reducibility. TPD of adsorbed reactants was used to investigate the heterogeneity of active site strengths present on the catalysts. X-ray diffraction (XRD) equipped with atmosphere and temperature control capabilities (up to 1200 °C) was used to study changes in catalyst crystallinity and phase transformation during calcination and reduction steps. H₂ chemisorption was used to measure Ni dispersion and metallic surface area.

Furthermore, XPS provided useful information on surface chemical states (i.e., oxidation state, coordination environment, and nature of catalytic active sites). In situ DRIFTS combined with TPD and TPRaction was conducted to identify the important surface species under the reaction conditions. Post-reaction characterization techniques using controlled-atmosphere sample handling capability of the surface and bulk characterization systems available such as XPS, and TEM were used to examine phase transformation, deactivation mechanisms, and change in microstructure of these catalysts. Additionally, TPO and TGA were performed to characterize carbonaceous species formed on catalyst surface during steam reforming of lower alkanes. Information acquired from all the characterization techniques above will offer a more complete picture of the characteristics of both Ni-based and Fe-based catalysts.
3.2.1 BET surface area measurement

The most common method of measuring surface area is the BET method developed by Brunauer, Emmett, and Teller. They proposed the following linearized BET isotherm, which is derived by equating the rate of condensation to the rate of evaporation as follows:

\[
\frac{P}{V(P_o - P)} = \frac{1}{V_mC} + \frac{(C - 1)P}{V_mC P_o}
\]

where \(V\) is the volume of gas adsorbed at pressure \(P\), \(V_m\) is the volume of gas adsorbed in monolayer, \(P_o\) is the saturation pressure of adsorbate gas at the experimental temperature, and \(C\) is a constant. Plotting \(P/V(P_o - P)\) vs \(P/P_o\) results in a straight line whose slope and intercept can be used to determine \(V_m\). With a knowledge of cross sectional area of adsorbing gas, the surface area of the catalyst can be calculated from \(V_m\) [12].

BET surface areas of calcined catalysts were measured by \(N_2\) adsorption-desorption at 77 K using a Micromeritics ASAP 2010 instrument. Before measurements, samples were degassed under vacuum at 130 °C overnight.

3.2.2 X-ray diffraction (XRD)

Determination of the crystal structure and identification of phases can be achieved using X-ray diffraction (XRD). XRD is particularly useful for the determination of change in crystallinity and phase transformation of species present in steam reforming and HTS catalysts during calcination and reduction steps. When electromagnetic radiation (X-rays) is incident upon a periodic array of scattering centers (lattice atoms), there are certain discrete directions for the incident ray that result in strong reflections.
This is because of constructive interference of the radiation scattered from each of the centers. The directions for which these strong reflections occur are related through Braggs law to the geometry of the arrangement. Therefore, measurements of the angles and intensities of the Bragg reflections can be used to deduce the arrangement and spacing of the scatterers. Additionally, line broadening of XRD peaks are inversely proportional to crystallite size and therefore can be used to estimate crystallite size in the range ~5-50nm using the Scherrer equation [105] as follows:

\[ d \text{ (nm)} = \frac{0.9\lambda}{B\cos\theta} \]

where \( \lambda \) is wavelength usually 1.54056 Å for Cu K\(_\alpha\) radiation, \( B \) is width of diffraction line at half of its maximum intensity, and \( \theta \) in radian is angle at the maximum intensity.

X-ray diffraction patterns of catalysts were obtained with a Scintag XDS diffractometer using Cu K\(_\alpha\) radiation operated at 45 kV and 20 mA. In situ XRD during reduction of the catalysts pre-calcined at 450 °C was performed using a Bruker D8 Advance X-ray diffractometer equipped with atmosphere and temperature control stage and using Cu K\(_\alpha\) radiation operated at 40 kV and 50 mA. In these experiments, XRD patterns were recorded every 50 °C with the ramp rate of 10 °C/min up to 800 °C under 5% H\(_2\)/N\(_2\).

3.2.3 Temperature-programmed desorption/reduction/oxidation(TPD/TPR/TPO)

Temperature-programmed techniques have been one of the most widely used methods for studying interactions between reactants and the catalyst surface. The methods involve the measurement of the rate of desorption (of adsorbed molecules), reduction, or oxidation as a function of temperature (linear temperature ramp). TPD can
provide information on the number of catalytic sites, the strength of adsorption bonds, and the nature of exposed sites. TPR can be used to determine the reducibility, distribution of reducible states, and the effect of metal catalyst modification by supports. TPO can be used to qualitatively and quantitatively characterize carbonaceous species formed on catalyst surface during hydrocarbon steam reforming.

TPD/TPR/TPO of catalysts was conducted using a laboratory-made gas flow system as shown in Figure 3.1. For TPR experiments, 50 mg of catalysts was initially placed in a 1/4 in. O.D. quartz U-tube reactor. The catalysts were then re-calcined under 10% O₂/He at 450 °C for 1 h followed by cooling to room temperature under Ar. The reduction was performed with 10% H₂/Ar (40 cm³/min). The temperature of the catalysts was raised using a ramp rate of 10 °C/min to 900 °C and held for 10 min. The effluent from the reactor was passed through a silica gel water trap to remove moisture formed during reduction. H₂ consumption was measured using a thermal conductivity detector (TCD) connected to a data-acquisition computer. TPO was performed with 50 mg of samples which were placed in a 1/4 in. O.D. quartz U-tube reactor and heated under He (40 cm³/min) at 200 °C for 30 min. to remove moisture followed by cooling to room temperature.
Figure 3.1: Schematic of TPD/TPR/TPO system
Subsequently, the temperature of the catalysts was raised under 1% O₂/He (40 cm³/min) with a ramp rate of 10 °C/min to 800 °C and held for 5 min. The desorbed species from the catalyst surface were monitored using a mass spectrometer (HP5890 GC-MS) under He carrier gas.

Sequential temperature-programmed coking/gasification/hydrogenation of catalysts was conducted with a Shimadzu GC-MS QP-5050. Prior to spectra collection, the catalysts were reduced in situ under 20% H₂/N₂ at 600 °C for 2 h. The coking was then performed by exposing the catalysts with 2% C₃H₈/He at 500 °C for 1 h followed by cooling to room temperature under He. Temperature-programmed gasification (TPGasification) experiments were initiated by raising the catalyst temperature under 2% H₂O/He with a ramp rate of 10 °C/min to 800 °C. Following cooling to room temperature, temperature-programmed hydrogenation (TPH) experiments were performed with 10% H₂/He. TPH profiles were collected while heating the catalysts with a ramp rate of 10 °C/min to 800 °C.

3.2.4 X-ray photoelectron spectroscopy (XPS)

XPS is a technique employed for chemical analysis of solid surfaces. This technique offers information on surfaces such as distribution, concentration, and chemical states for all elements. In XPS, a sample is irradiated by monochromatic X-rays under ultrahigh-vacuum conditions. Photoelectrons are ejected from various atomic shells with characteristic kinetic energy, which gives their binding energy according to the following equation: KE=\hbar\gamma-BE-\phi_{SP}
where KE is the kinetic energy, $h\gamma$ is the incident X-ray energy, BE is the binding energy, and $\phi_{sp}$ is the spectrometer work function. The binding energy is characteristic of the atomic number of the element. The chemical environment in which they exist affects the binding energies of elements. These changes in binding energies are called the “chemical shift” that gives information on the oxidation states of elements on the surface.

In this study, X-ray photoelectron spectra were used to determine the oxidation states of the components present in catalysts. XPS of reduced and post-reaction catalysts was performed with an AXIS Ultra XPS spectrometer with an Al anode operated at 14 kV and 10 mA. All samples were transferred to an XPS chamber using an inert glove box without exposing them to the atmosphere. Spectra were corrected using the C 1s signal located at 284.5 eV.

3.2.5 Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

DRIFTS is a surface sensitive technique for the analysis of trace quantities of materials. Unlike traditional solid sampling FTIR techniques, a sample does not need to be pelletized with KBr. Diffuse reflectance occurs when light impinges on the surface of a material and is partially reflected and transmitted. Light that passes into the material may be absorbed or reflected out again. Therefore, the radiation that reflects from an absorbing material is composed of surface-reflected and bulk re-emitted components, which summed are the diffuse reflectance of the sample. Figure 3.2 shows a DRIFTS system schematic used in this study.
Figure 3.2: Schematic of DRIFTS system
DRIFTS experiments were performed using a Bruker IFS66 instrument equipped with an MCT detector and a KBr beamsplitter. Catalysts were in situ reduced and then were placed in a sample cup inside a Spectratech diffuse reflectance cell equipped with KBr windows and a thermocouple that allowed direct measurements of the surface temperature. Spectra for each experiment were averaged over 1000 scans in the mid-IR range (400-4000 cm\(^{-1}\)) to a nominal 3 cm\(^{-1}\) resolution. Lanthanide-promoted sol-gel Ni/Al\(_2\)O\(_3\) catalysts were reduced under 20% H\(_2\)/N\(_2\) at 600 °C for 2 h. Prior to the collection of spectra, the catalysts were re-reduced in situ under 20% H\(_2\)/He at 450 °C for 1 h. The background spectra were taken at different temperature intervals under He. The adsorption of C\(_3\)H\(_8\) was performed at room temperature for 1 h followed by flushing under He for 30 min. The spectra were subsequently collected at different temperatures up to 450 °C.

Fe-based catalysts were reduced in situ under 20% H\(_2\)/He at 350 °C for 2 h followed by flushing under He for 30 min. Spectra for CO-TPD DRIFTS experiments were subsequently collected under CO by heating in steps up to 400 °C. For CO+H\(_2\)O-TPReaction experiments, spectra were taken under He before CO and H\(_2\)O were introduced at 400 °C.

3.2.6 Chemisorption

Chemisorption is a method for measuring metal surface area, dispersion, and crystallite size. By measuring the amount of gas adsorbed and knowing its stoichiometry of adsorption on the surface, one can calculate the metal dispersion. The metal dispersion
is the percentage of the active metal available for interaction with the adsorbate expressed as follows:

$$%D = \frac{(\text{Volume adsorbed})(\text{SF})(\text{atomic wt. of metal})}{22400 \times 100} \times \left(\% \text{wt of metal in the catalyst}\right)$$

where SF is the stoichiometry factor. In general, the 1:1 stoichiometry is widely accepted for \( \text{H}_2 \) adsorption on nickel; each surface Ni atom chemisorbs one hydrogen atom through the dissociation of a \( \text{H}_2 \) molecule. Moreover, the metal surface area can be estimated if an effective area of a metal atom is known.

Metal surface area (\( \text{m}^2/\text{g} \)) = \( (\text{Volume adsorbed})(\text{SF}) (N_{\text{avg}})(\text{effective area of metal})/22400 \)

where \( N_{\text{avg}} \) is Avogadro’s number.

\( \text{H}_2 \) chemisorption of catalysts was conducted using a Micromeritics ASAP 2010 Chemisorption System. Prior to adsorption measurements, approximately 0.2 g of calcined samples was reduced under \( \text{H}_2 \) at the desired reduction temperature for 2 h. Subsequently, the samples were cooled down to 35 °C followed by evacuation to \( 10^{-5} \) mmHg. The adsorption isotherms were measured at equilibrium pressures between 50-500 mmHg.

3.2.7 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is dedicated to micro structural analysis of solid materials down to the sub-nanometer scale. TEM is analogous to optical microscopy in that the photons are replaced by high-energy (\( >100 \text{ keV} \)) electrons and the glass lenses replaced by electromagnetic lenses. The electron beam passes an electron-transparent sample and an enlarged image is formed using a set of lenses. Since electrons
interact strongly with matter, electrons are attenuated as they pass through a solid requiring the samples to be prepared in very thin sections. The image is projected onto a Charged Coupled Device (CCD) camera for imaging. Image contrast is obtained by the interaction of the electron beam with the sample: a part of the electrons will be diffracted. By means of an aperture, one or more diffracted beams are selected for the formation of the image. In this way, one can distinguish between different materials, as well as image individual crystals and crystal defects. TEM images of post-reaction catalysts were taken with a Tecnai TF-20 operated at 100 kV. Samples were ultrasonically dispersed in ethanol, and a couple drops of the suspension were deposited on a standard 3 mm copper grid covered with a holey carbon film.

3.2.8 Thermogravimetric analysis (TGA)

TGA is a quantitative technique that measures the weight change of a catalyst placed in a quartz basket hung on the balance arm in a flow reactor where it contacts gaseous reactants. By using this method, carbon deposition during hydrocarbon steam reforming can be monitored continuously and the weight changes of catalysts can then be measured. When applied with temperature-programmed techniques, the minimal temperature at which the formation of carbon deposits starts can also be determined. TGA-TPReaction experiments were performed in a Perkin-Elmer TGA7. Catalysts were reduced in situ under 20% H₂/N₂ at 600 °C for 2 h followed by cooling to 250 °C under N₂. The reaction mixture (C₃H₈/H₂O/N₂, 30 cm³/min) with varied H₂O/C molar ratios of 0.167-0.333 was subsequently introduced to the reduced catalysts. The temperature
program was as follows: 1 min. at 250 °C, 10 °C/min ramp rate to 750 °C, and 5 min. at 750 °C.

3.3 Steady-state reactions

The catalysts synthesized and characterized as described in the previous sections were tested for their catalytic performance in steam reforming of lower alkanes and the HTS reaction. Figure 3.3 shows the reactor system for steady-state reaction experiments for steam reforming of lower alkanes and the WGS reaction. It consists of three main components: reactor, feed system, and analytical system. The reactor is made of 304 stainless steel with an outside diameter of 1/4 in. The catalyst was loaded into the reactor with a small amount of quartz wool placed at both ends of the bed. An Omega thermocouple was inserted into the catalyst bed to monitor the reaction temperature. The reactor was subsequently kept inside a laboratory-made furnace where the reaction temperature was controlled by a Dwyer temperature controller. The lines before and after the reactor were kept constant at 130 °C in order to prevent any condensation from the gas stream.

The gas feed system consists of various gas cylinders (Ar, H2, N2, CO, CO2, and C3H8). The delivery pressure of each gas cylinder was kept constant at 50 psi. Each gas stream was passed through an Alltech gas purifier packed with Drierite and 5A molecular sieve to remove moisture, traces of hydrocarbons and organics. The flow rates of all gases were subsequently controlled by Brooks mass flow controllers. The pressure of the feed stream was measured using a Noshok pressure gauge. In addition, steam was
introduced into the feed via a 300-cm³ Parker CPI stainless steel bubbler. To achieve the desired concentration of steam in the feed, the bubbler temperature was determined from the total gas flow rate and the H₂O/C molar ratio. The effluent gas was analyzed using an automated Shimadzu gas chromatograph (GC-14A) equipped with a thermal conductivity detector (TCD) using Ar (17 cm³/min) as the carrier gas. Both detector and injector were kept constant at 200 °C. The TCD current was set at 50 mA. A 1-cm³ sample loop was heated to 200 °C using a VICI temperature controller. Samples were injected into the GC via both VICI six-port valves controlled by automatic air-actuator switches. As shown in Figure 3.4, separations were performed using the TCD with two columns: Porapak Q (12 ft x 1/8 in. SS, 80/100 mesh) and Molecular Sieve 13X (5 ft x 1/8 in. SS, 60/80 mesh). A GOW-MAC 069-50 ruthenium methanizer operated at 350 °C was used with the FID for the sensitive determination of CO as low as 10 ppm. The light gases such as H₂ and N₂ were “isolated” in the molecular sieve column and were separated from the heavier ones in Porapak Q column. The temperature and the valve-switching programs for the GC are shown in Tables 3.1 and 3.2, respectively.

The Shimadzu CLASS-VP chromatography automated software system was employed to control the chromatograph, acquire data and analyze the acquired data. Generally, it is used to perform an integration analysis graphically on data to find, identify, and quantify peaks as well as to set up and run automated acquisition sequences.
Figure 3.3: Schematic of SR-WGS reactor system
Figure 3.4: The arrangement of columns and six-port valves for product separation
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial temperature (°C)</td>
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</tr>
<tr>
<td>Initial time (min.)</td>
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</tr>
<tr>
<td>Ramp rate (°C/min)</td>
<td>10</td>
</tr>
<tr>
<td>Final temperature (°C)</td>
<td>120</td>
</tr>
<tr>
<td>Final time (min.)</td>
<td>17.5</td>
</tr>
</tbody>
</table>

Table 3.1: GC temperature program.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Valve Number</th>
<th>Valve Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1</td>
<td>Inject</td>
</tr>
<tr>
<td>0.5</td>
<td>1</td>
<td>Load</td>
</tr>
<tr>
<td>3.15</td>
<td>2</td>
<td>Load</td>
</tr>
<tr>
<td>13.5</td>
<td>2</td>
<td>Inject</td>
</tr>
</tbody>
</table>

Table 3.2: GC valve-switching program.
The steady-state reaction experiments were performed using a fixed-bed flow stainless steel reactor (1/4 in. OD). The reaction conditions for propane steam reforming (dilution experiments) were as follows: 400-550 °C, H₂O/C = 1.3-2.7, and GHSV = 124,000-248,000 h⁻¹. Unless otherwise noted, lanthanide-promoted sol-gel Ni/Al₂O₃ catalysts were reduced in situ under 20% H₂/N₂ (50 cm³/min) at 600 °C for 2 h prior to the reaction. “Neat” experiments were also performed without N₂ dilution using 1/2 in. O.D. stainless steel flow reactor to avoid high pressure drop at 500-550 °C, 56,000 h⁻¹. The H₂O/C ratio was kept constant at 4. Demineralized distilled water was delivered by an Eldex metering pump (Model: A-10-S) connected with a 40 psi back pressure regulator and subsequently vaporized in a preheater which was operated above 150 °C. A column packed with ceramic beads was installed after the preheater to help C₃H₈ and steam mix effectively. The WGS reaction conditions were as follows: 300-400 °C, atmospheric pressure, H₂O/CO = 1, F_CO = 10 cm³/min, F_TOT = 100 cm³/min, GHSV = 3,200-9,500 h⁻¹. Fe-based catalysts were pre-reduced in situ under 20% H₂/N₂ (50 cm³/min) at 350 °C for 2 h.
CHAPTER 4

EFFECT OF LANTHANIDE PROMOTION ON CATALYTIC PERFORMANCE OF
SOL-GEL Ni/Al$_2$O$_3$ CATALYSTS IN STEAM REFORMING OF PROPANE

4.1 Introduction

Hydrogen is the ultimate clean energy carrier. When it is combusted, heat and water are the only products. When it is used as a fuel for fuel cells, then it has the potential of providing much higher efficiencies compared to combustion. Thus, hydrogen offers a potentially non-polluting and efficient fuel for today’s rising energy demands [1]. However, in the transition period before renewable sources of hydrogen can be developed, production of hydrogen from fossil fuels remains an important technology. Currently, steam reforming of natural gas, which is composed mainly of methane, is used to produce most of hydrogen in the U.S. and about half of the world’s hydrogen supply. Naphtha fractions with a final boiling point of less than 220 °C are also considered as suitable feedstocks [2] for hydrogen production. However, current Ni-based catalysts, which are used for natural gas steam reforming processes, suffer from catalyst deactivation by coke formation more severely when higher hydrocarbons are reformed at low steam/carbon ratios.
Although supported precious metals such as Pd, Pt, and Rh have been reported to be active and stable for steam reforming of hydrocarbons [106-111], the cost of the precious metals is still a major drawback. The low-cost and long-proven performance of Ni-based catalysts, therefore, warrant the effort to optimize these catalysts for steam reforming applications, particularly fuel processing technology from existing liquid fuels such as gasoline and diesel.

There is evidence in the literature pointing to an improvement in catalytic activity of Ni-based catalysts in hydrocarbon steam reforming with the addition of lanthanide elements [26, 27, 112]. Zhuang et al. [26] investigated the effect of cerium oxide as a promoter in supported Ni catalysts for methane steam reforming. It showed a beneficial effect by not only decreasing the carbon deposition rate, but also increasing the steam reforming activity. The authors believed that cerium oxide accelerated the reaction of steam with adsorbed species on the nickel surface, thus decreasing the carbon deposition as well as increasing or maintaining the catalytic activity. Su and Guo [27] also reported an improvement in catalytic activity and resistance to Ni sintering of Ni/Al₂O₃ catalysts doped with rare earth oxides in methane steam reforming. The growth of Ni particles and the formation of inactive NiO and NiAl₂O₄ phases were suppressed by the addition of rare earth oxides. Moreover, the oxides of heavy rare earth elements (Gd, Er, Dy) exhibited a more pronounced effect than those of the light ones (La, Pr, Nd).

The use of lanthanide-promoted Ni/Al₂O₃ catalysts in dry reforming of methane [113-116] and benzene hydrogenation [117] has also been reported. The effects of the addition of lanthanide oxides (La₂O₃ and CeO₂) and preparation procedures were investigated in the reforming of methane with carbon dioxide over impregnated Ni/Al₂O₃
catalysts [113]. When lanthanides were impregnated prior to nickel, an enhanced reducibility of nickel and a decrease in nickel particle size were observed. However, the reforming activity was not affected to a large extent by the impregnation order of nickel and lanthanides. The presence of CeO₂ (1-5 wt%) in impregnated Ni/γ-Al₂O₃ catalysts was found to reduce the chemical interaction between nickel and the alumina support, resulting in an increase in reducibility and higher nickel dispersion [114, 115]. Moreover, carbon deposition was greatly suppressed due to the oxygen storage capacity of CeO₂. The catalytic activity, sulfur tolerance, and thermal stability were remarkably improved after adding La, Sm, and Yb into Ni-B/Al₂O₃ catalysts for benzene hydrogenation [117]. The positive effect of lanthanide promotion was associated with easier reduction of nickel oxides, smaller nickel particles, and larger surface area of active nickel.

In this study, Ni/Al₂O₃ catalysts promoted with lanthanide elements (La, Ce, and Yb) were prepared by a modified sol-gel technique and were examined in propane steam reforming. Characterization was performed using the BET N₂ adsorption method, X-ray diffraction (XRD), temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), and H₂ chemisorption. In situ DRIFTS studies were also conducted to identify adsorbed species under C₃H₈ and C₃H₈ + H₂O flows as well as to elucidate the reaction pathways for propane steam reforming.

4.2 Physical properties of sol-gel catalysts

The effect of synthesis parameters on the physical properties of sol-gel Ni/Al₂O₃ catalysts is reported in Table 4.1. Parameters that were varied during the synthesis
included Ni content, pH of the resulting gels, and H$_2$O/ATB molar ratio. BET surface area of sol-gel Ni/Al$_2$O$_3$ catalysts is seen to decrease with increasing Ni contents possibly due to nickel aggregation to form larger particles on the Al$_2$O$_3$ support surface during thermal treatment. The decrease in surface area is even more pronounced at higher Ni contents. Furthermore, an increase in pH and H$_2$O/ATB ratio results in a decrease in surface area of 20 wt% Ni/Al$_2$O$_3$ catalysts. It is noted that a decrease in the pore diameter from 10.5 nm to 7.4 nm occurs when H$_2$O/ATB ratio is increased from 3.6 to 5.0. This phenomenon is related to an increase in cross-linking as a result of an increase in the extent of hydrolysis at high H$_2$O/ATB ratios [118].

BET surface areas of lanthanide-promoted sol-gel Ni/Al$_2$O$_3$ catalysts prepared at different lanthanide contents are listed in Table 4.2. In general, catalysts have a lower surface area than the pure support. At lower loading levels, the lanthanide-promoted catalysts exhibit a higher surface area than the unpromoted catalyst, but a loss in surface area with higher lanthanide content is observed with Ni-Ce/Al$_2$O$_3$ and Ni-Yb/Al$_2$O$_3$ catalysts possibly due to pore blockage by excess metal. In addition, an increase in calcination temperature from 450 °C to 600 °C causes a decrease in surface area of Ni-Ce/Al$_2$O$_3$ catalysts. The surface area of the catalyst calcined at 600 °C is 261 m$^2$/g compared to 304 m$^2$/g for the catalyst calcined at 450 °C.
<table>
<thead>
<tr>
<th>Ni content (wt%)</th>
<th>pH</th>
<th>H₂O/ATB ratio</th>
<th>Surface area (m²/g)</th>
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<tbody>
<tr>
<td>10</td>
<td>4.8</td>
<td>3.6</td>
<td>248</td>
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<td>15</td>
<td>4.8</td>
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<tr>
<td>20</td>
<td>4.8</td>
<td>5.0</td>
<td>248</td>
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Table 4.1: BET surface area of various sol-gel Ni/Al₂O₃ catalysts
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% Ni/Al₂O₃</td>
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</tr>
<tr>
<td>20% Ni-2% La/Al₂O₃</td>
<td>286</td>
</tr>
<tr>
<td>20% Ni-5% La/Al₂O₃</td>
<td>300</td>
</tr>
<tr>
<td>20% Ni-2% Ce/Al₂O₃</td>
<td>304</td>
</tr>
<tr>
<td>20% Ni-5% Ce/Al₂O₃</td>
<td>228</td>
</tr>
<tr>
<td>20% Ni-2% Yb/Al₂O₃</td>
<td>278</td>
</tr>
<tr>
<td>20% Ni-5% Yb/Al₂O₃</td>
<td>234</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>342</td>
</tr>
</tbody>
</table>

Table 4.2: BET surface area of lanthanide-promoted sol-gel Ni/Al₂O₃ catalysts calcined at 450 °C

4.3 Promotion effect on catalyst reducibility and nickel surface area

*X-ray diffraction.* The XRD patterns of calcined and reduced 20% Ni-2% Ce/Al₂O₃ catalysts are compared in Figure 4.1. The support calcined at 450 °C is relatively amorphous as evidenced by broad peaks that correspond to γ-Al₂O₃ (Figure 4.1(a)). The possible crystalline phases over the catalyst calcined at 450 °C are NiO, NiAl₂O₄, and γ-Al₂O₃ (Figure 4.1(b)). However, XRD results are not conclusive about
the presence of NiAl₂O₄. No cerium-related crystalline phases could be detected, suggesting that cerium species could be well dispersed on the alumina support undetectable by XRD. After in situ reduction under 5% H₂/N₂ at 600 °C, significant amounts of metallic nickel were formed as confirmed by the diffraction lines of a metallic nickel phase [(111), (200), (220)] at 2θ = 44.5°, 51.8°, and 76.4°, respectively (Figure 4.1(c)).

**Temperature-programmed reduction.** TPR experiments on lanthanide-promoted sol-gel Ni/Al₂O₃ catalysts were performed using 10% H₂/Ar as a reducing agent. As shown in Figure 4.2, the TPR profiles exhibit two peaks, representing two different reduction sites on all catalysts. A small low-temperature (LT) reduction peak around 400 °C could be attributed to the reduction of a well-dispersed and possibly amorphous NiO phase on the alumina support surface. On the other hand, a broad high-temperature (HT) reduction peak above 570 °C could be due to the bulk reduction of Ni in NiAl₂O₄ phase [119-121]. TPR results suggest that nickel species may exist in the form of NiAl₂O₄ as a result of the sol-gel preparation where nickel is incorporated into the alumina support network during gelation. For lanthanide-promoted catalysts calcined at 450 °C, the position of the HT peak maximum shifts toward lower temperatures compared to that of the unpromoted catalyst. This suggests that the presence of lanthanide elements helps facilitate the reduction of nickel species; the promotion effect is most evident on the Ni-Ce/Al₂O₃ catalyst. It is noted that the introduction of lanthanides to nickel catalysts showed no additional reduction peak under these conditions.
Figure 4.1: XRD patterns of: (a) sol-gel Al₂O₃ calcined at 450 °C (b) 20% Ni-2%Ce/Al₂O₃ catalyst calcined at 450 °C (c) 20% Ni-2%Ce/Al₂O₃ catalyst reduced at 600 °C.
Figure 4.2: TPR profiles of various sol-gel 20% Ni/Al₂O₃ catalysts promoted with 2 wt% lanthanide elements (calcined at 450 °C). The effect of calcination temperature on reducibility of 20% Ni-2% Ce/Al₂O₃ catalysts is shown as an inset.
In general, calcination temperature plays a major role on the strength of metal oxide and support interaction for supported metal catalysts, which in turn strongly affects the degree of reduction. The effect of calcination temperature on the catalyst reducibility of Ni-Ce/Al₂O₃ was also investigated. An increase in calcination temperature from 450 to 600 °C results in a shift of the HT peak maximum to a higher temperature around 680 °C. TPR results show that the interaction of Ni species with the alumina support becomes stronger at higher calcination temperatures, thereby suppressing the reduction of Ni species to metallic Ni [122, 123]. This could also be indicative of the formation of a nickel aluminate spinel at higher calcination temperatures.

_H₂ chemisorption._ H₂ chemisorption was performed to determine nickel dispersion and nickel surface area of the catalysts. Unless otherwise noted, the reduction was conducted under H₂ (UHP, 99.999%) at 600 °C for 2 h. The catalysts were then evacuated at 610 °C to remove adsorbed hydrogen from the surface and cooled to 35 °C. The first analysis was performed to measure both strong and weak sorption in combination whereas a repeat analysis was conducted to measure only weak (reversible) H₂ uptake. The chemisorption isotherm was obtained by plotting the difference in the volume of hydrogen adsorbed from the first and repeat analyses versus the hydrogen pressure and by extrapolating to zero pressure to obtain hydrogen uptake due to chemisorption on nickel. The nickel dispersion and nickel surface area were calculated assuming that one hydrogen atom is adsorbed on one surface nickel atom [18, 124, 125].
As listed in Table 4.3, the nickel dispersion is observed to be quite poor (2.3-6.4%) for all catalysts. The apparent low nickel dispersion on the high surface area of sol-gel alumina could be due to the formation of NiAl₂O₄, which is rather difficult to reduce and therefore is not available for H₂ chemisorption [126, 127]. The amount of H₂ chemisorbed on pure sol-gel alumina is negligibly small, thus no correction on H₂ uptake values was made. Furthermore, the method of dispersion calculations may not be quite applicable for these catalysts, since these calculation methods assume the supported metal to be present primarily on the surface (as a result of an impregnation process), whereas our catalysts are prepared by a modified sol-gel technique where some of the nickel metal can be in the alumina support matrix. The nickel dispersion and nickel surface area increase in the following order:

20% Ni-2% La/Al₂O₃ < 20% Ni/Al₂O₃ ≈ 20% Ni-2% Yb/Al₂O₃ < 20% Ni-2% Ce/Al₂O₃

Additionally, the nickel dispersion and nickel surface area are seen to decrease at higher lanthanide content; a decrease is more pronounced with Ni-Ce/Al₂O₃ and Ni-Yb/Al₂O₃ catalysts. This implies that higher amounts of lanthanides could cover or block nickel sites for hydrogen adsorption.

The effect of calcination and reduction temperatures on the nickel dispersion and nickel surface area of Ni/Al₂O₃ and Ni-Ce/Al₂O₃ catalysts is further examined. As reported in Table 4.4, there are three major exhibited by the H₂ chemisorption data: (i) For the catalysts calcined at 450 °C, the nickel dispersion and nickel surface area increase with increasing reduction temperature and reach a maximum at 600 °C. Further increase in reduction temperature to 700 °C leads to a decrease in both parameters. It is conceivable that growth of nickel crystallites becomes more prominent with higher
reduction temperatures, (ii) The nickel dispersion and nickel surface area increase with increasing reduction temperature for the catalysts calcined at 600 °C. In addition, the catalysts exhibit higher nickel dispersion and larger nickel surface area at the reduction temperature of 700 °C compared to those calcined at 450 °C. (iii) Regardless of calcination and reduction temperatures, Ni-Ce/Al₂O₃ catalysts possess higher nickel dispersion and larger nickel surface area than Ni/Al₂O₃ catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>%D³</th>
<th>MSA (m²/g)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% Ni/Al₂O₃</td>
<td>4.95</td>
<td>6.59</td>
</tr>
<tr>
<td>20% Ni-2% La/Al₂O₃</td>
<td>3.67</td>
<td>4.88</td>
</tr>
<tr>
<td>20% Ni-5% La/Al₂O₃</td>
<td>3.35</td>
<td>4.46</td>
</tr>
<tr>
<td>20% Ni-2% Ce/Al₂O₃</td>
<td>6.37</td>
<td>8.48</td>
</tr>
<tr>
<td>20% Ni-5% Ce/Al₂O₃</td>
<td>2.35</td>
<td>3.13</td>
</tr>
<tr>
<td>20% Ni-2% Yb/Al₂O₃</td>
<td>4.97</td>
<td>6.62</td>
</tr>
<tr>
<td>20% Ni-5% Yb/Al₂O₃</td>
<td>2.85</td>
<td>3.80</td>
</tr>
</tbody>
</table>

³ % nickel dispersion.

² Nickel surface area, m²/g.

Table 4.3: H₂ chemisorption data on various lanthanide-promoted sol-gel Ni/Al₂O₃ catalysts reduced under H₂ at 600 °C for 2 h.
Table 4.4: Effect of calcination ($T_{\text{cal}}$) and reduction ($T_{\text{red}}$) temperatures on nickel dispersion and surface area of sol-gel 20% Ni/Al$_2$O$_3$ and 20% Ni- 2% Ce/Al$_2$O$_3$ catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$T_{\text{cal}}$ (°C)</th>
<th>$T_{\text{red}}$ (°C)</th>
<th>%D$^a$</th>
<th>MSA (m$^2$/g)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% Ni/Al$_2$O$_3$</td>
<td>450</td>
<td>500</td>
<td>3.72</td>
<td>4.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>4.95</td>
<td>6.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>700</td>
<td>4.82</td>
<td>6.42</td>
</tr>
<tr>
<td>20% Ni- 2% Ce/Al$_2$O$_3$</td>
<td>600</td>
<td>500</td>
<td>3.32</td>
<td>4.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>5.25</td>
<td>6.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>700</td>
<td>5.40</td>
<td>7.19</td>
</tr>
<tr>
<td>20% Ni/Al$_2$O$_3$</td>
<td>450</td>
<td>500</td>
<td>5.17</td>
<td>6.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>6.37</td>
<td>8.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>700</td>
<td>6.22</td>
<td>8.28</td>
</tr>
<tr>
<td>20% Ni- 2% Ce/Al$_2$O$_3$</td>
<td>600</td>
<td>500</td>
<td>3.77</td>
<td>5.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>6.20</td>
<td>8.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>700</td>
<td>6.72</td>
<td>8.95</td>
</tr>
</tbody>
</table>

$^a$ % nickel dispersion.

$^b$ Nickel surface area, m$^2$/g.
X-ray Photoelectron Spectroscopy. XPS analysis was conducted to study the nature of surface nickel species over the catalysts after reduction under 20% H₂/N₂ at 600 °C for 2 h. The catalysts were transferred to the XPS chamber without exposing them to the atmosphere. The Ni 2p XPS spectra of reduced lanthanide-promoted catalysts are shown in Figure 4.3. The Ni 2p XPS spectra of the catalysts exhibit features that are assigned to Ni²⁺ with Ni 2p₃/₂ and Ni 2p₁/₂ binding energies at 855.8 and 873.3 eV, respectively and Ni⁰ with Ni 2p₃/₂ and Ni 2p₁/₂ binding energies at 852.7 and 870.2 eV, respectively [128-131]. The signal of Ni²⁺ species is likely to be due to NiAl₂O₄ although the possibility of a NiO phase cannot be excluded since the Ni 2p binding energies for these two species are very close together. The Ni 2p₃/₂ signal corresponding to Ni²⁺ is accompanied by a broader peak located at 860.8 eV due to a strong shake-up process [132]. Ni 2p XPS spectra imply that the reduction of nickel species to the metallic state in the sol-gel catalysts was not complete due to a strong interaction of nickel oxide with the alumina support. In addition, all catalysts show similar Ni 2p XPS spectra, suggesting that nickel species in these catalysts exist in a similar coordination environment. Deconvolution of the Ni 2p XPS spectra was performed by Gaussian-Lorentzian curve-fitting method to determine the peak areas for obtaining relative surface concentrations of nickel species. The ratio of peak areas $A_{Ni^0}/(A_{Ni^0}+A_{Ni^{2+}})$ is used to illustrate the degree of reducibility.
Figure 4.3: Ni 2p XPS spectra of lanthanide-promoted sol-gel 20% Ni/Al₂O₃ catalysts reduced at 600 °C.
As displayed in Table 4.5, a significant increase in the $A_{Ni}^0/(A_{Ni}^0+A_{Ni}^{2+})$ ratio for lanthanide-promoted Ni/Al$_2$O$_3$ catalysts is seen after reduction compared to that of the unpromoted catalyst, indicative of an enhancement in the catalyst reducibility with lanthanide promotion. This is in agreement with TPR results obtained with the lanthanide-promoted catalysts, which have shown a shift in the maximum of the high-temperature peak corresponding to the reduction of Ni in NiAl$_2$O$_4$ toward lower temperatures. For reduced Ni/Al$_2$O$_3$, only 27% of surface nickel is found in zero state while 73% is in the +2 state. In contrast, 68-89% of surface nickel is found in the metallic phase with 11-32% remaining in the oxide phase for reduced lanthanide-promoted catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$A_{Ni}^0/(A_{Ni}^0+A_{Ni}^{2+})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% Ni/Al$_2$O$_3$</td>
<td>0.37</td>
</tr>
<tr>
<td>20% Ni-2% La/Al$_2$O$_3$</td>
<td>0.62</td>
</tr>
<tr>
<td>20% Ni-2% Ce/Al$_2$O$_3$</td>
<td>0.64</td>
</tr>
<tr>
<td>20% Ni-2% Yb/Al$_2$O$_3$</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Table 4.5: Comparison of the $A_{Ni}^0/(A_{Ni}^0+A_{Ni}^{2+})$ XPS ratio of the catalysts after reduction at 600 °C.
4.4 Reaction performance in propane steam reforming

*Effect of synthesis parameters.* The effect of catalyst synthesis parameters on the catalytic activity of sol-gel Ni/Al₂O₃ catalysts at 500 °C and H₂O/C = 1.3 is shown in Table 4.6. The parameters examined are Ni content, pH and H₂O/ATB ratio. It is noted that H₂ yield is defined as (2 x moles of H₂ produced/total moles of hydrogen in the feed). As reported in Table 4.6, C₃H₈ conversion and H₂ yield are seen to increase with increasing Ni content and reach a maximum at 20 wt%, with C₃H₈ conversion and H₂ yield at 53% and 37%, respectively. Further increase in Ni content to 25 wt% leads to a decline in catalytic activity. Moreover, the variations of pH and H₂O/ATB ratio also have a pronounced effect on catalytic activity of 20% Ni/Al₂O₃ catalysts. The selectivities to C-containing products are also shown in Table 4.6. The C-containing products from propane steam reforming are CO, CO₂, and CH₄ with CO₂ being the main one. CO₂ selectivity is seen to increase with a decrease in CH₄ selectivity at lower C₃H₈ conversions. No CH₄ formation is observed at 10 wt%.

*Effect of lanthanide promotion.* Several sol-gel 20% Ni/Al₂O₃ catalysts promoted with lanthanide elements (La, Ce, Yb) were subsequently prepared at pH = 4.8 and H₂O/ATB = 3.6. The influence of lanthanide promotion (2 wt%) on catalytic performance at differing reaction temperatures is shown in Figure 4.4. C₃H₈ conversion (Figure 4.4(a)) and H₂ yield (Figure 4.4(b)) are seen to increase with increasing reaction temperature on all catalysts. Hydrogen yield that would be obtained at equilibrium is also included for comparison. 20% Ni-2% Ce/Al₂O₃ and 20% Ni-2% Yb/Al₂O₃ catalysts show an improvement in C₃H₈ conversion and H₂ yield compared to 20% Ni/Al₂O₃.
catalyst. Although 20% Ni-2% La/Al₂O₃ catalyst exhibits similar C₃H₈ conversion to 20% Ni/Al₂O₃ catalyst, it still shows an increased H₂ yield above 450 °C. At 500 °C, the highest C₃H₈ conversion (84%) and H₂ yield (50%) are achieved with 20% Ni-2% Yb/Al₂O₃ catalyst. The effect of lanthanide promotion is more evident at higher reaction temperatures. Moreover, heavier lanthanides exhibit a more pronounced effect than lighter ones; the catalytic activity at 500 °C increases in the following order: La < Ce < Yb.

When the performances in propane steam reforming at different lanthanide contents are compared at 500 °C (Table 4.7), reaction data show that C₃H₈ conversion and H₂ yield decrease with increasing lanthanide content from 2 wt% to 5 wt%. H₂ chemisorption data have also shown a decreasing trend of nickel surface area at higher lanthanide content. This indicates that the catalytic activity of lanthanide-promoted sol-gel Ni/Al₂O₃ catalysts is strongly related to nickel surface area. Thus, loss of activity with higher lanthanide content is due to the blockage of active sites by excess amounts of lanthanides introduced in the catalysts. It is noted that the distribution of C-containing products is not much affected by an increase in lanthanide content.
<table>
<thead>
<tr>
<th>Ni content (wt%)</th>
<th>pH</th>
<th>H₂O/ATB ratio</th>
<th>C₃H₈ conversion (%)</th>
<th>H₂ yield (%)</th>
<th>CO₂ (%)</th>
<th>CH₄ (%)</th>
<th>CO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
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<td>16</td>
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<td>15</td>
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<td>3.6</td>
<td>27</td>
<td>33</td>
<td>73</td>
<td>19</td>
<td>8</td>
</tr>
<tr>
<td>20</td>
<td>4.8</td>
<td>3.6</td>
<td>53</td>
<td>37</td>
<td>54</td>
<td>36</td>
<td>10</td>
</tr>
<tr>
<td>25</td>
<td>4.8</td>
<td>3.6</td>
<td>43</td>
<td>29</td>
<td>52</td>
<td>31</td>
<td>17</td>
</tr>
<tr>
<td>20</td>
<td>4.8</td>
<td>3.6</td>
<td>53</td>
<td>37</td>
<td>54</td>
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<td>3.6</td>
<td>27</td>
<td>26</td>
<td>68</td>
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<td>12</td>
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<td>20</td>
<td>4.8</td>
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<td>37</td>
<td>54</td>
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<td>7</td>
</tr>
<tr>
<td>20</td>
<td>4.8</td>
<td>5.0</td>
<td>23</td>
<td>23</td>
<td>77</td>
<td>15</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 4.6: Propane steam reforming reaction data obtained with sol-gel Ni/Al₂O₃ catalysts – effect of synthesis parameters.
Figure 4.4: Effect of reaction temperature on catalytic performance of lanthanide-promoted sol-gel 20% Ni/Al₂O₃ catalysts in propane steam reforming: (a) C₃H₈ conversion (b) H₂ yield [Reaction conditions: 400-500 °C, C₃H₈/H₂O/N₂ = 1/4/95, feed flow rate = 300 cm³/min, equal surface area reactions (9 m²)].
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>C\textsubscript{3}H\textsubscript{8} conversion (%)</th>
<th>H\textsubscript{2} yield (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO\textsubscript{2}</td>
</tr>
<tr>
<td>20% Ni/Al\textsubscript{2}O\textsubscript{3}</td>
<td>53</td>
<td>37</td>
<td>54</td>
</tr>
<tr>
<td>20% Ni-2%La/Al\textsubscript{2}O\textsubscript{3}</td>
<td>51</td>
<td>40</td>
<td>59</td>
</tr>
<tr>
<td>20% Ni-5%La/Al\textsubscript{2}O\textsubscript{3}</td>
<td>29</td>
<td>29</td>
<td>55</td>
</tr>
<tr>
<td>20% Ni-2%Ce/Al\textsubscript{2}O\textsubscript{3}</td>
<td>72</td>
<td>46</td>
<td>50</td>
</tr>
<tr>
<td>20% Ni-5%Ce/Al\textsubscript{2}O\textsubscript{3}</td>
<td>53</td>
<td>38</td>
<td>56</td>
</tr>
<tr>
<td>20% Ni-2%Yb/Al\textsubscript{2}O\textsubscript{3}</td>
<td>84</td>
<td>50</td>
<td>46</td>
</tr>
<tr>
<td>20% Ni-5%Yb/Al\textsubscript{2}O\textsubscript{3}</td>
<td>65</td>
<td>44</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 4.7: Reaction comparison for propane steam reforming (dilution experiments) at 500 °C [Reaction conditions: 500 °C, C\textsubscript{3}H\textsubscript{8}/H\textsubscript{2}O/N\textsubscript{2} = 1/4/95, feed flow rate = 300 cm\textsuperscript{3}/min, equal surface area reactions (9 m\textsuperscript{2})].

To further investigate catalytic performance at higher reaction temperature, steady-state reaction experiments were conducted at 550 °C. However, the feed flow rate was raised to 400 cm\textsuperscript{3}/min to avoid complete C\textsubscript{3}H\textsubscript{8} conversion. Interestingly, the highest C\textsubscript{3}H\textsubscript{8} conversion (80%) and H\textsubscript{2} yield (52%) are obtained with 20% Ni-2% Ce/Al\textsubscript{2}O\textsubscript{3} catalyst at 550 °C (Table 4.8). Furthermore, 20% Ni-2% La/Al\textsubscript{2}O\textsubscript{3} catalyst also shows a
significant improvement in steam reforming activity compared to 20% Ni/Al₂O₃ catalyst under these reaction conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>C₃H₈ conversion (%)</th>
<th>H₂ yield (%)</th>
<th>Selectivity (%)</th>
<th>CO₂</th>
<th>CH₄</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% Ni/Al₂O₃</td>
<td>48</td>
<td>36</td>
<td>48 21 31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% Ni-2%La/Al₂O₃</td>
<td>66</td>
<td>52</td>
<td>38 25 37</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% Ni-2%Ce/Al₂O₃</td>
<td>80</td>
<td>52</td>
<td>31 32 37</td>
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<td></td>
</tr>
<tr>
<td>20% Ni-2%Yb/Al₂O₃</td>
<td>70</td>
<td>50</td>
<td>33 30 37</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Table 4.8: Reaction comparison for propane steam reforming (dilution experiments) at 550 °C.

“Neat” experiments were performed with 20% Ni/Al₂O₃, 20% Ni-2% Ce/Al₂O₃, and 20% Ni-2% Yb/Al₂O₃ catalysts in propane steam reforming without N₂ dilution at the following conditions: 500-550 °C, H₂O/C = 4, total feed rate = 270 cm³/min, equal surface area reaction (18 m²). Demineralized distilled water was delivered by an Eldex metering pump (Model: A-10-S) connected with a 40 psi back pressure regulator and
subsequently vaporized in a preheater which was operated above 150 °C. A column packed with ceramic beads was installed after the preheater to help C₃H₈ and steam mix effectively. The steady-state reaction experiments were performed using 1/2 in. O.D. stainless steel flow reactor to avoid high pressure drop due to higher amounts of catalysts loaded in the reactor. Consistent with reaction data obtained from dilution experiments, 20% Ni-2% Yb/Al₂O₃ catalyst is seen to give the highest C₃H₈ conversion and H₂ yield at 500 °C (Table 4.9). On the other hand, at 550 °C, 20% Ni-2% Ce/Al₂O₃ catalyst exhibits higher C₃H₈ conversion and H₂ yield compared to 20% Ni-2% Yb/Al₂O₃ catalyst. Moreover, an increase in CO selectivity is observed at higher reaction temperature. This suggests an increased contribution from the reverse water-gas shift reaction (CO₂ + H₂ → CO + H₂O) to the overall reaction network. Another possible explanation is that at higher conversion, water becomes the limiting reactant, and leading to an increased formation of CO as opposed to CO₂ from the steam reforming reaction. Increased coking on the surface at higher temperatures could also lead to higher CO formation through the gasification of surface carbon.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>C₃H₈ conversion (%)</th>
<th>H₂ yield (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO₂</td>
<td>CH₄</td>
</tr>
<tr>
<td>20% Ni/Al₂O₃</td>
<td>500</td>
<td>35</td>
<td>14</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>43</td>
<td>18</td>
<td>69</td>
</tr>
<tr>
<td>20% Ni-2%Ce/Al₂O₃</td>
<td>500</td>
<td>43</td>
<td>15</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>95</td>
<td>31</td>
<td>58</td>
</tr>
<tr>
<td>20% Ni-2%Yb/Al₂O₃</td>
<td>500</td>
<td>59</td>
<td>19</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>83</td>
<td>27</td>
<td>58</td>
</tr>
</tbody>
</table>

Table 4.9: Reaction comparison for propane steam reforming (neat experiments).

*Effect of calcination and reduction temperatures.* Upon calcination at 450 °C, 20% Ni-2% Ce/Al₂O₃ catalyst exhibits higher H₂ yield compared to 20% Ni/Al₂O₃ catalyst at the reduction temperatures ranging from 500-700 °C (Figure 4.5(a)). An improvement in H₂ yield with cerium promotion is more evident at higher reduction temperature. Furthermore, the catalytic activity of both catalysts calcined at 450 °C is seen to go through a maximum at the reduction temperature of 600 °C and decreases at higher reduction temperature. By comparing the performance of 20% Ni-2% Ce/Al₂O₃ catalysts calcined at 450 and 600 °C, we see that the reduction temperature affects H₂ yield in a similar fashion (Figure 4.5(b)). The optimum reduction temperature is 600 °C regardless of calcination temperature. However, higher calcination temperature causes a decline in catalytic activity. This observation is in agreement with TPR and H₂
chemisorption results. When Ni-Ce/Al₂O₃ catalysts are calcined at higher temperature (600 °C), NiO interacts with Al₂O₃ to form a very stable NiAl₂O₄ spinel which is more difficult to reduce [133-137]. Our in-situ X-ray diffraction studies performed to observe the phase changes during reduction have shown incomplete reduction at lower temperatures while sintering of Ni was observed at higher temperatures [138].

Effect of gas hourly space velocity (GHSV). The catalytic performance of 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts in propane steam reforming was further investigated at various space velocities. The reaction conditions for these experiments were as follows: 500-550 °C, H₂O/C = 2. The variation of GHSV was performed by adjusting both the amount of the catalyst (10-20 mg) and the feed flow rate (200-400 cm³/min).
Figure 4.5: Effect of calcination and reduction temperatures on catalytic performance in propane steam reforming: [Reaction conditions: 550 °C, H₂O/C = 2, GHSV = 248,000 h⁻¹]: (a) Comparison between 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts calcined at 450 °C (b) Effect of calcination temperature on 20% Ni-2% Ce/Al₂O₃ catalysts.
Figure 4.6: Effect of GHSV on H₂ yield at 500-550 °C and H₂O/C = 2 in propane steam reforming over 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts.
As expected, H₂ yield increases with decreasing GHSV from 496,000 to 124,000 h⁻¹ over both catalysts (Figure 4.6). At 500 °C, the beneficial effect of cerium promotion becomes much more pronounced at lower GHSVs. At 550 °C, an improvement in H₂ yield with the addition of cerium is more evident for the whole range of GHSVs examined. The highest H₂ yield (50%) observed is achieved with 20% Ni-2% Ce/Al₂O₃ catalyst at 550 °C and 124,000 h⁻¹. C₃H₈ conversion rates at steady state were further normalized to surface nickel atoms, measured by H₂ chemisorption at 35 °C, in the form of turnover frequencies (TOFs). Table 4.10 compares average TOFs obtained with 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts at 500 and 550 °C. TOF is seen to increase with increasing reaction temperature. The increase is more pronounced with 20% Ni-2% Ce/Al₂O₃ catalyst. Furthermore, the higher activity of promoted catalysts is clearly seen when TOF values are compared for the 20% Ni-2% Ce/Al₂O₃ and 20% Ni/Al₂O₃ catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500 °C</td>
</tr>
<tr>
<td>20% Ni/Al₂O₃</td>
<td>0.35</td>
</tr>
<tr>
<td>20% Ni-2%Ce/Al₂O₃</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Table 4.10: Effect of reaction temperature on turnover frequency.
The variation of product selectivities with C$_3$H$_8$ conversion over 20% Ni/Al$_2$O$_3$ and 20% Ni-2% Ce/Al$_2$O$_3$ catalysts is shown in Figure 4.7(a-d). In this study, CO$_2$ selectivity is defined as the ratio of moles of CO$_2$ produced to the total moles of C-containing products (i.e., CO$_2$, CO, and CH$_4$) whereas H$_2$ selectivity is defined as 2 x moles of H$_2$ produced/total moles of hydrogen in the H-containing products, which are H$_2$ and CH$_4$. Interestingly, CH$_4$ selectivity is seen to increase at the expense of both H$_2$ and CO$_2$ selectivities at lower GHSV, i.e., higher conversions. This suggests that CO$_2$ methanation (CO$_2$ + 4H$_2$ → CH$_4$ + 2H$_2$O) becomes more appreciable at when residence time is increased, leading to an increased CH$_4$ selectivity. CO selectivity, on the other hand, is not much affected by the variation of C$_3$H$_8$ conversion over either catalyst.
Figure 4.7: Variation with C$_3$H$_8$ conversion of product selectivity over: (a) 20% Ni/Al$_2$O$_3$ at 500 °C (b) 20% Ni/Al$_2$O$_3$ at 550 °C (c) 20% Ni-2% Ce/Al$_2$O$_3$ at 500 °C (d) 20% Ni-2% Ce/Al$_2$O$_3$ at 550 °C.
4.5 DRIFTS studies

\[ C_3H_8-TPD/TPReaction \]. TPD/TPReaction experiments with DRIFTS were performed over reduced 20% Ni-2% Ce/Al2O3 catalyst, where strongly adsorbed propane was allowed to react with water. Adsorption of propane was carried out at room temperature for 1 h. The system was subsequently purged and heated under He and spectra were collected in steps under He flow up to 450 °C. The introduction of H2O was performed at 450 °C for different times on stream (i.e., 5, 10, and 15 min.) followed by He flushing before spectra were taken.

Figure 4.8 shows DRIFT spectra taken at 25, 100, 200, 250, 300, and 450 °C under He after C3H8 adsorption over reduced 20% Ni-2% Ce/Al2O3 catalyst. After propane adsorption and He flushing, bands remained at 2940, 2932 (shoulder), 2824, 1630, 1476, 1435 (shoulder), 1373, 1189, and 1103 cm\(^{-1}\) at room temperature. The band at 1630 cm\(^{-1}\) could be attributed to an olefinic C=C vibration [139, 140] and has been observed in a separate propylene adsorption/desorption DRIFTS experiment performed in our laboratory (Figure 4.9). However, bands typical of olefinic C=C stretching present above 3000 cm\(^{-1}\) were not observed after propane adsorption which leads us to assume that the band at 1630 cm\(^{-1}\) could be assigned as the O-H bending frequency of water as observed by Gates and co-workers [141]. The remaining bands are characteristic of adsorbed propylidyne [139, 142] and are rather equivalent to resultant spectra of propane adsorbed on a reduced Ir/Al2O3 catalyst [141]. In addition, a negative peak at 3750 cm\(^{-1}\), which is characteristics of surface hydroxyl groups on the alumina support, was observed [143, 144].
Figure 4.8: DRIFT spectra taken over reduced 20% Ni-2% Ce/Al₂O₃ catalysts after C₃H₈ adsorption; *H₂O was introduced for 5, 10, and 15 min. and the system was flushed under He for 5 min.
This indicates that the surface hydroxyl groups either interacted with propane or were consumed upon the adsorption of propane. Although the intensities of the bands at 2940 and 2824 cm\(^{-1}\) decreased at higher temperatures, they were thermally stable up to 450 °C. The features at 2940 and 2932 cm\(^{-1}\) are assigned to asymmetric CH\(_3\) stretching [\(\nu_{as}(CH_3)\)] and asymmetric CH\(_2\) stretching [\(\nu_{as}(CH_2)\)], respectively [139, 142, 145-147]. The feature at 2824 cm\(^{-1}\) could be attributed to either symmetric CH\(_2\) stretching [\(\nu_s(CH_2)\)] or symmetric CH\(_3\) stretching [\(\nu_s(CH_3)\)] [142, 148].

The features at 2940, 2824, 1476, 1437, 1373, 1189, 1103 cm\(^{-1}\) decreased in intensity with temperature and subsequently almost disappeared at 300 °C. These features could be associated with adsorbed ethylidyne/propylidyne species that were depleted upon the reaction with H\(_2\)O. At 450 °C and before the introduction of water, new bands at 1600 and 1374 cm\(^{-1}\) were present accompanied by two small C-H stretching bands at 2954 and 2904 cm\(^{-1}\). Although it is conceivable that new CH\(_3\) groups could be forming due to desorption/re-adsorption processes, a more likely explanation is that the features at 2954, 2904, 1600, and 1374 cm\(^{-1}\) are due to formate species [149, 150]. With the introduction of water at 450 °C, the bands associated with the formate species grew much stronger and were seen in higher intensity with time on stream. In the course of propane steam reforming, formate species are probably produced by the reaction of CO with the water introduced. In the absence of water, surface hydroxyl groups can serve as a source of oxygen to form formate species. Our formate band assignments are consistent with those which arise from adsorption of CO on 1% Au/ceria and 1% Pt/ceria catalysts [151]. Two additional features at 1455 and 1255 cm\(^{-1}\), which could be attributed to carbonate species, were also observed after H\(_2\)O exposure at 450 °C [149, 150].
In order to help in the band assignments for the C$_3$H$_8$-TPD/TPReaction experiment, propylene, water-only, and CO$_2$ adsorption with DRIFTS were also performed. Figure 4.9 shows DRIFT spectra taken at 25, 250, and 450 °C under He flow over reduced 20% Ni-2% Ce/Al$_2$O$_3$ catalyst during the C$_3$H$_6$-TPD experiment. The strong presence of the band at 1630 cm$^{-1}$ on the catalyst surface following propylene adsorption signals the C=C stretching vibration. Presence of olefinic C-H vibrations that would be expected above 3000 cm$^{-1}$ cannot be discerned from this spectrum due to a very broad feature in that region. It is possible that adsorbed propylene could be dehydrogenated on the surface, giving rise to water (surface hydroxyl groups), which would show an IR band around 1630 cm$^{-1}$ as well as a broad feature above 3000 cm$^{-1}$. The feature at 1373 cm$^{-1}$, which was quite prominent following propane adsorption, could not be observed after propylene adsorption. This observation supports the assignment of the band at 1373 cm$^{-1}$ to symmetric CH$_3$ bending [$\delta_s$(CH$_3$)] of propylidyne. This assignment is in agreement with what is reported by Shahid and Sheppard [142]. In addition, the feature at 2824 cm$^{-1}$ was absent, and the 2940 cm$^{-1}$ band was much weaker and disappeared very quickly at higher temperatures. The band at 1476 cm$^{-1}$, which was quite strong following propane adsorption was barely noticeable (~1456 cm$^{-1}$) after propylene adsorption. This observation makes us believe that this feature could be due to a methyl group, which may have a different orientation in species resulting from propylene adsorption. This explanation would also be consistent with our earlier assertion that propylidyne species are the predominant hydrocarbon derivatives on the surface following propane adsorption, but this is not necessarily the case following propylene adsorption.
Figure 4.9: DRIFT spectra taken over reduced 20% Ni-2% Ce/Al₂O₃ catalysts after C₃H₆ adsorption at room temperature.
Figure 4.10: DRIFT spectra taken over reduced 20% Ni-2% Ce/Al₂O₃ catalysts after CO₂ adsorption at room temperature.
From DRIFT spectra of CO\textsubscript{2}-TPD over the reduced 20% Ni-2% Ce/Al\textsubscript{2}O\textsubscript{3} catalyst, bands at 3619, 2355, 2325, 1643, 1543 (shoulder), 1438, 1387 (shoulder), 1229, and 1084 cm\textsuperscript{-1} are seen at room temperature (Figure 4.10). The bands at 3619, 1643, 1438, and 1229 cm\textsuperscript{-1} are assigned to bicarbonate species and decrease in intensity significantly at 250 °C [149, 150, 152]. Conversely, carbonate species are characterized by the shoulder bands at 1543, and 1387 cm\textsuperscript{-1} as well as the 1084 cm\textsuperscript{-1} band [149, 150, 152]. In addition, the only other feature observed is a doublet at 2355 and 2325 cm\textsuperscript{-1}, which corresponds to adsorbed CO\textsubscript{2} [153, 154]. The disappearance of carbonate and bicarbonate species at higher temperatures leads us to believe that formate and carbonate species observed from the C\textsubscript{3}H\textsubscript{8}-TPD/TPReaction experiment are the result of the surface transformation of propylidyne species rather than from the re-adsorption of CO\textsubscript{2}.

\textit{C\textsubscript{3}H\textsubscript{8} + H\textsubscript{2}O-TPReaction}. C\textsubscript{3}H\textsubscript{8} + H\textsubscript{2}O-TPReaction with DRIFTS was also performed over reduced 20% Ni-2% Ce/Al\textsubscript{2}O\textsubscript{3} catalyst. C\textsubscript{3}H\textsubscript{8} was adsorbed at room temperature for 1 h. The system was then purged under He for 30 min. and H\textsubscript{2}O was subsequently introduced for 5 min. at room temperature followed by He flushing for 5 min. The system was heated and DRIFT spectra were collected in steps under He flow up to 450 °C. It is noted that H\textsubscript{2}O was re-introduced at each temperature for 5 min. followed by He flushing before taking spectra.

After C\textsubscript{3}H\textsubscript{8} and H\textsubscript{2}O introduction at room temperature, bands remained at 3750-3500 (very broad), 2940, 2824, 2055, 1630, 1435 (weak), 1373 (weak), and 1255 (weak) cm\textsuperscript{-1} (Figure 4.11). The broad band around 3750-3500 cm\textsuperscript{-1} is characteristic of the OH stretching region while the feature at 2055 cm\textsuperscript{-1} is assigned as linearly adsorbed CO on
the catalyst surface and disappeared above 200 °C [155-157]. Compared to the DRIFT spectrum after C\textsubscript{3}H\textsubscript{8} adsorption at room temperature, the intensity of the band located at 1630 cm\textsuperscript{-1} increased significantly when H\textsubscript{2}O was introduced at room temperature. In a separate water-TPD experiment performed in our laboratory (not shown), a large band at 1630 cm\textsuperscript{-1} was attributed to adsorbed water. This band decreased in intensity at higher temperatures and eventually shifted to 1600 cm\textsuperscript{-1} at 450 °C. It is intuitive that the band at 1600 cm\textsuperscript{-1} could be a surface species which is produced from the reaction of C\textsubscript{3}H\textsubscript{8} with H\textsubscript{2}O and a formate species is a likely possibility. The features at 2940 and 2824 cm\textsuperscript{-1} were seen in much lower intensity and disappeared above 250 °C whereas the bands at 2954 and 1455 cm\textsuperscript{-1} started to appear at 200 °C and grew stronger at higher temperatures. Furthermore, two additional bands at 2904 and 1374 were seen at 450 °C. It is evident that most surface species such as formate and carbonate ions are formed upon the reaction of adsorbed C\textsubscript{3}H\textsubscript{8} and H\textsubscript{2}O above 250 °C.

Based on the observed surface specie transformations from in situ DRIFTS studies, the major reaction pathways for adsorbed propane in the presence of steam over reduced sol-gel Ni-Ce/Al\textsubscript{2}O\textsubscript{3} catalysts are proposed and are illustrated in Figure 4.12. The first step is believed to be adsorption of propane on metallic nickel sites to form propylidyne. To a lesser degree, adsorbed propane can further decompose into hydrocarbon fragments (i.e., CH\textsubscript{x}) and even carbon oxides in the presence of adsorbed water. Carbon deposition, especially at higher temperatures, also is a possibility as seen through our coking studies [138]. During this step, it is likely that the formation of carbon monoxide could be occurring on nickel sites. Adsorbed water from the catalyst can combine with adsorbed hydrocarbon fragments or adsorbed carbon monoxide to form
formate species. It is also possible that adsorbed hydrocarbon fragments could react with other sources of oxygen (hydroxyls, ceria) to form formates in the absence of water, as observed at 450 °C (Figure 4.8). Additionally, it is possible that water can dissociatively adsorbed to produce gaseous hydrogen and surface oxygen species. These surface oxygen species have been found to react with methane to form CO and hydrogen in methane steam reforming over various oxide supports, including ceria [158-160]. Unfortunately, we cannot obtain information pointing to the dissociative adsorption of water to form hydrogen from the DRIFTS experiments. However, the contribution from hydroxyls created from adsorbed water is expected to be much higher than that from surface oxygen. The thermal decomposition of adsorbed formates can result in the formation of carbon dioxide and hydrogen, or the formation of carbon monoxide and hydroxyl groups [150]. Moreover, the fraction of the formate remaining adsorbed could react with hydroxyl groups arising from adsorbed water to form carbonates and hydrogen at higher temperatures. While the DRIFTS experiments do not specifically indicate the participation of other surface intermediates, it could be possible that adsorbed species such as oxygen atoms, hydrogen atoms, and hydroxyl groups could also be spilling over to the nickel surface from the alumina support or ceria, thus enhancing the overall adsorption and participation of water.
Figure 4.11: DRIFT spectra taken over reduced 20% Ni-2% Ce/Al₂O₃ catalysts after C₃H₈ + H₂O adsorption.
Figure 4.12: Mechanistic steps during propane steam reforming over reduced Ni-Ce/Al₂O₃ catalyst as observed using in situ DRIFTS.
4.6 Summary

Sol-gel 20% Ni/Al₂O₃ catalysts promoted with lanthanide elements (La, Ce, and Yb) were studied with regard to their activity for the steam reforming of propane. The beneficial effect is induced upon low-content lanthanide promotion (2 wt%) of Ni/Al₂O₃ catalysts in catalytic performance under reaction conditions with and without N₂ dilution. Among the lanthanide elements examined, cerium is found to be very effective in improving the steam reforming activity. The better catalytic performance of lanthanide-promoted catalysts is partially attributed to easier reduction of nickel species to a metallic state. The pretreatment conditions (i.e., calcination and reduction temperatures) also markedly affect nickel surface area. High calcination temperature retards the catalyst reducibility due to a strong interaction of NiO and the Al₂O₃ support. Regardless of calcination temperature, the optimum reduction temperature is found to be 600 °C to obtain the best catalytic performance with respect to C₃H₈ conversion and H₂ yield. Furthermore, an increase in nickel surface area measured by H₂ chemisorption at 35 °C is apparently observed with the incorporation of cerium. In situ DRIFTS results show that ethylidyne/propylidyne species are formed after C₃H₈ adsorption at room temperature and are depleted upon the reaction with H₂O at 450 °C. Adsorbed species on Ni⁰ sites under C₃H₈ + H₂O flow are formate and carbonate ions which further decompose to CO, CO₂, and H₂.
5.1 Introduction

Steam reforming (SR) of hydrocarbons has seen increasing interest due to the necessity of efficient and cost-effective reforming technologies for hydrogen production for fuel cell applications. In practice, SR of hydrocarbons, especially that of methane, is performed at high temperature and low pressure over Ni-based catalysts. However, the high temperature required may favor several routes to the formation of carbon deposits such as the Boudouard reaction and methane/hydrocarbon decomposition. Additionally, Ni catalysts tend to agglomerate and then lose their active surface area under steam reforming conditions, resulting in short catalyst lifetimes. Therefore, novel preparation and promotion techniques that could resist rapid catalyst deactivation by coking and sintering are essential.

Much effort has been placed on development of Ni catalysts with improved resistance to coke formation by adding promoters. Alkali metals such as K₂O and CaO have been shown to improve coking resistance by enhancing carbon gasification but with the expense of a reduction in catalytic activity [2, 8]. The introduction of small amounts
of molybdenum or tungsten (0.5 wt% MoO$_3$ or WO$_3$) into Ni catalysts has shown to increase the coking resistance without a decrease in catalytic activity \[23, 25, 45, 46, 161\]. The mechanism of coke minimization on molybdenum-promoted Ni catalysts was proposed as follows: Mo$^{+n}$ on the nickel surface is first oxidized to Mo$^{+(n+2)}$, which then reacts with adsorbed Ni-C or Ni-CH$_x$ yielding CO and H$_2$, and is finally reduced back to Mo$^{+n}$ \[46\].

Alternatively, lanthanides appear to be promising promoters since they can inhibit coke formation without sacrificing the catalytic activity \[26, 112, 114\]. Zhuang et al. \[26\] investigated the effect of cerium oxide as the promoter in MgAl$_2$O$_4$-supported Ni catalysts for methane steam reforming at 550 °C. Cerium promotion showed a beneficial effect by not only decreasing the rate of carbon deposition but also increasing the catalytic activity. Wang and Lu \[114\] stated that the addition of CeO$_2$ into Ni/$\gamma$-Al$_2$O$_3$ catalysts enhanced the nickel dispersion and reactivities of carbon deposits, leading to an improvement in the catalytic activity and stability in carbon dioxide reforming of methane. An increase in sintering resistance by adding lanthanides into supported Ni catalysts was also reported \[27, 162\]. Incorporation of lanthanides (4 wt%) suppressed the growth of Ni crystallites and the formation of inactive NiO and NiAl$_2$O$_4$ phases \[27\]. Furthermore, oxides of heavier lanthanides (Gd, Er, and Dy) exhibited a more pronounced effect than those of lighter ones (La, Pr, Nd). Teixeira and Giudici \[162\] suggested that the sintering rate of small nickel crystallites, particularly for narrow initial crystallite size distributions and high initial dispersions in coprecipitated Ni/Al$_2$O$_3$, was facilitated at high temperatures when steam was present. However, the growth of nickel
crystallites under reduction and reaction conditions could be inhibited by lanthanum promotion.

In this study, lanthanide-promoted Ni/Al₂O₃ catalysts were prepared and evaluated with regard to their activity and stability for the steam reforming of propane. Characterization was performed using X-ray photoelectron spectroscopy (XPS), in situ X-ray diffraction (XRD), temperature-programmed oxidation (TPO), transmission electron microscopy (TEM), thermogravimetric analysis-temperature-programmed reaction (TGA-TPReaction), and sequential temperature-programmed coking/gasification/hydrogenation. Using the information obtained, possible deactivation mechanisms of lanthanide-promoted sol-gel Ni/Al₂O₃ catalysts in propane steam reforming are discussed.

5.2 Catalytic activity and stability for propane steam reforming

Effect of lanthanide addition. Lanthanide-promoted sol-gel 20% Ni/Al₂O₃ catalysts were evaluated with regard to activity and stability in propane steam reforming at 500-550 °C. Propane conversion and % activity loss data (inset) are presented in Figure 5.1. The feed percentages of these experiments were C₃H₈/H₂O/N₂ = 1/4/95. To ensure that steady-state reaction conditions do not allow the system to approach equilibrium-limited regime, GHSV was increased at higher temperatures. As shown in Figure 5.1(a), at 500 °C and 124,000 h⁻¹, 20% Ni-2% Ce/Al₂O₃ and 20% Ni-2% Yb/Al₂O₃ catalysts exhibit an increase in propane conversion whereas 20% Ni-2% La/Al₂O₃ catalyst shows similar steam reforming activity compared to 20% Ni/Al₂O₃
catalyst. More importantly, the addition of lanthanide elements leads to a significant improvement in catalyst stability as evidenced by a smaller percentage of activity loss. At 500 °C, the loss of catalytic activity increases in the following order:

Ni-Yb/Al₂O₃  (7%) < Ni-Ce/Al₂O₃ (12%) < Ni-La/Al₂O₃ (19%) < Ni/Al₂O₃ (23%)

However, an increase in activity loss becomes more evident with increasing reaction temperature possibly due to more severe catalyst deactivation by sintering and coke formation as shown in Figure 5.1(b). Interestingly, the highest propane conversion is achieved with 20% Ni-2% Yb/Al₂O₃ catalyst at 500 °C while 20% Ni-2% Ce/Al₂O₃ catalyst is the best-performing catalyst with regard to catalytic activity and stability at 550 °C. It is conceivable that a beneficial effect of cerium promotion on improvement in coking resistance is more pronounced at elevated temperatures, thus resulting in more stable catalysts. An enhancement in stability of cerium-containing Ni-based catalysts as a result of a reduction in carbon deposition during reforming processes has been reported earlier [26, 115, 163].

Effect of H₂O/C ratio. The effect of H₂O/C ratio on catalytic performance of 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts in propane steam reforming was investigated at 550 °C and 248,000 h⁻¹. The H₂O/C ratio was varied in the range of 1.3-2.7 by keeping the propane flow rate constant at 6 cm³(STP)/min. As shown in Figure 5.2(a), C₃H₈ conversion is seen to increase with increasing H₂O/C ratio. An increase in catalytic activity is more evident with 20% Ni-2% Ce/Al₂O₃ catalyst; 47% and 99% C₃H₈ conversion were obtained at H₂O/C ratios = 1.3 and 2.7, respectively. A significant improvement in catalyst stability is apparent at higher H₂O/C ratios when cerium is present in the catalysts [Figure 5.2(b)].
Figure 5.1: $C_3H_8$ conversion as a function of time on stream observed with various catalysts under the reaction conditions: (a) $T = 500 \, ^\circ C$, $H_2O/C = 1.3$, GHSV = 124,000 h$^{-1}$ (b) $T = 550 \, ^\circ C$, $H_2O/C = 1.3$, GHSV = 186,000 h$^{-1}$. The activity loss of the same set of catalysts is shown as insets.
Figure 5.2: Effect of H$_2$O/C ratio on catalytic activity and stability of 20% Ni/Al$_2$O$_3$ and 20% Ni-2% Ce/Al$_2$O$_3$ catalysts in propane steam reforming: (a) C$_3$H$_8$ conversion (b) Activity loss [Reaction conditions: 550 °C, F(C$_3$H$_8$) = 6 cm$^3$/min, GHSV = 248,000 h$^{-1}$, W$_{cat}$ = 10 mg].
On the other hand, an improvement in the catalyst stability of 20% Ni/Al₂O₃ catalysts is barely noticeable with increasing H₂O/C ratios. At 550 °C and H₂O/C = 2.7, 20% Ni-2% Ce/Al₂O₃ catalyst lost only 1% of its initial activity (TOS = 1 h) after steady state was reached while 20% Ni/Al₂O₃ catalyst gave 62% activity loss. Fig. 5.3 shows plots of H₂ formation rate at 550 °C as a function of time on stream observed with 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts at different H₂O/C ratios. A decline in H₂ formation rate is seen over both catalysts at lower H₂O/C ratios possibly due to catalyst deactivation by coke formation. At H₂O/C = 2.7, 20% Ni/Al₂O₃ catalyst still exhibits a pronounced reduction in H₂ formation rate in the first 15 hours whereas the Ni-Ce catalyst shows a very stable performance. Reaction results indicate that a high H₂O/C ratio coupled with cerium promotion is very effective in enhancing catalytic activity as well as preventing the activity loss.
Figure 5.3: H₂ formation rate at 550 °C as a function of time on stream observed at differing H₂O/C ratios over 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts.
5.3 Deactivation characteristics of sol-gel catalysts

Re-oxidation of metallic nickel sites. Figure 5.4 shows the Ni 2p region of the XPS spectra of sol-gel 20% Ni/Al₂O₃ catalysts promoted with 2 wt% La, Ce, and Yb after being exposed to the propane steam reforming reaction medium at 500 °C for 20 h. The Ni 2p XPS spectra of the catalysts exhibit features that are assigned to Ni²⁺ with Ni 2p3/2 and Ni 2p1/2 binding energies at 855.8 and 873.3 eV, respectively and Ni⁰ with Ni 2p3/2 and Ni 2p1/2 binding energies at 852.7 and 870.2 eV, respectively [128-131]. The signal of Ni²⁺ species is likely to be due to NiAl₂O₄ although the possibility of a NiO phase cannot be excluded since the Ni 2p binding energies for these two species are very close together. The Ni 2p₃/2 signal corresponding to Ni²⁺ is accompanied by a broader peak located at 860.8 eV due to a strong shake-up process [132]. Deconvolution of the Ni 2p XPS spectra was performed by Gaussian-Lorentzian curve-fitting method to determine the peak areas for obtaining relative surface concentrations of nickel species. The ratio of peak areas $\frac{A_{\text{Ni}^0}}{A_{\text{Ni}^0} + A_{\text{Ni}^{2+}}}$ is used to illustrate the degree of reduction before and after reaction. As displayed in Table 5.1, a decrease in the $\frac{A_{\text{Ni}^0}}{A_{\text{Ni}^0} + A_{\text{Ni}^{2+}}}$ ratio is seen after being exposed to the propane steam reforming atmosphere compared to freshly reduced pre-reaction catalysts. This suggests a partial oxidation of metallic nickel sites during the reaction. Since the Ni 2p binding energies for NiAl₂O₄ and NiO are very close together, it is not possible to determine if the re-oxidation to +2 state leads to the formation of NiO species. In addition, 20% Ni-2% La/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts contain more of the Ni species in a metallic phase (~50%) compared to 20% Ni/Al₂O₃ catalyst (32%) after being subjected to the propane steam reforming atmosphere.
Figure 5.4: Ni 2p XPS spectra of reduced catalysts after being exposed to the propane steam reforming atmosphere at 500 °C for 20 h.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$A_{\text{Ni}}^0/(A_{\text{Ni}}^0+A_{\text{Ni}}^{2+})$</th>
<th>Pre-reaction (reduction)</th>
<th>Post-reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% Ni/Al$_2$O$_3$</td>
<td>0.37</td>
<td></td>
<td>0.32</td>
</tr>
<tr>
<td>20% Ni-2% La/Al$_2$O$_3$</td>
<td>0.62</td>
<td></td>
<td>0.51</td>
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<tr>
<td>20% Ni-2% Ce/Al$_2$O$_3$</td>
<td>0.64</td>
<td></td>
<td>0.50</td>
</tr>
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<td>20% Ni-2% Yb/Al$_2$O$_3$</td>
<td>0.60</td>
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<td>0.33</td>
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Table 5.1: Comparison of the ratio of XPS peak areas $A_{\text{Ni}}^0/(A_{\text{Ni}}^0+A_{\text{Ni}}^{2+})$ of the catalysts before and after 20-h propane steam reforming.

*Ni sintering.* The sintering of Ni crystallites in lanthanide-promoted sol-gel 20% Ni/Al$_2$O$_3$ catalysts during reduction was studied from a determination of the mean Ni crystallite size by *in situ* XRD. The XRD patterns of 20% Ni-2% Yb/Al$_2$O$_3$ catalyst during reduction under 5% H$_2$/N$_2$ are shown in Figure 5.5. The pre-calcined catalyst is relatively amorphous as evidenced by broad peaks at room temperature. The possible crystalline phases are NiO, NiAl$_2$O$_4$, and $\gamma$-Al$_2$O$_3$. No ytterbium-related crystalline phases could be detected, suggesting that Yb species could be well dispersed on the alumina support undetectable by XRD. As the reduction temperature was increased to 450 °C, a metallic Ni phase starts to appear. The diffraction lines of Ni (111), (200), and (220) are seen to grow in intensity with further increase in reduction temperature up to
700 °C. *In situ* XRD results indicate that high reduction temperatures (above 500°C) necessary to reduce nickel species to a metallic state due to a strong interaction of nickel oxide with the alumina support. Nickel crystallite diameters of different lanthanide-promoted 20% Ni/Al₂O₃ catalysts were calculated from line broadening of Ni (111) diffraction line using the Scherrer equation [105] and are listed in Table 5.2. Ni crystallite diameter of the catalysts is found to increase with increasing reduction temperature. Compared to unpromoted catalyst, Ni crystallites are much smaller in lanthanide-promoted samples at all reduction temperatures. This suggests that the presence of lanthanide elements in sol-gel Ni/Al₂O₃ catalysts helps improve the sintering resistance of nickel crystallites during reduction.
Figure 5.5: XRD patterns of 20% Ni-2% Yb/Al₂O₃ catalysts during *in situ* reduction under 5% H₂/N₂.
### Table 5.2: Effect of reduction temperature on nickel crystallite diameter (nm) of lanthanide-promoted sol-gel 20% Ni/Al₂O₃ catalysts.

<table>
<thead>
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<th>Catalyst</th>
<th>Reduction temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500</td>
</tr>
<tr>
<td>20% Ni/Al₂O₃</td>
<td>29</td>
</tr>
<tr>
<td>20% Ni-2% La/Al₂O₃</td>
<td>16</td>
</tr>
<tr>
<td>20% Ni-2% Ce/Al₂O₃</td>
<td>16</td>
</tr>
<tr>
<td>20% Ni-2% Yb/Al₂O₃</td>
<td>12</td>
</tr>
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</table>

The stabilizing effect of lanthanides to prevent Ni sintering is associated with a surface phenomenon in which lanthanides, located mostly on the catalyst surface, could act as a spacer by separating Ni crystallites after reduction. BET surface area measurements show that the addition of lanthanides results in an increase in surface area. The BET surface area of a freshly calcined 20% Ni/Al₂O₃ catalyst is 209 m²/g whereas catalysts promoted with 2% lanthanides possess the BET surface area of 278-304 m²/g. It is also possible that a substantial fraction of lanthanides could be present inside the nickel crystallites. Topsoe et al. [164] reported that the existence of strain created by the occluded Al₂O₃ phase in the iron lattice led to a shift of the equilibrium iron particle size toward smaller particles. As a result, the presence of alumina in ammonia-synthesis iron
catalysts inhibited the growth of iron particles. Similarly, lanthanides could also cause strain in the nickel lattice and this is subsequently responsible for the formation of smaller nickel crystallites after reduction. Figure 5.6 displays the XRD patterns of 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts reduced at 700 °C. α-Al₂O₃ was used as an internal standard to investigate a change in the lattice parameter of the metallic Ni phase when cerium is added in sol-gel 20% Ni/Al₂O₃ catalysts. The peak maxima of Ni(111) and (200) diffraction lines of 20% Ni-2% Ce/Al₂O₃ catalyst shift to lower diffraction angles (2θ) compared to those of the unpromoted sample. The calculated lattice parameters are 3.5239 and 3.5278 Å in 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts reduced at 700 °C, respectively. It is noted that the lattice parameter of pure nickel, obtained from ICDD PDF database (PDF 4-850), is 3.5238 Å. This suggests that cerium could be embedded in the nickel lattice, thus preventing the growth of Ni crystallites.

It is known that sintering is an important cause of deactivation of Ni-based catalysts under steam reforming conditions. The sintering process can be affected by many parameters including temperature, chemical environment, catalyst composition and structure, and support morphology [165-167]. The sintering rate of Ni crystallites was considerably enhanced by high temperature and the presence of water in the feed gas [162, 168]. Moreover, sintering of the catalysts with a lower Ni loading was found to be slower and they exhibited a greater loss in Ni surface area compared to those with a higher Ni loading [165]. Type of support also plays a role on the thermal stability of active metal phase, thus affecting the sintering process. Nickel was found to be much
more stable on alumina compared to silica in a hydrogen atmosphere at 700 °C, partially due to a stronger metal-support interaction for Ni/Al₂O₃ catalysts [168].

_Coke formation._ Our reaction results indicate that the introduction of lanthanide elements in sol-gel 20% Ni/Al₂O₃ catalysts enhances steam reforming activity and stability significantly. It is likely that lanthanide promotion strongly affects the coking process under steam reforming conditions, thus improving the catalyst resistance to coking. To investigate the nature and amount of carbonaceous species formed on the surface during reaction, TPO and TEM were performed with 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts after 20 h propane steam reforming. TGA-TPReaction experiments were conducted to determine the temperature of coking initiation. In addition, coking studies were performed using sequential temperature-programmed coking/gasification/hydrogenation experiments.
Figure 5.6: Comparison of XRD patterns of 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts reduced at 700 °C: (a) 2θ = 42-46° (b) 2θ = 50-54°.
**TPO experiments.** TPO profiles of carbon deposited on 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts after 20 h propane steam reforming at 500 °C, H₂O/C = 1.3 are shown in Figure 5.7. TPO profiles of carbon deposited on both catalysts are similar. There are mainly two peaks observed, indicative of two types of carbonaceous species having different reactivity toward oxidation. A low-temperature peak at 360 °C could be assigned to amorphous carbon, which is highly reactive and easily oxidized from the catalyst surface [26, 115, 169-171]. A larger peak at 640 °C could be due to graphitic carbon, which is more stable and oxidized at higher temperature. Although the temperatures at which the CO₂ is eluted from the surface are identical for the two catalysts, the amount of CO₂ evolution from the oxidation of carbon deposited on 20% Ni/Al₂O₃ catalyst is much higher compared to 20% Ni-2% Ce/Al₂O₃ catalyst, suggesting a much larger amount of carbon deposited on Ni-only catalyst. As displayed in the inset, the amounts of carbon deposited, obtained by integrating the TPO curves, are 1.7 and 0.2 mg /m² on 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts, respectively. The amount of carbon deposited on the catalyst is reduced by approximately 90% upon cerium promotion. Furthermore, the formation of graphitic carbon is markedly suppressed when cerium is present as indicated by a smaller value of the ratio of the high-temperature (640 °C) peak area to the low-temperature (360 °C) peak area.

The effect of cerium as a promoter on coke minimization can be attributed to its unique properties as an oxygen carrier. The redox properties of ceria and the high lability of lattice oxygen are among the most important factors which contribute to the catalytic reactivity of CeO₂ in oxidation reactions [172]. Under steam reforming conditions, the presence of cerium could accelerate the reaction of steam with adsorbed
species on the nickel surface [26]. Subsequently, surface carbon species are quickly converted to products, decreasing the accumulation of carbon deposited on the catalysts.

**TEM experiments.** TEM was conducted to further characterize the structure of carbon deposited on 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts after 20 h propane steam reforming at 500 °C. As shown in Figure 5.8, there is clear evidence of significant amounts of carbon filaments covering nickel particles on unpromoted catalyst. Most of them exhibit some degree of curvature possibly due to an unequal diffusion of graphitic carbon through nickel particles [173]. Conversely, no carbon filaments are seen on post-reaction 20% Ni-2% Ce/Al₂O₃ catalyst. This indicates that carbon deposition and fiber growth are greatly suppressed due to the addition of cerium in Ni/Al₂O₃ catalysts. The nickel particles remained relatively small with a diameter ranging between 10 and 15 nm and homogeneously distributed. The morphology of a filament obtained with 20% Ni/Al₂O₃ catalyst is shown in Figure 5.9. A nickel particle is seen at the tip of the carbon filament. Upon the carbon filament formation, the deformation of the nickel particle occurred, resulting in the appearance of a pear shape [116, 174]. Moreover, the diameter of the carbon filament formed on the unpromoted sample is about 50 nm which is roughly the same as that of the Ni particle at the tip of the carbon filament. This suggests that the size of nickel particles determines the width of carbon filaments. The growth of carbon filaments has been observed previously with nickel particle sizes in the range of 10-60 nm [169].
Figure 5.7: TPO profiles of carbon deposited on 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts. Calculated carbon formation rates and ratios of 360 °C and 640 °C peak areas are shown as insets.
Figure 5.8: TEM images of carbon deposited on catalysts after 20 h propane steam reforming over 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts.
Figure 5.9: The morphology of carbonaceous species on 20% Ni/Al$_2$O$_3$ and 20% Ni-2% Ce/Al$_2$O$_3$ catalysts after propane steam reforming.
It is intuitive that larger nickel particles located at the filament tips could remain immobile and cannot contribute for steam reforming activity, causing rapid catalyst deactivation as observed on 20% Ni/Al₂O₃ catalyst. In contrast to carbon filaments formed on unpromoted catalyst, the morphology of carbon deposited on 20% Ni-2% Ce/Al₂O₃ catalyst is quite different. Carbon appears to be “extruded” while the nickel particle remains on the alumina support surface.

TGA-TPReaction experiments. As previously discussed, TPO and TEM results clearly indicate that addition of cerium to sol-gel 20% Ni/Al₂O₃ catalysts considerably improves resistance to coking. A temperature-programmed reaction technique (i.e., steam reforming of hydrocarbons) coupled with thermogravimetric analysis was also performed to investigate the coking resistance of Ni-based catalysts. The introduction of small amounts of MoO₃ (0.5-2 wt%) [175, 176] or K₂O [177] into Ni-based catalysts was reported to increase the coking initiation temperature when steam ratio was increased, which implies an improvement in coking resistance.

The effect of H₂O/C ratio on the weight changes on reduced 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts during the TPRaction of propane with steam is shown in Figure 5.10. An increase in weight due to coke formation during propane steam reforming on 20% Ni-2% Ce/Al₂O₃ catalyst is less pronounced compared to 20% Ni/Al₂O₃ catalyst at all steam ratios. At H₂O/C ratio = 0.1, 77% weight increase is obtained with 20% Ni-2% Ce/Al₂O₃ catalyst at 750 °C whereas the weight increase reaches 102% on unpromoted catalyst. The amount of carbon deposited decreases with increasing steam ratio, suggesting that more coke is gasified at higher concentrations of
steam on both catalysts. Furthermore, an increase in steam ratio causes an increase in the temperature of coking initiation. As listed in Table 5.3, a pronounced increase in coking initiation temperature is clearly seen when cerium is present in sol-gel Ni/Al₂O₃ catalysts. Additionally, the beneficial effect of cerium promotion is more evident at higher steam ratios.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H₂O/C ratio</th>
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<tbody>
<tr>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>20% Ni/Al₂O₃</td>
<td>430</td>
</tr>
<tr>
<td>20% Ni-2% Ce/Al₂O₃</td>
<td>486</td>
</tr>
</tbody>
</table>

Table 5.3: Effect of steam/carbon ratio on coking initiation temperature on 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts.
Figure 5.10: Effect of steam ratio on the temperature of coking initiation during propane steam reforming over 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts.
Sequential temperature-programmed coking/gasification/hydrogenation.

Propane decomposition with 2% C$_3$H$_8$/He at 500 °C and subsequent TPGasification of carbon deposited with 2% H$_2$O/He followed by TPH with 10% H$_2$/He were performed with reduced 20% Ni/Al$_2$O$_3$ and 20% Ni-2% Ce/Al$_2$O$_3$ catalysts. Figure 5.11 shows the changes in the concentrations of various carbon-containing species in propane decomposition. Compared to 20% Ni/Al$_2$O$_3$ catalyst, the intensity of propane increases with time on stream more noticeably over 20% Ni-2% Ce/Al$_2$O$_3$ catalyst. This suggests that there are markedly smaller amounts of carbon-containing products formed as a result of propane decomposition on 20% Ni-2% Ce/Al$_2$O$_3$ catalyst. Moreover, the formation of CH$_4$ and C$_2$ species is seen to start approximately at 3 min. and increases rapidly as the time progresses. However, after 6 min., the formation of CH$_4$ decreases with time on stream while C$_2$ species signal increases. It is conceivable that the formation of C$_2$ species is enhanced with time on stream due to the recombination of CH$_4$ molecules. Additionally, CO, CO$_2$, and H$_2$O were not detected within 1 h of propane decomposition at 500 °C.

TPGasification profiles of carbon deposited following propane decomposition are shown in Figure 5.12. It is seen that gasification of carbon deposited with 2% H$_2$O/He results in the formation of CO and CO$_2$. A decline in H$_2$O concentration is accompanied by CO and CO$_2$ evolution. The combined peak area under the CO and CO$_2$ evolution curves of 20% Ni-2% Ce/Al$_2$O$_3$ catalyst is considerably smaller compared to that of 20% Ni/Al$_2$O$_3$ catalyst. This shows that there is much less accumulation of carbon species from propane decomposition when cerium is present in sol-gel Ni/Al$_2$O$_3$ catalysts. The gasification mechanism of carbon deposited on nickel has been proposed
to be controlled by the diffusion of carbon through the metal [178-180]. Since the
gasification reaction proceeds at the same rate as the diffusion of carbon through nickel,
back diffusion of carbon to the nickel surface becomes the rate-determining step [64]. In
case of steam gasification, H₂O is believed to dissociatively adsorb on the surface of
nickel particles to form mobile surface oxygen species, which further react with carbon
atoms to form CO and CO₂. Our TPGasification profiles show that 20% Ni-2% Ce/Al₂O₃
catalyst exhibits a higher gasification temperature (570 °C) compared to 20% Ni/Al₂O₃
catalyst (535 °C). This suggests that the carbon diffusion rate could be retarded due to a
decrease in mobility of carbonaceous species upon the incorporation of cerium in nickel
particles.

Following TPGasification experiments, the catalysts were cooled down to
room temperature under He. TPH experiments were then conducted with 10% H₂/He to
further characterize deposited carbon left on the catalyst surface after steam gasification.
As displayed in Figure 5.13, TPH profiles show a peak of CH₄ and C₂ species over both
catalysts, indicating that there was some carbon that could not be completely gasified.
The hydrogenation of this “residual” carbon deposited starts approximately at 550 °C and
is complete at 800 °C on both catalysts. The peak maxima of CH₄ and C₂ species appear
at 650 and 770 °C, respectively. Furthermore, the peak area integrated under the curves
of CH₄ and C₂ species is lower with 20% Ni-2% Ce/Al₂O₃ catalyst compared to 20%
Ni/Al₂O₃ catalyst. This suggests that a higher amount of carbon deposited is removed
from the surface of 20% Ni-2% Ce/Al₂O₃ catalyst after steam gasification. Cerium
promotion could also enhance gasification of carbonaceous species due to high mobility
of its lattice oxygen.
Figure 5.11: Changes in the concentrations of various carbon-containing species as a function of time on stream in propane decomposition at 500 °C over 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts.
Figure 5.12: TPGasification profiles of carbon deposited following propane decomposition.
Figure 5.13: TPH profiles of carbon deposited left after H₂O gasification. The inset shows the comparison of the peak area of CH₄ and C₂ species formed during TPH over 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts.
Coking models during steam reforming. Based on information obtained from characterization results, coking models during propane steam reforming over sol-gel Ni/Al₂O₃ and Ni-Ce/Al₂O₃ catalysts are proposed similar to that reported by Baker et al. [181] and Snoeck et al. [174, 182]. For Ni/Al₂O₃ catalyst, the formation of carbon filaments is believed to cause rapid catalyst deactivation. The mechanism of carbon filament growth for propane steam reforming on nickel involves various steps (i.e., surface reactions, dissolution/segregation, carbon diffusion through nickel, and precipitation) [174, 181-183]. The decomposition of propane to hydrocarbon fragments (i.e., CHₓ and carbon atoms) originally occurs on the nickel surface as illustrated in Figure 5.14. Carbonaceous species further dissolve and diffuse through the nickel particle accompanied by the precipitation at the rear of the nickel particle with formation of a carbon filament. As the carbon filament begins to grow, the deformation of the nickel particle takes place. The appearance of a distorted nickel particle is affected by the relative rates of nucleation of carbon filaments and of carbon diffusion through nickel as well as the difference in diffusional path lengths on the metal/carbon interface. A pear-shaped nickel particle as observed from TEM studies could be due to a much faster nucleation rate with high diffusional path lengths at elevated temperature. Snoeck et al. [174] reported that the metal/support interaction must be overcome to lift the particle at places where there is no carbon excretion. Consequently, the formation of a pear shape takes place as the nickel particle is lifted strongly far from the support near the gas/metal interface.

In contrast, the addition of cerium enhances the adsorption of water, resulting in higher concentrations of active surface oxygen. The gasification of adsorbed carbon
from hydrocarbon fragments on the nickel surface is so efficient that the surface carbon species can be quickly converted to products and therefore the accumulation rate of carbon deposited is reduced [26]. Additionally, dissolution and diffusion of carbon species through nickel particles are greatly inhibited by the incorporation of cerium. The nucleation process to form carbon filaments is therefore retarded due to decreased mobility of carbon. TEM studies have shown that there were no carbon filaments detected over Ni-Ce/Al₂O₃ catalyst after 20 h propane steam reforming. Unlike Ni/Al₂O₃ catalyst, nickel particles on Ni-Ce/Al₂O₃ catalyst still remain on the alumina support rather than being strongly lifted far from it. Indeed, a small amount of carbon species spreading out around nickel particles is seen with the presence of cerium instead of carbon filaments having the same diameter as nickel particles.
Figure 5.14: Coking models during propane steam reforming over Ni/Al\textsubscript{2}O\textsubscript{3} and Ni-Ce/Al\textsubscript{2}O\textsubscript{3} catalysts.
5.4 Summary

This study has examined the effect of lanthanide promotion on catalytic performance of sol-gel nickel catalysts supported on alumina in steam reforming of propane. The presence of lanthanide elements (i.e., La, Ce, and Yb) is found to enhance the catalytic activity and stability significantly. This is partially due to the fact that lanthanides help retard the growth of nickel crystallites as well as the re-oxidation of metallic nickel sites during the reaction. Coke formation is likely a major cause of catalyst deactivation as suggested by an improvement in the reaction performance at higher steam/carbon ratios. In particular, the catalysts promoted with cerium remain highly active and stable for 20 h when excess steam is introduced into the feed. It appears that cerium promotion greatly inhibits carbon deposition due to enhanced water adsorption and effective gasification. As evidenced by TEM studies, the incorporation of cerium prevents the formation of carbon filaments by reducing the dissolution and diffusion of carbonaceous species through nickel particles.
CHAPTER 6

CHROMIUM-FREE IRON-BASED CATALYSTS: PREPARATION, CHARACTERIZATION, AND CATALYTIC PERFORMANCE IN THE HIGH-TEMPERATURE WATER-GAS SHIFT REACTION

6.1 Introduction

The water-gas shift (WGS) reaction is an important step in the production of H₂, where CO, which is produced from hydrocarbon steam reforming or coal gasification, is reacted with water to give H₂ and CO₂. The water–gas shift reaction is exothermic and thermodynamically limited at high temperatures:

\[
\text{CO} (\text{g}) + \text{H}_2\text{O} (\text{g}) \leftrightarrow \text{CO}_2 (\text{g}) + \text{H}_2 (\text{g}), \Delta H (298 \text{ K}) = -41.2 \text{ kJ/mol.}
\]

There has been renewed interest in the WGS reaction in recent years because of its necessity in conjunction with fuel cell power generation. The high-temperature shift (HTS) reaction is industrially performed at 320-450 °C using Fe-Cr oxide catalysts, while the low-temperature shift (LTS) reaction is conducted at 200-250 °C. The LTS catalysts commonly used are Cu/ZnO/Al₂O₃ or precious metal-based catalysts. The WGS reactor currently represents the largest volume of any catalyst in a fuel processor due to the slow kinetics at temperatures where the equilibrium is favorable [70].

Development of Fe-Cr catalysts with improved activity and stability has been pursued in the last two decades [94, 98-102, 184-192]. However, existing WGS catalyst
formulations are not yet commercially viable for use in coal-based fuel processors for fuel cell applications due to many disadvantages such as their sensitivity to air and low activity of Fe-Cr catalysts, which dictates higher temperature of operation. Thus, development of novel WGS catalysts with superior performance and low cost will have an impact on the widespread applications of fuel cell systems. Andreev et al. [99] studied the effect of the addition of CuO, CoO, and ZnO (5 wt%) on the activity of Fe-Cr catalysts. The Cu-promoted sample was found to be the most active at 380 °C. Kappen et al. [101] investigated the state of the Cu promoter (0.17-1.5 wt%) in Fe-Cr catalysts. It was found that Cu was in the metallic phase under the WGS reaction conditions. However, it reoxidized easily when exposed to the atmosphere. Rhodes et al. [102] examined the promotion of Fe-Cr catalysts with 2 wt% B, Cu, Ba, Pb, Hg, and Ag. A beneficial effect of adding Hg, Ag, or Ba was observed between 350-440 °C. This could be due to their different ionic sizes compared to that of Fe$^{2+}$, influencing the electronic structure of the active Fe$^{3+}$ center. Despite its high WGS activity, it is unlikely that the toxic Hg-promoted catalyst will be considered as a commercial HTS catalyst. Although Fe-Cr catalysts have been widely used in the HTS reaction, the role of the Cr$_2$O$_3$ addition on the stabilization of the catalyst structure is still unclear. Edwards et al. [100] proposed a model for the high stabilizing effect of chromium whereby a shell of chromium enriched material is formed on each catalyst grain, but the mechanism by which promotion occurs is still uncertain.

It is known that the activation process can play an important role on the activity and stability of catalysts. Rethwisch et al. [93] investigated the effect of catalyst treatment on catalytic activity over 16.8 wt% Fe$_3$O$_4$ supported on graphite. It was found
that the treatment of the catalyst in CO/CO$_2$ at 390 °C prior to the reaction increased the WGS activity. In contrast, the catalyst treatment in H$_2$/H$_2$O caused the growth of magnetite particles, leading to a decrease in catalytic activity. Gonzalez et al. [94] studied the influence of thermal treatments and reduction processes on the WGS activity of Fe-Cr catalysts. The active phase, Fe$_3$O$_4$, can be obtained from partial reduction of Fe$_2$O$_3$. However, over-reduction to form metallic Fe should be avoided since it results in a loss of catalytic activity. The authors concluded that reduction under either H$_2$/N$_2$ or CO/N$_2$/H$_2$/H$_2$O at temperatures below 500 °C should be performed to obtain higher activity without over-reduction of Fe$_2$O$_3$.

Even though chromium oxide has been used as a stabilizer in industrial HTS catalysts, its replacement with more benign components is highly desirable due to environmental concerns related to chromium. Araujo and Rangel [103] investigated the catalytic performance of Al-doped Fe-based catalyst with small amounts of copper (%wt Cu ≈ 3) in the HTS reaction. The aluminum and copper-doped catalyst showed similar catalytic activity compared to the commercial Fe-Cr catalyst even at more severe conditions (H$_2$O/CO = 0.4, 350 °C). Costa et al. [104] subsequently examined the use of thorium instead of chromium in iron- and copper-based catalysts for the HTS reaction. It was found that the thorium and copper-doped catalyst was more active than the commercial Fe-Cr catalyst at H$_2$O/CO = 0.6 and 370 °C. Its high activity was attributed to an increase in surface area by thorium. The authors concluded that the non-toxic thorium and copper-doped catalyst is a promising HTS catalyst.

Consequently, it is apparent that innovative chromium-free iron-based catalysts that can overcome these drawbacks (i.e., low activity at low temperatures, sintering,
sulfur poisoning, and pyrophoric nature) will have a significant impact in many processes, in particular those that target hydrogen production from coal. In this study, we examine the effect of various catalyst preparation variables on catalytic performance in the HTS reaction to develop chromium-free iron-based catalysts that are highly active and stable. Catalyst characterization was performed using BET surface area measurements, temperature-programmed reduction (TPR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The reaction mechanism of the HTS reaction over Fe-based catalysts is also discussed.

6.2 Reaction experiments for the high-temperature water-gas shift reaction

Effect of promoters. It is believed that the function of chromium in commercial HTS formulations is to stabilize magnetite from sintering, thus enhancing the activity and stability of iron catalysts [2, 193]. However, the use of chromium poses additional complications due to harmful effects of Cr\textsuperscript{6+} on human health such as cancer risk and lung damage [194]. Therefore, development of chromium-free catalytic system is necessary. Generally speaking, it is conceivable that any metal that has a similar ionic radius to Fe\textsuperscript{3+} (0.69 Å) could easily incorporate into the hematite lattice to form a solid solution instead of segregating into another phase. Based on this concept, aluminum, manganese, and gallium were chosen to replace chromium. The ionic radii of metals investigated in this study are as follows: Al\textsuperscript{3+} (0.675 Å), Mn\textsuperscript{3+} (0.72 Å), Cr\textsuperscript{3+} (0.755 Å), Ga\textsuperscript{3+} (0.76 Å) [195]. The addition of manganese and gallium causes a decrease in WGS activity whereas the presence of aluminum results in an improvement in WGS activity of
Fe catalysts as shown in Table 6.1. However, the CO conversion achieved with Fe-Al catalyst is still lower than that obtained over Fe-Cr catalyst. Fe-Al catalysts promoted with first-row transition metals (copper, cobalt, zinc) were subsequently prepared using a coprecipitation-impregnation method by keeping the Fe/promoter ratio constant at 20. As shown in Table 6.1, although addition of Zn does not provide any higher activity compared to Fe-Al catalyst, promotion with Co and Cu leads to significantly higher CO conversion, with Fe-Al-Cu catalyst giving the highest activity. More importantly, Fe-Al-Cu catalyst not only matches the activity of Fe-Cr catalyst, but surpasses it. The promotion of Fe catalysts is seen to increase the surface area (Table 1), although it is clear that the change in activity with the promoters cannot be explained solely by the variation in surface area.

The effect of various synthesis variables (i.e., Fe/Al molar ratio, Fe/Cu molar ratio, pH of precipitation medium, calcination and reduction temperatures) on the activity and stability of the catalysts was examined to improve the catalytic performance of Fe-Al-Cu catalysts.
Table 6.1: BET surface area measurements and % CO conversion over Fe-based catalysts.

<table>
<thead>
<tr>
<th>Catalysta</th>
<th>Surface area (m²/g)</th>
<th>CO conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-only</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td>Fe-Ga</td>
<td>31</td>
<td>12</td>
</tr>
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<td>Fe-Mn</td>
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<tr>
<td>Fe-Cr</td>
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<tr>
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<tr>
<td>Fe-Al-Cu</td>
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</tbody>
</table>

Effect of Fe/Al molar ratio. A first series of Fe-Al catalysts was prepared at differing Fe/Al molar ratios from 5 to 20. The pH of precipitation medium and calcination temperature were kept constant at 9 and 450 °C, respectively. Table 6.2 shows that the WGS activity of Fe-Al catalysts increases with decreasing Fe/Al molar ratio (or at higher Al contents) and reaches a maximum at Fe/Al = 10. Further addition of Al (Fe/Al = 5) causes a significant drop in WGS activity, possibly due to segregation of aluminum into another phase.
**Effect of pH of precipitation medium.** A second series of Fe-Al catalysts was subsequently prepared at various pH values of the precipitation medium. The Fe/Al molar ratio and calcination temperature were kept constant at 10 and 450 °C, respectively. pH is the major factor to control the precipitation rate of different species in the mixture of catalyst precursors. Lower pH values of the precipitation medium could favor the precipitation of aluminum species whereas the precipitation rate of iron species becomes faster at higher pH values. Reaction results indicate that the optimum pH value of the precipitation medium is 9 for forming the solid solution of aluminum species in iron precipitates.

**Effect of calcination temperature.** A third series of Fe-Al catalysts was therefore synthesized at Fe/Al = 10 and pH = 9. CO conversion of Fe-Al catalysts prepared at various calcination temperature ranging from 350-500 °C is also listed in Table 6.2. The catalytic activity of Fe-Al catalysts is seen to go through a maximum at 450 °C. Higher calcination temperature results in a decrease in WGS activity possibly due to loss of surface area caused by sintering. It is concluded that the best-performing Fe-Al catalyst with regard to WGS activity can be prepared at the following conditions: Fe/Al molar ratio = 10, pH = 9, and calcination temperature = 450 °C.

**Effect of Fe/Cu molar ratio.** As displayed in Table 6.2, the WGS activity of Fe-Al-Cu catalysts increases with decreasing Fe/Cu molar ratio (or at higher Cu contents) until it reaches a maximum at Fe/Al = 20. A further decrease in Fe/Cu molar ratio causes a drop in WGS activity.
Effect of reduction temperature. Generally, pretreatment conditions such as reduction temperature and reducing atmosphere strongly affect the active form of a catalyst, which in turn, influence its catalytic performance. The effect of reduction temperature on WGS activity of Fe-based catalysts was examined with 20% H\textsubscript{2}/N\textsubscript{2} as a reducing agent. As shown in Figure 6.1, the WGS activity of all catalysts is seen to go through a maximum and drops at higher reduction temperatures, possibly due to over-reduction of magnetite at higher temperatures.

Although Fe-Al catalyst shows similar activity to Fe-only catalyst at reduction temperature below 300 °C, it shows an improvement in catalytic activity at higher reduction temperatures, with Fe-only catalyst showing almost negligible WGS activity when it is reduced at 450 °C. This indicates the beneficial effect of aluminum on stabilizing the magnetite phase. Although all three catalysts exhibit a maximum in activity with increasing reduction temperature, the maximum for the Fe-Al-Cu catalyst takes place at a much lower reduction temperature (250 °C) compared to Fe-only and Fe-Al catalysts (350 °C). It appears that a reduction temperature of 250 °C is not high enough to convert all of hematite to magnetite in Fe-only and Fe-Al catalysts whereas it is sufficient for Fe-Al-Cu catalyst. Moreover, the Fe-Al-Cu catalyst reduced at 350 °C rapidly deactivates during the first 10 h as shown in the inset of Figure 6.1. However, the loss of activity can be prevented for a larger extent by reducing the catalyst at a lower catalyst (250 °C) as CO conversion is seen to decrease more slowly and remains constant for 20 h.
<table>
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<th>Catalyst</th>
<th>Fe/Al</th>
<th>Fe/Cu</th>
<th>pH</th>
<th>T&lt;sub&gt;cal&lt;/sub&gt; (°C)</th>
<th>CO conversion (%)</th>
</tr>
</thead>
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<td>9</td>
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<td>40</td>
<td>9</td>
<td>450</td>
<td>37</td>
</tr>
</tbody>
</table>

Table 6.2: Reaction comparison for the high-temperature water-gas shift reaction - effect of synthesis variables [Reaction conditions: 400 °C, CO/H<sub>2</sub>O/N<sub>2</sub> = 1/1/8, feed flow rate = 100 cm<sup>3</sup>/min, equal weight reactions (0.1 g), in situ reduction at 350 °C under 20% H<sub>2</sub>/N<sub>2</sub> for 2 h].
Figure 6.1: Effect of reduction temperature on WGS activity of Fe-based catalysts [Reaction conditions: 400 °C, CO/H_2O/N_2 = 1:1:8, feed flow rate = 100 cm^3/min, equal weight reactions (0.1 g)]. An inset shows catalytic activity as a function of time on stream of Fe-Al-Cu catalysts reduced at 250 and 350 °C.
Figure 6.2: Effect of reaction temperature on WGS activity of Fe-based catalysts.
Effect of reaction temperature. Fe-based catalysts were compared in the HTS reaction at 300-400 °C and H₂O/CO = 1. The effect of reaction temperature on WGS activity of Fe-based catalysts in the HTS reaction is shown in Figure 6.2. Compared to Fe-only catalyst, all promoted catalysts exhibit higher WGS activity for the whole range of reaction temperature investigated. The WGS activity of all catalysts is seen to increase with increasing reaction temperature. Furthermore, the beneficial effect of Cu promotion on activity enhancement is more pronounced at lower reaction temperatures. It is noted that H₂ and CO₂ are the only products from these reaction experiments; no CH₄ formation is detected.

Effect of gas hourly space velocity (GHSV). The effect of GHSV on CO conversion in the HTS reaction at 400 °C over Fe-based catalysts reduced at 250 °C is shown in Figure 6.3. As the space velocity is decreased, CO conversion increases. At the highest space velocity studied (9500 h⁻¹), Fe-only and Fe-Al catalysts exhibit similar WGS activity. CO conversions are 17%, 39%, and 54% over Fe-Al, Fe-Cr, and Fe-Al-Cu catalysts, respectively. At lower space velocities, Fe-Al catalyst gives slightly higher CO conversion than Fe-only catalyst whereas the equilibrium CO conversion (78%) is obtained over Fe-Al-Cu catalyst. Within the range of GHSV investigated, the WGS activity of Fe-based catalysts increases in the following order: Fe-only ≤ Fe-Al << Fe-Cr < Fe-Al-Cu.
Figure 6.3: Effect of GHSV on CO conversion at 400 °C of Fe-based catalysts.
6.3 Change in catalyst reducibility

To further examine the change in catalyst reducibility with promotion, TPR was performed with 10% H₂/Ar over various Fe-based catalysts calcined at 450 °C. As depicted in Figure 6.4, there are two main reduction peaks observed above 300 °C. A low-temperature (LT) reduction peak is assigned to the reduction of hematite (Fe₂O₃) to magnetite (Fe₃O₄). A broad high-temperature (HT) reduction peak is attributed to the reduction of magnetite (Fe₃O₄) to FeO. The HT reduction peak has a shoulder possibly due to the reduction of the outer layers of FeO particles forming metallic Fe. The addition of Al and Cr into Fe catalysts leads to a shift of the HT peak maximum to higher temperatures. This suggests that the addition of Al and Cr stabilizes magnetite and prevents its further reduction to undesirable FeO or metallic Fe. An additional reduction peak, assigned to the reduction of Cr⁶⁺ to Cr³⁺, is seen at 270 °C for Fe-Cr catalyst [94]. Upon Cu promotion, the position of the LT peak maximum shifts toward much lower temperature, around 300 °C, suggesting that Cu facilitates the formation of magnetite. An additional reduction peak is also seen on Fe-Al-Cu catalyst at 220 °C. This could be due to the reduction of Cu²⁺ to metallic Cu [103, 104]. It is noted that the formation of magnetite is slightly enhanced by the presence of Co and Zn.
Figure 6.4: TPR profiles of various Fe-based catalysts calcined at 450 °C.
6.4 Change in crystallinity and phase transformations during reduction

_Calcined catalysts._ The XRD patterns of catalysts calcined at 450 °C are displayed in Figure 6.5. Hematite (Fe₂O₃) is the only crystalline phase detected. No separate Al- and Cr-containing crystalline phases are observed on the calcined samples, suggesting that Al and Cr could exist in solid solution within the hematite lattice upon the catalyst preparation. XRD peaks of all promoted catalysts are much broader than Fe-only catalyst, suggesting that hematite crystallites in these catalysts are significantly smaller. The crystallite sizes of hematite were further calculated from line broadening of Fe₂O₃ (104) diffraction line using the Scherrer equation [105]. As shown in Table 6.3, the addition of Al and Cr in Fe catalysts helps improve the sintering resistance of hematite as confirmed by much smaller crystallite sizes of hematite at all calcination temperatures. In addition, the effect of calcination temperature on crystallinity of Fe-Al catalysts in shown in an inset. The catalyst calcined at 350 °C is relatively amorphous. As the calcination temperature is increased, Fe-Al catalysts become more crystalline.

_Reduced catalysts._ Phase transformations that took place during the reduction in Fe-based catalysts were further investigated by an _in situ_ XRD technique. The corresponding d spacings and (hkl) values for the diffraction lines of iron-containing species using the International Centre for Diffraction Data (ICDD) PDF database are given in Table 6.4. No phase transformation occurs in Fe-Al catalyst below 250 °C; the only crystalline phase observed is hematite (Figure 6.6). At 300 °C, hematite begins to reduce to magnetite (Fe₃O₄), which is further reduced to inactive FeO above 600 °C. In contrast, the Fe-Al-Cu calcined at 450 °C is amorphous.
Figure 6.5: XRD patterns of various Fe-based catalysts calcined at 450 °C. The effect of calcination temperature on crystallinity of Fe-Al catalysts is shown as an inset.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>d (nm)</th>
<th>Calcination temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>350</td>
</tr>
<tr>
<td>Fe</td>
<td>34</td>
<td>36</td>
</tr>
<tr>
<td>Fe-Al</td>
<td>n.d.²</td>
<td>26</td>
</tr>
<tr>
<td>Fe-Cr</td>
<td>n.d.²</td>
<td>23</td>
</tr>
</tbody>
</table>

n.d.² = not determined since Fe₂O₃(104) diffraction line was not well resolved.

Table 6.3: Effect of calcination temperature on hematite crystallite diameter of Fe-based catalysts.
<table>
<thead>
<tr>
<th>Phase</th>
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<th>2θ</th>
<th>(hkl)</th>
</tr>
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<tr>
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<td>24.14</td>
<td>(012)</td>
</tr>
<tr>
<td></td>
<td>2.700</td>
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<td></td>
<td>2.519</td>
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<td></td>
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<td>1.485</td>
<td>62.51</td>
<td>(440)</td>
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<td>36.04</td>
<td>(111)</td>
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<td>1.433</td>
<td>65.02</td>
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Table 6.4: Major peaks in the XRD patterns of identified phases during *in situ* reduction of Fe-based catalysts.
Figure 6.6: *In situ* XRD patterns during reduction of Fe-Al and Fe-Al-Cu catalysts.
Magnetite is observed at much lower temperature (200 °C) in Fe-Al-Cu catalyst and it is subsequently reduced to metallic Fe at 450 °C. This implies that the presence of Cu in Fe-based catalysts enhances the reduction of magnetite to metallic Fe considerably. Table 6.5 summarizes the reduction temperature at which each crystalline iron-containing phase is detected in various Fe-based catalysts. Compared to Fe-Al and Fe-Cr catalysts, FeO is detected at lower reduction temperature (500 °C) for the Fe-only catalyst. This is in good agreement with TPR results. The presence of Al and Cr in Fe catalysts stabilizes the magnetite phase and prevents its further reduction to FeO. This also indicates that the HT reduction peak observed with Fe-Al-Cu catalyst is due to the reduction of magnetite to metallic Fe. The crystallite sizes of various Fe-based catalysts reduced at differing temperatures (300-450 °C) were also calculated from line broadening of Fe₃O₄ (311) diffraction line and are listed in Table 6.6. It can be seen that magnetite crystallite sizes increase with increasing reduction temperature. The presence of Al and Cr significantly inhibits the growth of magnetite crystallites.

6.5 Investigation of active sites and oxidation states

*Pre-reaction XPS.* In order to investigate the nature of active sites and oxidation states of species upon promotion, XPS was performed with calcined and reduced catalysts. Figure 6.7(a) shows Fe 2p X-ray photoelectron spectrum of calcined Fe-only catalysts. Hematite (710.9 eV) is the only iron species observed on the surface of calcined catalysts. After reduction at 350 °C, magnetite (710.3 eV) is the major species detected. Metallic (706.3 eV) phase is clearly seen on reduced Fe-only (Figure 6.7b) and Fe-Al-Cu (Figure 6.7e) while it is markedly suppressed on both Fe-Cr (Figure 6.7c) and
Fe-Al (Figure 6.7d). Consistent with TPR and in situ XRD results, the addition of Al and Cr in Fe catalysts helps stabilize the magnetite phase. Compared to Fe-Al-Cu catalyst reduced at 350 °C, there is no metallic Fe observed after reduction at 250 °C (Figure 6.7f). This is in good agreement with reaction results; Fe-Al-Cu catalyst becomes less stable when reduced at 350 °C due to over-reduction of magnetite to metallic Fe.

<table>
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<tr>
<th>Catalyst</th>
<th>Reduction temperature (°C)</th>
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<tr>
<td></td>
<td>Fe₃O₄</td>
</tr>
<tr>
<td>Fe</td>
<td>300</td>
</tr>
<tr>
<td>Fe-Al</td>
<td>300</td>
</tr>
<tr>
<td>Fe-Cr</td>
<td>300</td>
</tr>
<tr>
<td>Fe-Al-Cu</td>
<td>200</td>
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</tbody>
</table>

n.d.ᵃ = not detected.

Table 6.5: Phase transformations in Fe-based catalysts as a function of reduction temperature.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>d (nm)</th>
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<tr>
<td></td>
<td>300</td>
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<tr>
<td>Fe</td>
<td>49</td>
</tr>
<tr>
<td>Fe-Al</td>
<td>32</td>
</tr>
<tr>
<td>Fe-Cr</td>
<td>32</td>
</tr>
<tr>
<td>Fe-Al-Cu</td>
<td>25</td>
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</table>

Table 6.6: Effect of reduction temperature on magnetite crystallite diameter of Fe-based catalysts.

As shown in Figure 6.8, Cr is found to have two oxidation states in the calcined sample: Cr$^{6+}$ (579.3 eV) and Cr$^{3+}$ (576.5 eV) with Cr$^{6+}$ being the main phase. After reduction at 350 °C, Cr$^{6+}$ is reduced to Cr$^{3+}$, which is also observed in the TPR profile of Fe-Cr catalyst. Cu is found in the +2 state in the calcined sample (Figure 6.9). After reduction at 350 °C, all copper oxide is converted to a metallic Cu phase (932.2 eV). It is noted that aluminum is found to exist in +3 state in calcined Fe-Al catalyst and no notable change is observed after reduction.
Figure 6.7: Fe 2p X-ray photoelectron spectra of various Fe-based catalysts: (a) calcined Fe-only (b) reduced Fe-only (c) reduced Fe-Cr (d) reduced Fe-Al (e) Fe-Al-Cu reduced at 350 °C (f) Fe-Al-Cu reduced at 250 °C.
Figure 6.8: Cr 2p spectra of calcined and reduced Fe-Cr catalysts.
Figure 6.9: Cu 2p spectra of calcined and reduced Fe-Al-Cu catalysts.
**Post-reaction XPS without the pre-reduction step.** Post-reaction XPS characterization shows that hematite is converted primarily to magnetite and a lesser extent to FeO as shown in Figure 6.10 (a). Additionally, CuO is seen to reduce to metallic Cu on the post-reaction catalyst (Figure 6.10b). This indicates that catalysts are reduced under the reaction medium; however, the presence of FeO suggests that they may be “over-reduced”. To further examine the impact of the pre-reduction step on the catalytic performance, steady-state reaction experiments at 400 °C were performed with Fe-Al and Fe-Al-Cu catalysts. Although catalysts that are not pre-reduced still exhibit WGS activity, they are less active than pre-reduced catalysts (250 °C, 20% H2/N2) as compared in Table 6.7. A significant increase in catalytic activity is observed with Fe-Al-Cu catalysts.

<table>
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<tr>
<th>Catalyst</th>
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<th>CO conversion (%)</th>
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<tr>
<td>Fe-Al</td>
<td>No pre-reduction</td>
<td>15</td>
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<tr>
<td></td>
<td>Reduction at 350 °C, 2 h</td>
<td>25</td>
</tr>
<tr>
<td>Fe-Al-Cu</td>
<td>No pre-reduction</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Reduction at 250 °C, 2 h</td>
<td>54</td>
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Table 6.7: Effect of the pre-reduction step on catalytic performance of Fe-Al and Fe-Al-Cu catalysts.
Figure 6.10: Comparison of pre- and post-reaction XPS of Fe-Al-Cu catalysts without the pre-reduction step: (a) Fe 2p (b) Cu 2p.
6.6 DRIFTS studies

Surface species formed as a result of CO adsorption over reduced catalysts were examined using DRIFTS. Figure 6.11 shows DRIFT spectra under CO flow taken at various temperatures up to 400 °C over reduced Fe-only and Fe-Al-Cu catalysts. At room temperature, bands at 2173, 2110, 1608, 1391, and 1215 cm\(^{-1}\) are observed under CO flow. The bands at 2173 and 2110 cm\(^{-1}\) are assigned to gas-phase CO and weakly adsorbed CO, respectively [150, 196, 197]. It is plausible that the oxidation of adsorbed CO and/or the Boudouard reaction could produce CO\(_2\). The features at 1608, 1391, and 1215 cm\(^{-1}\) are attributed to bicarbonate species, which are formed upon the adsorption of CO\(_2\) [149, 150]. Bicarbonate bands are much more intense on reduced Fe-Al-Cu catalyst compared to those observed on reduced Fe-only catalyst. Subsequent heating under He results in an appearance of a doublet at 2358 and 2327 cm\(^{-1}\), which signals the formation of CO\(_2\) [153, 154]. These bands grow much stronger with increasing temperature up to 400 °C. Moreover, they are seen at much lower temperature (75 °C) over reduced Fe-Al-Cu catalyst, suggesting that the presence of Al and Cu helps reduce the energy barrier of CO\(_2\) formation.

DRIFTS experiments of the CO+H\(_2\)O TPRaction were further conducted to investigate adsorbed species during the WGS reaction and to elucidate the reaction mechanism. Figure 6.12 displays CO+H\(_2\)O TPRaction DRIFT spectra over reduced Fe-Al-Cu catalyst. The bands at 2173 cm\(^{-1}\) (gas-phase CO) and 2110 cm\(^{-1}\) (weakly-adsorbed CO) are seen under CO flow at room temperature. Under He flow, the band at 2173 cm\(^{-1}\) disappears completely at room temperature.
Figure 6.11: CO-TPD DRIFT spectra of reduced Fe-only and Fe-Al-Cu catalysts.
Figure 6.12: CO+H₂O-TPReaction DRIFT spectra of the reduced Fe-Al-Cu catalyst.
In addition, the intensity of the band at 2110 cm\(^{-1}\) decreases gradually with increasing temperature. At 400 °C, no adsorbed species are observed under He flow.

After CO is re-introduced at 400 °C for 10 min., a doublet, characterized the formation of CO\(_2\), at 2358 and 2327 cm\(^{-1}\) appears. The intensity of these bands decreases whereas that of the CO bands (2173 and 2110 cm\(^{-1}\)) increases with time on stream, suggesting that surface oxygen is being depleted during the reaction. After H\(_2\)O introduction at 400 °C, the catalyst is re-oxidized by oxygen, which is produced from the dissociation of H\(_2\)O. Interestingly, the bands at 2358-2327 cm\(^{-1}\) re-appear after H\(_2\)O exposure with much higher intensity compared to those before introducing water. However, their intensity continues to decrease with time on stream as previously observed. Most importantly, these bands grow much strongly on reduced Fe-Al-Cu catalyst after H\(_2\)O exposure compared to reduced Fe-only catalyst as shown in Figure 6.13. This suggests that activity difference observed over the two catalysts could be due to the more rapid regeneration of the active sites over the Cu-promoted catalysts.

Two possible reaction mechanisms of the HTS reaction on Fe-based catalysts have been proposed: associative and regenerative (redox) [97]. The associative mechanism involves the adsorption of CO and H\(_2\)O on the catalyst surface, therefore leading to the formation of an intermediate (i.e., formate), which further decomposes to CO\(_2\) and H\(_2\). The redox mechanism can be visualized as a cyclic change in the oxidation state of magnetite upon the adsorption of CO and H\(_2\)O. The redox mechanism seems to be the predominant reaction pathway due to the unique capabilities of magnetite to exchange an electron between Fe\(^{2+}\) and Fe\(^{3+}\) rapidly.
Figure 6.13: Comparison of CO+H₂O-TPRreaction DRIFT spectra taken under CO flow of Fe-only and Fe-Al-Cu catalysts.
Magnetite is known to have an inverse spinel structure [198, 199]. It consists of Fe$^{3+}$ located in tetrahedral sites with Fe$^{2+}$ and Fe$^{3+}$ equally occupying octahedral sites while the oxygen atoms form a face-centered cubic lattice (fcc) within a spinel. The arrangements of iron and oxygen atoms in magnetite can be written as Fe$^{3+}$ (A) Fe$^{3+}$ (B) Fe$^{2+}$ (B)(O$^{2-}$)$_4$, where A and B refer to tetrahedral and octahedral sites, respectively. Fast electron hopping between Fe$^{2+}$ and Fe$^{3+}$ locating in octahedral sites in magnetite has been confirmed by Mössbauer spectroscopy [164, 200] and isotopic labeling studies [201]. Furthermore, the water-gas shift reaction over Fe-Cr catalysts was well described by the kinetics of surface oxygen removal by CO and H$\textsubscript{2}$ and surface oxygen incorporation from CO$_2$ and H$_2$O, indicating that the redox mechanism is a primary pathway for the water-gas shift reaction over magnetite [202, 203]. Our \textit{in situ} DRIFTS results also indicate that the WGS reaction over Fe-based catalysts occurs via the redox mechanism as depicted in Figure 6.14. The catalyst surface undergoes successive reduction and oxidation cycles by CO and H$_2$O to produce CO$_2$ and H$_2$, respectively, with Fe$^{3+}$ and Fe$^{2+}$ occupying the octahedral sites in the magnetite structure constituting a “redox” pair.

The role of copper in HTS catalysts for the water-gas shift reaction is still uncertain. Rhodes et al. [192] reported that copper enhanced the WGS activity by modifying the electronic properties of coprecipitated Fe-Cr catalysts. Their TPR studies using 5% H$_2$/Ar and 5% CO/He showed that no additional feature was observed with coprecipitated Fe-Cr-Cu catalyst, suggesting that CuO and Cr$_2$O$_3$ could exist in solid solution within the magnetite structure. Moreover, no discrete Cr$_2$O$_3$ or CuO phase was observed in the reduced sample while CuO was found to segregate on the surface of the post-reaction sample [100]. However, it is also possible that under the WGS reaction
atmosphere copper could provide new active sites similar to those in Cu/ZnO/Al₂O₃ catalysts, which are extensively used for the LTS reaction, methanol synthesis, and methanol steam reforming. Andreev et al. [99] reported that the addition of 5 wt% CuO and CoO in coprecipitated Fe-Cr catalysts enhanced the reaction rate and shifted the maximum of the conversion curve to lower temperatures compared to unpromoted samples.

It is worth noting that our Fe-Al-Cu catalysts were prepared by a coprecipitation-impregnation method by which the catalyst surface could be enriched in copper upon the impregnation step. As previously discussed, TPR, in situ XRD, and XPS results clearly indicate that copper is in a metallic form after reduction. The sintering of metallic Cu could also contribute to loss of the WGS activity when catalysts are reduced at higher temperatures. In situ DRIFTS results suggests that the differences in catalytic performance can be due to rate differences in redox steps of the WGS reaction over Fe-based catalysts. Moreover, a two-fold increase in WGS activity of Fe-Al catalysts due to Cu promotion makes us suspect that Cu could also provide additional active sites for the water-gas shift reaction (Table 6.7). Thus, it is possible that the combination of magnetite and metallic copper could contribute to high activity of Fe-Al-Cu catalysts. The effect of catalyst preparation methods (i.e., coprecipitation, 1-step vs coprecipitation-impregnation, 2-step) and the role of copper promoter are being further investigated to clarify this issue.
Figure 6.14: Redox mechanism of the WGS reaction over Fe-based catalysts.
6.7 Summary

Chromium-free iron-based HTS catalysts that are highly active and stable were prepared by adding both aluminum and copper using a coprecipitation-impregnation method. Many catalysts synthesis variables, including Fe/promoter ratio, pH of the precipitation medium, calcination temperature, and reduction temperature, have been shown to affect the catalyst performance significantly. Steady-state reaction experiments have shown that the effect of Cu promotion on the activity enhancement is much more pronounced at low reaction temperatures. Over-reduction of Fe-based catalysts to form metallic Fe is seen to lead to a drastic decrease in catalytic activity. Characterization results using BET, TPR, XRD, and XPS strongly indicate that aluminum, which is a promising chromium replacement, acts as a textural promoter by stabilizing magnetite and retarding its further reduction to FeO or metallic Fe. Copper, which is believed to be a structural promoter, improves the WGS activity by enhancing the reduction of hematite to magnetite markedly. Its promotional effect due to formation of additional active sites is also a strong possibility. Moreover, strong evidence gained from in situ DRIFTS studies (coupled with TPR-Reduction experiments) suggests that the WGS reaction on iron-based catalysts occurs through a redox process. It is conceivable that Cu may promote the WGS activity by enhancing the rate of the re-oxidation step.
RECOMMENDATIONS

- Novel approaches to catalyst promotion for additional activity, selectivity, and stability of nickel-based catalysts should be developed to achieve high nickel surface area, increased carbon gasification rates, and nickel-metal alloys to inhibit coking and sintering. In this study, addition of lanthanides (i.e., lanthanum, cerium, and ytterbium) has shown a significant improvement in catalytic activity. In particular, sol-gel Ni-Ce/Al₂O₃ catalysts were found to remarkably suppress the rate of carbon deposition but maintain their activity in steam reforming of propane. However, little is known for the role of enhanced steam adsorption on cerium-promoted catalysts. A beneficial effect was also reported with the promotion of molybdenum and tin. Studies on multi-promoter catalytic systems that provide optimal metal dispersion and resistance to coking and sulfur are still limited. The introduction of small amounts of molybdenum or tin on mixed oxide supports (i.e., alumina-ceria) could be a promising approach to tackle the coking problem. In addition, metals aimed specifically to either alloy or electronically interact with nickel to improve sulfur tolerance should be explored. Potential candidates include rhenium and iron since they have been reported to enhance sulfur tolerance of supported nickel catalysts.
The effect of sol-gel parameters such as type of metallic precursor and solvent, gelation time and temperature, as well as pretreatment conditions should be further studied to improve catalytic performance. We should keep in mind that precise control of the size, structure, and location of domains within a catalyst is necessary. Therefore, new methods of catalyst synthesis should be developed to establish molecular control over the structure, location, and promoter distribution of catalysts to give optimum activity, selectivity, and stability. Innovative preparation methods based on Layered Double Hydroxides (LDHs) or hydrotalcite-like compounds, which posses versatile acid-base and redox properties where metal-support interaction can be carefully fine-tuned during synthesis, should be examined for their effects on coking and sulfur resistance.

Evaluation of catalyst durability (>100 h time-on-stream) under realistic steam reforming conditions with the presence of olefins/aromatics and sulfur compounds should be attempted. Fundamental chemical interactions that contribute to deactivation by coking and sulfur should be identified using characterization techniques such as controlled-atmosphere XPS, in situ DRIFTS, TPO, TGA, DSC, and TEM.

Steady-state and transient isotopic labeling studies using $^{13}$C$_3$H$_8$ and D$_2$O should be performed to obtain kinetic parameters such as abundance of adsorbed surface intermediates, surface coverage, and reactivity distribution, thus gaining insights into the reaction mechanism of hydrocarbon steam reforming over nickel-based catalysts.
With the success of replacing toxic chromium in high-temperature shift iron-based catalysts with aluminum, there is incentive to further develop these catalysts for the water-gas shift reaction of coal-derived synthesis gas. Although many synthesis variables have been optimized in this work, namely, iron/promoter molar ratio, pH of the precipitation medium, calcination and reduction temperatures, other catalyst preparation parameters such as type of iron precursor and precipitating agent as well as aging time should also be examined. Considerable effort is needed to elucidate the role of copper promoter on activity enhancement. Microcalorimetry techniques can be employed to measure heat of adsorption of adsorbed reactants on the catalyst surface and could open up surface thermodynamics to molecular level studies. Mössbauer spectroscopy, which has been widely applied to studies of iron-containing catalysts, provides valuable information on oxidation states, magnetic fields, lattice symmetry, and lattice vibrations of iron-based catalysts. This capability is extremely important because it can reveal the identity of iron phases in a catalyst after different treatments and phase transformations upon promotion. It is also employed to follow the kinetics of bulk reactions and to determine sizes of iron particles in applied magnetic field, giving a complete picture of the structure of catalysts.
BIBLIOGRAPHY


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APPENDIX

SAMPLE CALCULATIONS

Definition of Relative Response Factor (Dilution experiments):

\[ X_i = \text{component } i \ [\text{C}_3\text{H}_8, \text{H}_2\text{O}, \text{CO}_2, \text{H}_2, \text{CH}_4, \text{CO}], \ A_{Xi} = \text{peak area of component } i \]

\[
RF(X_i/N_2) = \frac{\text{moles of } X_i / A_{Xi}}{\text{moles of } N_2 / A_{N2}}
\]

\[
\text{mol}\% X_i = \frac{RF(X_i/N_2)(A_{Xi})}{\sum RF(X_i/N_2)(A_{Xi})} \times 100
\]

Feed Stream Analysis \( (F_{N_2,\text{feed}} = 285 \text{ cm}^3(\text{STP})/\text{min}) \):

\[
\sum RF(X_i/N_2)(\text{peak area of } X_i) = RF(\text{C}_3\text{H}_8/N_2)(A_{\text{C}_3\text{H}_8}) + RF(\text{H}_2\text{O}/N_2)(A_{\text{H}_2\text{O}}) + A_{N2}
\]

\[
= (0.567)(10524) + (0.474)(50821) + 520913
\]

\[
= 550969
\]

\[
\text{mol}\% \text{C}_3\text{H}_8,\text{feed} = \frac{5967/550969 \times 100}{550969}
\]

\[
= 1.1\%
\]

\[
\text{mol}\% \text{H}_2\text{O,feed} = \frac{24089/550969 \times 100}{550969}
\]

\[
= 4.4\%
\]

\[
\text{mol}\% N_2,\text{feed} = 100-1.1-4.4 = 94.5\%
\]

then gives,

\[
F_{\text{C}_3\text{H}_8,\text{feed}} = (1.1)(285)/94.5 = 3.3 \text{ cm}^3(\text{STP})/\text{min}
\]

\[
F_{\text{H}_2\text{O,feed}} = (4.4)(285)/94.5 = 13.3 \text{ cm}^3(\text{STP})/\text{min}
\]
Product Stream Analysis @ Steady-State:

\[
\sum RF(X_i/N_2)\text{(peak area of } X_i) = RF(C_3H_8/N_2)(A_{C3H8}) + RF(H_2O/N_2)(A_{H2O}) + A_{N2} +
RF(H_2/N_2)(A_{H2}) + RF(CO_2/N_2)(A_{CO2}) + RF(CO/N_2)(A_{CO}) + RF(CH_4/N_2)(A_{CH4})
\]

\[
= (0.567)(2496)+(0.474)(19649)+508498+(0.070)(310000)+(1.797)(3750)+(0.943)(1595) + (0.314)(15882)
\]

\[
= 554157
\]

mol% C\textsubscript{3}H\textsubscript{8},\text{prod} = \frac{1415}{554157} \times 100 = 0.2%

Similarly,

mol% H\textsubscript{2}O,\text{prod} = 1.7%

mol% N\textsubscript{2},\text{prod} = 91.8%

mol% H\textsubscript{2} = 3.9%

mol% CO\textsubscript{2} = 1.2%

mol% CO = 0.3%

mol% CH\textsubscript{4} = 0.9%

N\textsubscript{2}-balance:

\[
F_{N2,\text{prod}} = \frac{285}{0.918} = 310.4 \text{ cm}^3\text{(STP)/min}
\]

which gives

\[
F_{C3H8,\text{prod}} = 0.6 \text{ cm}^3\text{(STP)/min}
\]

\[
F_{H2O,\text{prod}} = 5.3 \text{ cm}^3\text{(STP)/min}
\]

\[
F_{H2} = 12.1 \text{ cm}^3\text{(STP)/min}
\]

\[
F_{CO2} = 3.7 \text{ cm}^3\text{(STP)/min}
\]

\[
F_{CO} = 0.9 \text{ cm}^3\text{(STP)/min}
\]

\[
F_{CH4} = 2.8 \text{ cm}^3\text{(STP)/min}
\]

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\% C_3H_8 Conversion = (moles of carbon converted / total moles of carbon in the feed) \times 100
= (3.3-0.6)/3.3 \times 100
= 81.8% \\

\% H_2O Conversion = (moles of H_2O converted / moles of H_2O in the feed) \times 100
= (13.3-5.3)/13.3 \times 100
= 60.1% \\

\% \text{H}_2 \text{ Yield} = (2*\text{moles of H}_2 \text{ produced} / \text{total moles of H in the feed}) \times 100
= (2)(12.1)/ [(8)(3.3)+(2)(13.3)] \times 100
= 45.7% \\

\% \text{H}_2 \text{ Selectivity} = (2*\text{moles of H}_2 \text{ produced} / \text{total moles of H in H}_2 \text{ and CH}_4) \times 100
= (2)(12.1)/ [(2)(12.1)+(4)(2.8)] \times 100
= 68.4% \\

\% \text{CO}_2 \text{ Selectivity} = (\text{moles of carbon in CO}_2 / \text{total moles of carbon in CO}_2, \text{CH}_4, \text{and CO}) \times 100
= (3.7)/(3.7+2.8+0.9) \times 100
= 50% \\

\% \text{C Balance} = (\text{total moles of carbon in the products} / \text{total moles of carbon in the feed}) \times 100
= [(3)(0.6)+3.7 +2.8+0.9]/[(3)(3.3)] \times 100
= 93% \\

\% \text{H Balance} = (\text{total moles of hydrogen in the products} / \text{total moles of hydrogen in the feed}) \times 100
= [(8)(0.6)+(2)(5.3)+(2)(12.1)+(4)(2.8)]/[(8)(3.3)+(2)(13.3)] \times 100
= 96%
Definition of Relative Response Factor (Neat experiments):

\[ X_i = \text{component } i \text{ [H}_2\text{O, CO}_2, \text{H}_2, \text{CH}_4, \text{CO}], A_{Xi} = \text{peak area of component } i \]

\[ \text{RF}(X_i/C_3H_8) = \frac{\text{RF}(X_i/N_2)}{\text{RF}(C_3H_8/N_2)} \]

\[ \text{mol}\% X_i = \frac{\text{RF}(X_i/C_3H_8)(A_{Xi})}{\sum \text{RF}(X_i/C_3H_8)(A_{Xi})} \times 100 \]

Feed Stream Analysis (\(F_{C_3H_8} = 20.8 \text{ cm}^3\text{(STP)/min})

\[ \sum \text{RF}(X_i/C_3H_8)(\text{peak area of } X_i) = \text{RF}(\text{H}_2\text{O/C}_3\text{H}_8)(A_{\text{H}_2\text{O}}) + A_{C_3H_8} \]

\[ = (0.837)(788188) + 54119 \]

\[ = 713832 \]

\[ \text{mol}\% C_3H_8,\text{feed} = \frac{54119}{713832} \times 100 \]

\[ = 7.6\% \]

\[ \text{mol}\% \text{H}_2\text{O,feed} = 100 - 7.6 = 92.4\% \]

\[ F_{\text{H}_2\text{O,feed}} = \frac{(92.4)(20.8)}{7.6} \]

\[ = 252.9 \text{ cm}^3\text{(STP)/min} \]

Product Stream Analysis @ Steady-State:

\[ \sum \text{RF}(X_i/N_2)(\text{peak area of } X_i) = A_{C_3H_8} + \text{RF}(\text{H}_2\text{O/C}_3\text{H}_8)(A_{\text{H}_2\text{O}}) + \]

\[ \text{RF}(\text{H}_2/C_3\text{H}_8)(A_{\text{H}_2}) + \text{RF}(\text{CO}_2/C_3\text{H}_8)(A_{\text{CO}_2}) + \text{RF}(\text{CO/C}_3\text{H}_8)(A_{\text{CO}}) + \text{RF}(\text{CH}_4/C_3\text{H}_8)(A_{\text{CH}_4}) \]

\[ = 8581 + (0.836)(565623) + (0.123)(1699041) + (3.171)(21007) + (1.665)(6036) + (0.554)(59016) \]

\[ = 799782 \]

\[ \text{mol}\% C_3H_8,\text{prod} = \frac{8581}{799782} \times 100 \]

\[ = 1.1\% \]
Similarly,

\[
\text{mol}\% \text{ H}_2\text{O}_{\text{prod}} = 59.1\%
\]

\[
\text{mol}\% \text{ H}_2 = 26.1
\]

\[
\text{mol}\% \text{ CO}_2 = 8.3
\]

\[
\text{mol}\% \text{ CO} = 1.2
\]

\[
\text{mol}\% \text{ CH}_4 = 4.2
\]

O-balance:

\[
252.9 = [0.591 + (0.083)(2) + 0.012]F_{\text{prod}}
\]

\[
F_{\text{prod}} = 329 \text{ cm}^3(\text{STP})/\text{min}
\]

\[
F_{\text{C}_3\text{H}_8, \text{prod}} = 3.6 \text{ cm}^3(\text{STP})/\text{min}
\]

\[
F_{\text{H}_2\text{O}, \text{prod}} = 194.4 \text{ cm}^3(\text{STP})/\text{min}
\]

\[
F_{\text{H}_2} = 85.9 \text{ cm}^3(\text{STP})/\text{min}
\]

\[
F_{\text{CO}_2} = 27.3 \text{ cm}^3(\text{STP})/\text{min}
\]

\[
F_{\text{CO}} = 3.9 \text{ cm}^3(\text{STP})/\text{min}
\]

\[
F_{\text{CH}_4} = 13.8 \text{ cm}^3(\text{STP})/\text{min}
\]

\[
\% \text{ C}_3\text{H}_8 \text{ Conversion} = \left( \frac{\text{moles of carbon converted}}{\text{total moles of carbon in the feed}} \right) \times 100
\]

\[
= \frac{20.8-3.6}{20.8} \times 100
\]

\[
= 82.7\%
\]

\[
\% \text{ H}_2\text{O} \text{ Conversion} = \left( \frac{\text{moles of H}_2\text{O converted}}{\text{moles of H}_2\text{O in the feed}} \right) \times 100
\]

\[
= \frac{252.9-194.4}{252.9} \times 100
\]

\[
= 23.1\%
\]
% H₂ Yield = (2*moles of H₂ produced / total moles of H in the feed) x 100

= (2)(85.9) / [(8)(20.8)+(2)(252.9)] x 100

= 25.6%

% H₂ Selectivity = (2*moles of H₂ produced / total moles of H in H₂ and CH₄) x 100

= (2)(85.9) / [(2)(85.9)+(4)(13.8)] x 100

= 75.7%

% CO₂ Selectivity = (moles of carbon in CO₂ / total moles of carbon in CO₂, CH₄, and CO) x 100

= (27.3)/(27.3+13.8+3.9) x 100

= 60.7%

% C Balance = (total moles of carbon in the products / total moles of carbon in the feed)x 100

= [(3)(3.6)+27.3+13.8+3.9]/[(3)(20.8)] x 100

= 90%

% H Balance = (total moles of hydrogen in the products / total moles of hydrogen in the feed)x 100

= [(8)(3.6)+(2)(194.4)+(2)(85.9)+(4)(13.8)]/[(8)(20.8)+(2)(252.9)] x 100

= 96%