REFORMING OF METHANE ON Rh/HEXAALUMINATE CATALYSTS IN A STAGNATION-FLOW REACTOR

by

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ABSTRACT

The present work reports the synthesis, characterization, and performance of reforming catalysts based upon dispersed rhodium particles on strontium-substituted hexaaluminate supports. As confirmed by electron microscopy and X-ray diffraction, the Sr-substituted hexaaluminate provides a plate-like support structure that resists sintering and occlusion of the Rh. The hexaaluminates are synthesized using an alumoxane-based process as well as coprecipitation of appropriate nitrates. Rhodium is dispersed using impregnation with metal-nitrate salts. The total surface area and metal dispersion of the fabricated catalysts are measured before and after an accelerated aging process to evaluate the thermal stability of hexaaluminate-based catalysts.

The performance and catalytic activity of the Sr-hexaaluminate supported Rh is evaluated using a stagnation-flow reactor. A combination of experiment and modeling is used to investigate heterogeneous dry-reforming chemistry in a stagnation-flow reactor. The stagnation-flow configuration enables microprobe sampling of the compositional boundary layer adjacent to the catalyst surface. This configuration also enables efficient modeling of the catalytic chemistry as well as the coupled effects of convective and diffusive transport within the boundary layer. The active catalyst is rhodium, which is supported on strontium-substituted hexaaluminate. The modeling considers detailed reaction mechanisms that include 42 heterogeneous reactions among 12 surface species and 6 gas-phase species. Model-based experimental interpretation is used to refine previously published reaction mechanisms, which also incorporate partial oxidation and steam reforming.
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Chapter 1

INTRODUCTION

Diminishing reserves of fossil fuels necessitate efficient utilization of natural gas reserves. One technical process that has attracted much attention in recent years is to reform methane, a major component of abundant natural gas reserves, into carbon monoxide and hydrogen. Table 1.1 shows a typical makeup of natural gas. The mixture of carbon monoxide and hydrogen is often referred to as synthesis gas and can be used as feedstock for other catalytic processes such as Fischer-Tropsch synthesis of liquid fuels or production of methanol [1]. Converting the methane into liquid fuels carries the advantage of facilitated transportability, an important aspect when much of the world's natural gas is located in remote areas. Alternatively, the hydrogen component of synthesis gas can be separated from the carbon monoxide and used in a fuel cell. The fuel cell is an efficient device that produces electrochemical energy, but often requires pure hydrogen to operate. Upstream reforming is often used to produce the hydrogen required for low-temperature proton exchange membrane (PEM) fuel cells. In the case of high-temperature solid oxide fuel cells (SOFC) upstream reforming can be used to generate the required hydrogen, or in-situ reforming can be used to produce the hydrogen directly at the site of the electrochemical reactions.

The conversion of methane to synthesis gas occurs via several paths. Catalytic partial oxidation (CPOX) of methane, represented globally by Reaction 1.1, is one of the more energy efficient paths because of the exothermicity of the reaction. CPOX produces syngas in the required ratio for Fischer Tropsch synthesis without the use of downstream shift reformers. Downstream shift reformers use the water-gas-shift reaction to alter the ratio of hydrogen to carbon monoxide. The water-gas-shift reaction is represented globally by Reaction 1.2.
Table 1.1: Typical composition of natural gas

<table>
<thead>
<tr>
<th>Component</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0.9647</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.0164</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0.0019</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>0.0005</td>
</tr>
<tr>
<td>C₅H₁₂</td>
<td>0.0002</td>
</tr>
<tr>
<td>N₂</td>
<td>0.0045</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0091</td>
</tr>
</tbody>
</table>

\[ \text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \]  \hspace{1cm} (1.1)

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]  \hspace{1cm} (1.2)

Downstream shift reactors might be used in a steam reforming process, represented globally by reaction 1.3. Steam reforming methane to synthesis gas is particularly appealing for fuel cell applications because of the high ratio of hydrogen to carbon monoxide found in the products. Much of the world’s existing hydrogen comes from the steam reforming process being carried out in large scale industrial reactors. The steam reforming process is endothermic, meaning that external heat input is required to drive the reaction.

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \]  \hspace{1cm} (1.3)

Dry reforming is another path to converting methane to synthesis gas. The dry-reforming process is also endothermic and is represented globally by Reaction 1.4. Dry reforming has become particularly appealing recently because it utilizes the greenhouse gas carbon dioxide as the co-reactant. It also produces syngas in a ratio that is ideally suited to Fischer-Tropsch synthesis of liquid fuels. However, the danger of forming carbon deposits via the Boudouard reaction is much higher for the dry reforming process. The Boudouard reaction is represented in reaction 1.5.
\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad (1.4) \]

\[ 2\text{CO} \rightarrow \text{C} + \text{CO}_2 \quad (1.5) \]

It is frequently the case that these pathways to syngas production proceed in parallel. Researchers have also studied mixing the inlet streams to use two or more co-reactants [2, 3, 4, 5]. Ashcroft et al. investigated combining catalytic partial oxidation with dry reforming, noting that the combination of processes may allow the use of natural gas reserves that contain significant quantities of CO\textsubscript{2} [2]. Mixing the exothermicity of a process like catalytic partial oxidation with the endothermicity of a process like dry reforming can result in thermally neutral processes that are attractive from an engineering standpoint. The combination of partial oxidation and steam reforming is often referred to as auto-thermal reforming and has been explored recently for fuels other than methane [4].

1.1 Rh as a Catalyst for Converting Methane to Synthesis Gas

A variety of catalysts for reforming methane to synthesis gas have been studied recently. The catalysts use transition metals such as nickel, ruthenium, rhodium, palladium, platinum, and others as the active phase. Such metals are used because the surfaces readily accept or donate electrons in making bonds. A range of carriers and promoters are also used to disperse the active phase or chemically increase activity. Typically, large-scale industrial reactors utilize the non-noble metal nickel as the active phase because it is the more economically viable option. However, for specialized applications utilizing compact, short-contact-time reactors, the noble metals of the platinum group provide excellent conversions at relatively low metal loadings. In particular, the highly active metal rhodium has attracted much research interest.
1.1.1 Rh as a Partial-Oxidation Catalyst

There is significant prior literature on the use of Rh as the active phase in a partial-oxidation catalyst. It is generally agreed that Rh is the best-performing material for carbon-free operation. The high activity and stability of Rh for catalytic partial oxidation make it an ideal candidate for short-contact-time reactors designed for distributed generation of hydrogen. The short contact times translate to compact reactor sizes.

Hu and Ruckenstein published a thorough review on the partial oxidation and dry reforming of methane to synthesis gas [6]. The review covers the recent efforts by researchers to use different metals and different supports for partial oxidation and dry reforming. The review also examines the reaction pathways for catalytic partial oxidation and optimization of process conditions that can lead to greater catalyst stability. More recently, Enger et al published a thorough review on partial oxidation catalysts that focuses on the reaction pathways of partial oxidation over transition-metal based catalysts [7].

The high activity of Rh as a partial oxidation catalyst was studied by Schmidt and coworkers [8]. They studied the performance of Rh-based catalysts and compared the results to previous experiments conducted using Pt catalysts. Excellent conversions and a high selectivity to H₂ are reported for the Rh-based catalysts. In a later publication, Schmidt et al. studied a variety of different metals for the conversion of methane to synthesis gas by partial oxidation [9]. The metals included in this study were Ni, Pt, Ir, Pd, Pd-La₂O₃, Fe, Co, Re, and Ru. Schmidt and co-workers report optimal conversion, close to equilibrium, on both Rh- and Ni-based catalysts. However, the Rh-based catalyst was more stable at the reaction temperature of 1000 °C. The Ni catalysts in this study suffered from deactivation due to metal volatilization and loss of active surface area at the high reaction temperature.

The use of Rh as a partial-oxidation catalyst may also benefit parallel processes (steam reforming, dry reforming) in regards to carbon-free operation. Carbon deposits are of particular concern when dry reforming methane. Rhodium as the active metal for steam reforming and dry reforming has been extensively studied primarily because
of its high activity and propensity towards carbon-free operation. Some recent efforts by researchers on this subject are highlighted in the next section.

1.1.2 Rh as a Reforming Catalyst

Several rigorous studies on the use of Rh as a reforming catalyst have been published. Catalytic steam reforming (Reaction 1.3) of methane on nickel catalysts to produce hydrogen is a widely used commercial process that is well established. A thorough review of the process is published by Rostrup-Nielsen et al. [10]. Rostrup-Nielsen and Bak Hansen [11] conducted studies on steam-reforming and dry-reforming of methane over various transition metals and ranked them according to activity. The researchers characterize activity by turnover frequency which is defined as the reforming rate normalized by the number of available metal sites [1]. The sequence of activity is reported by Rostrup Nielsen and Bak-Hansen to be:

\[
\text{Ru, Rh} > \text{Ir} > \text{Ni, Pt, Pd} \tag{1.6}
\]

Rostrup-Nielsen and Bak Hansen also report that rhodium and ruthenium show a greater selectivity to carbon-free operation during steam reforming in the temperature range of 577-847 °C, as no carbon was formed during operation with these metals [11]. Carbon formation was measured by thermogravimetric analysis.

Reforming catalysts using non-noble metal catalysts is practical from an industrial standpoint but rapid deactivation is observed [12]. Rhodium has received attention as a catalyst for dry reforming because its high activity and low propensity for carbon formation [11] make it an ideal catalyst for chemical-energy transmission systems [12]. Richardson compared commercial Rh and Ru catalysts and noted Rh as the more-stable catalyst under dry-reforming conditions. Bradford and Vanice published a thorough review of carbon dioxide reforming of methane [13]. In comparing the different types of metals, it is noted that in general Ru, Rh, and Ir exhibit much less carbon formation than Ni, Pd, and Pt.
Ashcroft et al. studied different noble metals for CO$_2$ reforming of methane [2]. They report that for stoichiometric dry reforming of methane most platinum group metals are comparable in their performance. However, when Ni is used as the active metal in stoichiometric dry reforming, rapid deactivation is observed. They show that rhodium, in addition to iridium, are particularly stable. Ashcroft et al measured the stable performance of these active phases under dry-reforming conditions in a silica reactor for over 200h.

Solymosi and co-workers studied the catalytic reaction of methane with carbon dioxide over alumina-supported platinum group metals [14]. They ranked the specific activities of the different metals. The specific activities decreased in the order: Ru, Pd, Rh, Pt and Ir.

\[
Ru > Pd > Rh > Pt > Ir \quad (1.7)
\]

The ranking according to Solymosi et al. is slightly different from the ranking reported by previous researchers but in general it is agreed that Rh is a high-performance metal for dry-reforming methane. Solymosi and co-workers also report on the abilities of the metal to dissociate carbon dioxide. Carbon dioxide is pulsed over a reduced catalyst while products of the dissociation are detected downstream. They report that the ranking of catalyst’s ability to dissociate CO$_2$ was consistent with the activity ranking.

1.1.3 Conclusion

Rhodium as the active metal in a catalyst for converting methane to synthesis gas is one that shows high activity and a propensity to carbon-free operation. The use of rare and expensive metals such as Rh in large industrial scale reactors is impractical. However, such attributes are desirable for the active phase of the catalyst when designing reactors for high-performance applications that are small in size and require the ability to perform for long periods of time without required regeneration of the catalysts. Additionally, the high activity for both partial oxidation and reform-
ing of methane make it an ideal catalyst for autothermal operation. The preceding studies highlight the demonstrated capabilities as discovered by previous researchers of rhodium in comparison other possible noble metal and non-noble metal catalysts.

1.2 Rh Catalyst Supports Under Reforming Conditions

Recent focus has been directed at the effects of the catalyst carrier, or support, on the active metal Rh. The catalyst carrier, often a metal oxide, must be a stable high-surface-area material that can preserve well-dispersed metal phases under harsh operating conditions [1]. Care must be taken in selecting a support as research has shown that the support can influence the activity of the catalyst. For example, reforming catalysts using supports that contain ceria are known to have high activities because of the oxygen-storage capabilities of the support. In the case of converting methane to synthesis gas using Rh, researchers have focused on how the support effects the dispersion and stability of Rh. The next section highlights some of the results of those studies.

Differing conclusions have been reported on the role of the support in methane-reforming reactions using Rh. Some researchers have concluded that the reforming activity is independent of support. Erdohelyi et al [15] studied the effects of support on Rh catalysts for CO₂ reforming of methane. They report that there is no effect of support on the methane dry-reforming activity. Similarly, Bitter et al [16] also report that for Rh-based catalysts under dry reforming of methane, the activity is determined by the number of available Rh sites and the support plays no role in the actual chemistry of conversion.

Tsipouriari et al. studied reforming of methane with carbon dioxide to synthesis gas over supported Rh catalysts [17]. They report on the dependence of the CO₂ reforming reaction on Rh crystallite size and suggest that the support may play a role in determining the Rh structure (i.e. crystallite size). In a highly cited study, Wei and Iglesia [18] studied dry-reforming and steam-reforming of methane on rhodium and investigated kinetics as well as the influence of metal loading and support on dispersion and turnover frequency. Wei and Iglesia report that the identity of the
oxide surface on which Rh clusters are supported does not influence CH$_4$ turnover rates but does influence the size of Rh clusters for a given Rh content, thereby indirectly influencing turnover rates. This conclusion is in agreement with the results of Tsipouriari et al. Mark and Maier [19] also report that there is no detectable effect of the nature of the support on dry-reforming reaction rates and that the sole influence of the support is to stabilize the metal surface area.

In contrast to these findings, Wang and Ruckenstein have previously shown that the oxide support can influence reforming activity. They studied the effects of support on converting methane to synthesis gas both under partial-oxidation conditions [20] and dry-reforming conditions [21]. The study is focused on the differences between reducible oxides and irreducible oxides as catalyst supports. Wang and Ruckenstein report that reducible oxides (CeO$_2$, Nb$_2$O$_5$, Ta$_2$O$_5$, TiO$_2$, and ZrO$_2$) show low conversions while irreducible oxides (MgO and $\gamma$-Al$_2$O$_3$) show high activity and stability. Other reducible oxides (La$_2$O$_3$, SiO$_2$, and Y$_2$O$_3$) studied displayed high activity initially but a slow decline during time on stream. There is clear evidence that similarly loaded catalysts with different supports show different activity.

Zhang and coworkers report that the specific activity of Rh catalysts depends on the support employed [22]. In order of decreasing activity the supports they studied were YSZ > Al$_2$O$_3$ > TiO$_2$ > SiO$_2$ > La$_2$O$_3$ > MgO. They conclude that the activity is correlated with the acidity characteristics of the carrier and its ability to dissociate CH$_4$. Zhang et al. correlate dry-reforming activity over Rh/$\gamma$-Al$_2$O$_3$ with Rh crystallite diameter [22] and found that a reduction in Rh particle size results in an enhanced rate of deactivation. Wang and Ruckenstein [21] measured CO$_2$ reforming activity for different Rh crystallite sizes by varying the loading. They reported a decrease in turnover frequency with an increase in mean Rh crystallite diameter. Zhang et al. attribute the decreased turnover number to a greater availability of low coordination metal sites over which carbon deposition is favored [22]. They also report that increased Rh loading leads to decreased dispersion which yields lower CH$_4$ turnover rates.

Wei and Iglesia were the first to report that methane steam-reforming turnover rates increased with Rh dispersion through the range of dispersions measured (25-50
percent). Additionally, their data show that turnover rates and the effect of Rh morphology (i.e. dispersion) are identical for steam and dry reforming on rhodium. This is important because many of the findings of dry reforming could be carried over to steam reforming of methane. In a recently published article Jones et al. [23] reported increased turnover frequencies with increased dispersion for CH$_4$-H$_2$O reforming over Rh.

The role of the support in reforming chemistry as published in the literature is unclear. However, researchers tend to be in agreement on the fact that the support may indirectly affect activity by influencing the morphology of the rhodium it is supporting. One area the literature lacks is studying the use of the thermally stable hexaaluminates in reforming reactions. Little data exists showing the effects of a hexaaluminate support on Rh structure and reforming activity.

1.3 Hexaaluminate Catalysts and Catalyst Supports

Hexaaluminates are a promising alternative catalyst for catalytic combustion and catalytic partial oxidation. The two processes are exothermic processes that typically take place at high temperatures. Sidwell and others focused on the use of hexaaluminates as catalysts during the catalytic combustion of methane [24, 25]. Zhu et al. studied the partial oxidation of methane over RhSr-substituted catalysts and reported the increased stability of the hexaaluminate based catalysts [26]. Gardner et al used BaNi-hexaaluminate catalysts during catalytic partial oxidation of n-tetradecane [27] and also reported on the increased stability of hexaaluminate catalysts as compared to conventional washcoat catalysts.

Hexaaluminates have also been used as a thermally stable support material. Majocchi et al reported on the activity and selectivity of Rh-hexaaluminate-based catalysts for partial oxidation of methane to synthesis gas [28]. Ferrandon reported on the ability of a hexaaluminate-supported Rh-based catalyst to retain surface area under simulated aging of catalysts [4].

We have shown in a previous work that hexaaluminate catalyst supports resist
surface area loss [29], a necessary feature for the high temperatures required to operate dry reforming or autothermal reforming of methane. The high-temperature thermal stability of hexaaluminates is attributable to the sintering resistance of the underlying structure.

1.3.1 Hexaaluminate Structure

The hexaaluminate structure as shown in Figure 1.1 is composed of two closely spaced spinel blocks that are separated by mirror planes containing large cations. A range of cation substitutions has been reported in the literature including Ba, Sr, Ca, Ni, Mg and La. The hexaaluminate crystal structure is fundamentally different from that of $\gamma$-$\text{Al}_2\text{O}_3$ because of the addition of a large cation into the crystal structure along the $c$-axis. Studies have shown that the addition of this cation suppresses crystal growth and oxygen ion diffusion in the [0 0 1] direction and results in a thin plate-like morphology. The crystal shape and preferential diffusion route of oxide ions allows the hexaaluminate to retain large surface areas at high temperatures [30]. In contrast, the $\gamma$-$\text{Al}_2\text{O}_3$ undergoes a phase transformation at high temperatures to $\alpha$-$\text{Al}_2\text{O}_3$, a low-surface-area phase.

Substituting an active metal into one of the sites of the hexaaluminate structure provides a catalyst that resists sintering of the active metal at high temperatures since it is embedded in the lattice of the catalyst material. Manganese-substituted hexaaluminates in particular have shown high activity and thermal stability for catalytic combustion. Substituted hexaaluminates are often used when sintering or volatilization of the active phase are a concern.

1.3.2 Hexaaluminates Used for Steam- and Dry-Reforming of Methane

There is prior literature on the use of hexaaluminates, both as supports and as reforming catalysts. Machida et al. studied steam reforming over hexaaluminate-supported nickel catalysts with three different cation substitutions: barium, strontium, and calcium [31]. Because excess steam is needed to suppress carbon deposition on Ni, a stable catalyst-support structure is important. Of the three alternatives stud-
Fig. 1.1: Illustration of strontium hexaaluminate crystal structure.
ied by Machida, the Sr-substituted hexaaluminate displayed the greatest resistance to high-temperature sintering.

Additionally, Machida et al. conducted methane-steam reforming experiments on the various types of hexaaluminate-supported nickel catalysts. They compared the performance to that of standard steam-reforming catalysts (12 wt-% Ni/Al₂O₃) and commercially available steam-reforming catalysts (16 wt-% Ni/CaO-Al₂O₃). No differences were observed by the authors in activity or selectivity. However, Machida et al. reported a dependence of carbon deposition on steam-to-carbon ratio for the Al₂O₃-based catalysts that was not observed for the hexaaluminate based catalysts. Carbon deposition was scarcely detected for the hexaaluminates over the range of steam-to-carbon ratios examined (1.0 < H₂O/C < 5.0). Machida proposed that the cation substitutions enhanced steam adsorption and thus suppressed carbon deposition. The low amount of carbon deposition on the hexaaluminates is also attributed to the high nickel surface area of hexaaluminate supported catalysts.

Ferrandon and Krause reported on the catalytic reforming activity and excellent thermal stability of Ca-substituted hexaaluminates supporting Rh as the active metal [4]. They studied autothermal reforming of gasoline surrogates and applied a simulated aging technique to measure the ability of Rh catalyst supports to retain surface area after the aging technique. Of the supports tested the Ca-based hexaaluminate was one catalyst support that did not experience a severe loss of surface area after the simulated aging process.

The use of hexaaluminates as catalysts has been studied in the dry reforming of methane, which has a close relationship with steam reforming [11, 18]. Xu et al. [32] studied the use of hexaaluminate-supported nickel catalysts with various mirror plane substitutions (Ca, Sr, Ba, and La) for dry-reforming of methane. They investigated the activity and stability of these catalysts and found that they are highly active and retain their activity with no signs of deactivation over a reaction time of 18 h. Yokota et al. [33] also investigated the use of hexaaluminates as catalysts for methane-steam/C⁰₂ reforming as well as catalytic oxidation. They used a barium-nickel substituted hexaaluminate (BaNiAl₁₁O₁₉) and compared the catalytic activity and stability to the conventional Ni/Al₂O₃ catalyst. Results of the activity and
stability tests show that although the conventional catalysts have a greater initial activity, the methane conversion for these catalysts decreases over a period of 70 hours due to carbon deposition. Meanwhile, the hexaaluminate catalysts maintain a steady level of methane conversion over the time of the test and no carbon deposition was measured by thermogravimetric analysis.

1.3.3 Conclusion

Hexaaluminates are a thermally stable material that have seen successful use in applications such as catalytic combustion and partial oxidation of methane. The thermal stability is directly attributable to the underlying crystal structure of the hexaaluminate. A large cation substitution into the mirror plane of the crystal lattice suppresses growth in the [0 0 1] direction resulting in a plate-like morphology and stable surface areas at elevated temperatures. Hexaaluminates also show promise as thermally stable supports for steam-reforming or dry-reforming catalysts but there is much left to be understood about their effects on Rh dispersion.

1.4 Development of Elementary Reaction Mechanisms

Significant research on conversion of methane to synthesis gas is focused on the underlying elementary chemistry or the reaction pathways. A recent review article published by Enger et al. [7] highlights recent efforts in the literature towards understanding the reaction pathways for catalytic partial oxidation on various metals. Additionally, the review on dry reforming published by Bradford and Vannice [13] focuses much attention on the reaction pathways and kinetics underlying dry reforming methane to synthesis gas.

Deeper understanding of reaction pathways can lead to development of valid elementary reaction mechanisms. Optimization of processes and reactor geometries can be facilitated through the use of computational models that incorporate the elementary reaction mechanisms. Using such a mechanism in reactor models enables rapid numerical experimentation of wider fuel-processing windows, including a wide
blending of steam reforming, dry reforming, and catalytic partial oxidation reactant mixtures. The next section highlights some of the recent findings of various researchers on reaction pathways and elementary-mechanism development.

1.4.1 Previous Mechanistic Studies on the Partial Oxidation of Methane on Rh

For catalytic partial oxidation of methane to synthesis gas, two pathways are proposed in the literature, a direct pathway and an indirect pathway. In the direct pathway, the syngas is a direct product of the reactions occurring on the catalyst surface. Evidence of a direct pathway lies in the fact that syngas is obtained at relatively short contact times. In the indirect pathway, the methane is first completely oxidized and then the products of the combustion reaction (CO$_2$ and H$_2$O) serve to reform the remaining methane by one of the global reforming reactions (Reactions 1.3 and 1.4). In practice, catalytic partial oxidation is likely a combination of the two, but researchers have used computational modeling of reactor systems to probe the underlying processes at certain conditions in an effort to develop elementary reaction mechanisms.

Schwiedernoch et al. proposed a competition between partial oxidation and methane reforming [34]. The dominance of one pathway over another relies on the oxygen coverage of the surface. Mhadeshwar and Vlachos developed a Cl microkinetic model that predicts a combination of partial oxidation and combustion to produce CO and H$_2$O [35]. The H$_2$O then proceeds to steam reform the remaining methane to produce hydrogen. The model results are probed to determine the degree of surface coverage located on catalysts within a tube reactor. The two models both speculate that the amount of surface oxygen is high at the entrance to the reactor and subsequently reduces as one moves towards the exit of the reactor.

Some of the most recent studies on methane conversion to syngas have been carried out by Donazzi et al. in a two-part study focusing on the methane reforming results in an annular reactor [5, 36]. The experimental results from these studies have been utilized by Maestri et al. in developing microkinetic models for optimizing reactor geometries and process operating parameters. Maestri et al carry out a reaction
path analysis on the microkinetic model results to gain a deeper understanding of the underlying chemical processes [37]. The results of reaction-path analysis by Maestri et al. supports the indirect route to syngas production. Maestri et al. conclude that at the entrance to a monolith reactor there is a section where the methane is combusted to CO₂ and H₂O. Combustion in this regime occurs due to the high coverage of the surface by atomic adsorbed oxygen. This conclusion is in agreement with previous speculation by Schwiedernoch and Deutschmann [34]. The entrance regime is followed by an intermediary section where formation of syngas occurs in parallel with regular combustion. In the final reaction zone the steam reforming and water-gas shift reactions dominate [37].

The dominant reaction pathways that underly catalytic partial oxidation of methane to synthesis gas are well documented. Elementary mechanisms have been published that accurately predict the performance of CPOX reactors. Taylor et al. tested several mechanisms in a stagnation-flow configuration and reported on the abilities of elementary reaction mechanisms in predicting boundary-layer species profiles [38].

Because the reaction mechanisms are elementary in nature the global reactions for steam or CO₂ reforming are included. The next section highlights some recent efforts to elucidate the elementary reactions involved in reforming methane to synthesis gas using H₂O or CO₂ as the co-reactant.

1.4.2 Previous Mechanistic Studies on Steam- and Dry-reforming of Methane

Steam reforming reaction pathways were recently studied by Maestri et al [39]. Similar to their work with partial oxidation, a C1 microkinetic model was validated against experimental data for steam reforming methane. The experimental data is obtained from an annular reactor that is able to achieve high space velocities, high reaction temperatures and better isothermal conditions than standard fixed-bed reactors [40]. Following model validation, a reaction path analysis based on the model predictions for steam-reforming methane was carried out.

In the pathway proposed by Maestri et al., the steam reforming process begins
with adsorption of the reactant species CH₄ and H₂O (Reactions 1.8 and 1.9). In the following series of reactions an asterisk designates a surface site. Methane is reduced to atomic adsorbed carbon (C*) through a series a hydrogen abstraction steps (Re-
actions 1.10-1.13) and the resulting atomic adsorbed hydrogen can then recombine to form gas phase hydrogen (Reaction 1.14). Adsorbed steam molecules dissociate to OH* and H* (Reaction 1.15) and the OH* oxidizes C* to produce CO* (Reaction 1.16) which can desorb into the gas phase. The adsorbed CO can then further react with adsorbed hydroxyl radicals to produce adsorbed CO₂ (Reaction 1.17). The rate determining step for this pathway is reported to be adsorbed methyl dehydrogenation (Reaction 1.11).

\[
\text{CH}_4 + * \rightarrow \text{CH}_4^* \quad (1.8)
\]

\[
\text{H}_2\text{O} + * \rightarrow \text{H}_2\text{O}^* \quad (1.9)
\]

\[
\text{CH}_4 ^* + * \rightarrow \text{CH}_3^* + \text{H}^* \quad (1.10)
\]

\[
\text{CH}_3 ^* + * \rightarrow \text{CH}_2^* + \text{H}^* \quad (1.11)
\]

\[
\text{CH}_2 ^* + * \rightarrow \text{CH}^* + \text{H}^* \quad (1.12)
\]

\[
\text{CH} ^* + * \rightarrow \text{C}^* + \text{H}^* \quad (1.13)
\]

\[
\text{H}^* + \text{H}^* \rightarrow \text{H}_2 + 2^* \quad (1.14)
\]
\[ \text{H}_2\text{O}^* + \* \rightarrow \text{OH}^* + \text{H}^* \] (1.15)

\[ \text{C}^* + \text{OH}^* \rightarrow \text{CO}^* + \text{H}^* \] (1.16)

\[ \text{CO}^* + \text{OH}^* \rightarrow \text{CO}_2^* + \text{H}^* \] (1.17)

Wei and Iglesia [18] also studied the reaction pathways of steam-reforming methane. Experimental data was obtained in a standard tubular-reactor configuration. In such a configuration the catalyst, which may be coated onto a monolith or diluted with inert particles, is placed a stainless steel or quartz reactor tube. Reactant mixtures flow over the catalyst and products are measured at the exit of the reactor tube either by gas chromatography or mass spectrometry. An illustration of such a configuration is shown in Figure 1.2.

Based on experimental data, Wei and Iglesia proposed a common mechanism for both steam- and dry-reforming of methane. The pathway they propose is largely similar to the pathway proposed by Maestri et al. The major difference is that in the pathway proposed by Wei and Iglesia, the oxidation of the surface adsorbed carbon occurs by surface adsorbed atomic oxygen (Reaction 1.18). The surface-adsorbed atomic oxygen in this case originates from the dissociation of OH* (Reaction 1.19).

\[ \text{C}^* + \text{O}^* \rightarrow \text{CO}^* + \text{Rh}^* \] (1.18)

\[ \text{OH}^* + \* \rightarrow \text{O}^* + \text{H}^* \] (1.19)

Schadel et al. also developed an elementary reaction mechanism for steam reforming of methane on Rh [41]. The model predictions were validated against ex-
Typical Flow Reactor

Fig. 1.2: Standard tubular-reactor configuration for evaluation of catalyst activity.

Experimental data obtained in a tubular flow reactor but no reaction path analysis was carried out.

The elementary reaction mechanism for dry reforming of methane on transition metals has also been previously studied. A comprehensive review of the dry-reforming process, including mechanism development, is provided by Bradford and Vannice [13]. Rostrup-Nielsen and Bak-Hansen [11] investigated dry reforming of methane on transition metals. They proposed a pathway that began with the adsorption of methane (Reaction 1.8) and carbon dioxide (Reaction 1.20). Similar to the steam-reforming pathway, the methane decomposes (Reactions 1.10-1.13) and produces surface carbon. The adsorbed CO₂ dissociates according to Reaction 1.21, and the resulting O* oxidizes the surface carbon (Reaction 1.18). Similar pathways were proposed by Erdohelyi [15], Efstatthiou [42], and Wei and Iglesia [18].
\[ \text{CO}_2 + \star \rightarrow \text{CO}_2^\star \] (1.20)

\[ \text{CO}_2^\star + \star \rightarrow \text{CO}^\star + \text{O}^\star \] (1.21)

Mark and Maier [19] proposed a different, two-step pathway. In their pathway, the decomposition of methane onto the surface produces surface carbon that is reacted with gas phase CO\(_2\) to produce 2CO (Reaction 1.22).

\[ \text{C}^\star + \text{CO}_2 \rightarrow 2\text{CO} + \text{Rh}^\star \] (1.22)

Recently, Maestri and others have published a C\(_1\) microkinetic model [37] that includes dry-reforming pathways. Similar to their reaction pathways for steam reforming methane, the oxidation of surface carbon occurs by surface hydroxyl radicals (Reaction 1.16) [39]. This is in contrast to oxidation by adsorbed oxygen as proposed by previous researchers.

Methane conversion rates for the two processes are often the same regardless of co-reactant. This result suggests that the rate determining step will involve methane. Wei and Iglesia [18] proposed an elementary surface mechanism that is limited by the initial activation of a C-H bond. A number of experimental studies in the temperature range 873 K to 1073 K supported this claim. Arrhenius plots showed that forward CH\(_4\) reaction rates are identical when using steam as to when using CO\(_2\) as the co-reactant. The rate constant is also similar to that of CH\(_4\) decomposition on the same catalyst, indicating that the limiting elementary reaction step in reforming methane is the initial activation of a C-H bond with a Rh site.

Kinetic-isotope experiments are also independent of co-reactant. For example, replacing H\(_2\)O with D\(_2\)O did not influence steam-reforming rates indicating that water activation, reaction of C\(^\star\) with hydroxyl groups, and hydrogen desorption are not kinetically relevant. Chemisorbed hydrogen and CO coverage are expected to be neg-
ligible at typical CH$_4$-reforming temperatures (873 K-1100 K). Thus the co-adsorbed products do not influence the number of Rh atoms available for CH$_4$ activation. Jones et al. [23] performed a more-rigorous theoretical study of steam reforming on noble metals and found that at low temperatures the CO-formation step is kinetically the most important reaction step. However, as temperatures increase the rate-limiting step switches to dissociative methane adsorption which is in agreement with the results of Wei and Iglesia.

1.4.3 Conclusion

There is significant prior research on the pathways to producing synthesis gas from methane which will aid in further developing elementary reaction mechanisms. Partial oxidation of methane is proposed to occur via an indirect or direct route. Evidence for the indirect and direct routes to syngas exists. However, most researchers agree that in practice some combination of the two is likely to occur.

The pathways to dry-reforming and steam-reforming methane are also debated. Researchers propose several pathways where the oxidation of surface carbon occurs either by surface-adsorbed oxygen [18] or surface-adsorbed hydroxyl radicals [39]. A third pathway for dry-reforming methane proposes that the surface carbon is reacted with gas-phase CO$_2$ to produce gas-phase CO [19]. Deeper understanding of the pathways to producing syngas can be assisted by generation of experimental data.

1.5 Stagnation-Flow Reactor

Data for validating proposed reaction mechanisms is largely measured in a tube reactor configuration (Figure 1.2). This configuration is practical as an industrial reactor but makes measurement of gas-species compositions within the boundary layer close to the surface difficult. This work utilizes an experimentally accessible surface in a so-called "stagnation-flow" configuration to validate and develop a proposed elementary reaction mechanisms that encompasses global partial oxidation, steam reforming, and dry reforming [43].
The stagnation-flow reactor introduced in a previous publication [29] is a useful tool in understanding underlying catalytic chemical processes. Figure 1.3 contrasts simplified illustrations of a commonly used tube-reactor configuration and a stagnation-flow configuration. In the stagnation-flow reactor, premixed reactants impinge upon a catalytically active stagnation surface. Reactants (CO₂ and CH₄) are consumed at the surface while products (CO and H₂) diffuse away from the surface. The diffusion causes changes in the local gas composition and the formation of a chemical boundary layer. Changes within the chemical boundary-layer can be measured by gas-phase sampling with a quartz microprobe that traverses the boundary layer.

The stagnation-flow similarity creates a one-dimensional flow field where temperature and species profiles within the boundary layer do not vary with radial position [44]. The one-dimensional nature enables rapid numerical modeling with elementary gas-phase and surface chemical kinetics included. The reduced computation times facilitate rapid evaluation and development of existing reaction mechanisms [38]. The gas-phase chemical boundary-layer profiles can also be used to infer surface-reaction rate constants as shown by Sidwell and others [24, 25].

![Typical Flow Reactor](image1.png) ![Stagnation Flow Reactor](image2.png)

**FIG. 1.3:** Comparison of a) typical flow reactor configuration and b) stagnation flow configuration.

The stagnation-flow geometry has little, if any, value as a practical catalytic re-
actor; its primary purpose is to facilitate study of interactions between a catalytic surface and the adjacent gas-phase boundary layer. By exposing the catalytic surface to direct experimental observation, valuable fundamental knowledge can be garnered. The unique data gathered from stagnation-flow experiments can be incorporated directly into models that provide quantitative design insight for the practical configurations [45, 26].

1.5.1 Previous Kinetic Studies Using Stagnation-Point Flows

Stagnation flows have been used in several studies to validate elementary surface-reaction mechanisms and gas-phase reaction mechanisms. Ikeda et al. [46] used stagnation flows to study surface kinetics of hydrogen-air combustion on platinum surfaces. Experiments were carried out that measured major gas-phase species concentrations as a function of distance normal to the catalytic surface. These measurements were performed using a quartz sampling probe that fed into a gas chromatograph. In their study, the authors first examined the overall surface reaction rate through a range of operating conditions by employing the stagnation point-flow simplification where the overall surface rate is equal to the molar diffusive flux of species \( i \) at the surface. The molar diffusive flux \( J_i \) can be calculated using the measured concentration gradients in the axial direction \( \left( \frac{dX_i}{dy} \right) \), mole-weighted average binary diffusion coefficients \( D_i \), the pressure \( p \), and the universal gas constant \( R \) as shown in Equation 1.23.

\[
\text{Rate} = J_i = -D_i \left( \frac{dX_i}{dy} \right) \frac{p}{RT}
\]  

Equation 1.23

Ikeda et al. reported that the overall rate increases with increasing equivalence ratio and temperature in the range studied (\( 0.5 < \phi < 3.0 \) and \( 489 \text{ K} < T < 928 \text{ K} \)). The equivalence ratio, \( \phi \), is defined as the fuel/oxidizer ratio for a given experiment divided by the stoichiometric fuel/oxidizer ratio. They used these findings in the more-detailed studies of a proposed elementary surface reaction mechanism. The authors simplified the mechanism at various equivalence-ratio ranges to produce rate expressions based on experimentally measurable parameters such as gas properties
at the catalytic surface. They simplified the rate expressions based on findings in the experiments with the overall surface-reaction rate summarized above. The rate expressions were used along with the experimentally produced results to produce Arrhenius plots which gave pre-exponential factors and activation energies. The resulting kinetic parameters could then be compared to results in the literature. Ikeda et al. report that in general the rate constants for their experimentally produced results were lower than those deduced from the literature. However, the values deduced from the literature were based on surfaces exposed to high vacuum cleaning procedures, thus the discrepancies indicate that there is some dependence of the rate on surface coverage. Suggestions for modification of the elementary surface reaction mechanism were not proposed.

Khadiya and Glumac [47] also used stagnation-point flames and measurements of gas-phase composition in the boundary layer to validate surface-chemistry models. They measured compositions using laser induced fluorescence but the subsequent analysis is similar to that of Ikeda et al. The molar diffusive fluxes were obtained against a range of experimental variables: substrate temperature, pressure, and equivalence ratio. The authors reported that the values of the molar diffusive flux as predicted by their elementary surface-reaction mechanism were in general greater than those observed experimentally for nearly all experimental conditions, but trends were similar. Khadiya and Glumac state that this is the product of an overprediction in the destruction probability of OH and that a higher sticking probability of adsorbed oxygen or a lower sticking probability of adsorbed hydrogen is required in the surface mechanism. This accounts for the quantitative deviation of experimentally produced and modeled results. It was also found that the variation in molar diffusive flux with pressure deviated qualitatively as well. The authors propose that this is because the model overpredicts the density of free surface sites and thus overpredicts OH destruction at low pressures.

Sidwell et al. [25] employed stagnation surfaces to study catalytic combustion of methane over hexaaluminate surfaces. A quartz microprobe was used with a mass spectrometer to produce boundary-layer gas-phase species composition profiles. Accompanying numerical models were used to estimate global surface-reaction rates. Sidwell et al. came to the conclusion that the hexaaluminate catalyst surface con-
sumes methyl radicals to suppress gas-phase reactions. The conclusion was arrived at by changing the sticking coefficient of CH$_3$ to one in the model. Such a sticking coefficient implies a 100 percent probability of methyl radicals adsorbing on the surface of the catalyst. This resulted in good agreement between experimental results and modeled results. In another study by Sidwell [24], stagnation surfaces were employed to modify a previously developed elementary surface-reaction mechanism for the combustion of methane over Pd/hexaaluminate surfaces. A sensitivity analysis of species showing poor agreement between modeled and experimental results is performed to identify those reactions in the mechanism which require further study.

Taylor et al. [38] studied catalytic partial oxidation on Pt in a stagnation-flow reactor. In their study they use Raman spectroscopy to measure the concentration of CH$_4$ along the centerline of a chemically reacting stagnation-point flow. The experimentally measured results are compared to results obtained from a numerical model incorporating elementary surface reaction mechanisms. The strengths and weaknesses in predicting stagnation-flow-reactor results for a number of different mechanisms are reported.

1.5.2 Conclusion

The stagnation-flow reactor measurements coupled with numerical models that incorporate elementary heterogeneous reaction mechanisms is a useful tool for understanding the underlying chemical processes present in catalytic reforming and combustion. The preceding section highlights some recent efforts by researchers using the stagnation-flow configuration for elementary reaction mechanism development.

1.6 Summary of Results

In this work we have fabricated a number of catalysts based on the Rh-hexaaluminate catalyst system. The catalysts are fabricated using a number of techniques and are characterized to confirm hexaaluminate formation and Rh-metal impregnation. The catalysts are exposed to harsh operating conditions meant to mimic time on stream.
The catalysts are characterized after exposure to these conditions and compared to the untested materials. The primary objective of the characterization is to evaluate thermal stability of the fabricated catalysts.

Catalyst chemical activity is tested in a stagnation-flow reactor. The stagnation-flow reactor provides a means to measure gas-phase compositions immediately adjacent to the catalyst surface. Such measurements are not available in practical reactor configurations (e.g. channel monoliths or porous foams). Moreover, the stagnation-flow similarity enables efficient mathematical modeling of the chemically reacting boundary layers. By analyzing boundary-layer measurements taken in the stagnation-flow reactor at various experimental conditions, rate constants are developed that extend a previously published elementary mechanism to modeling dry reforming of methane on Rh. With these new parameters reasonable agreement is obtained between simulated and experimental results. The model results can then be used to assist interpretation of the fundamental reaction pathways, providing quantitative insight about the overall reforming processes.
Chapter 2

RESEARCH APPROACH

This chapter describes in detail the experimental and numerical methodology used in this work. The first section of this chapter describes the methods used in synthesis of hexaaluminate catalyst supports and subsequent impregnation by the active metal Rh. A number of diagnostic techniques are used to characterize the catalysts used in this work. The objective of using the diagnostic techniques is to confirm proper synthesis and also to evaluate the thermal stability of fabricated catalysts as compared to commercial catalysts. The second section describes the methods used for characterization.

The third section describes a stagnation-flow reactor (SFR) which is used in this work to test the catalysts for catalytic activity. In addition, the SFR is used to provide experimental data for development of a published chemical reaction mechanism. Aspects of reactor development and operation are included in this section. Errors associated with experimental measurements are also described in this section.

The experimental results obtained from the stagnation-flow reactor are interpreted using a multi-step heterogeneous elementary reaction mechanism. Model-based interpretation is used to further develop untested aspects of a published mechanism. The modeling results in this paper are computed using the SPIN application of the CHEMKIN software package [48, 49, 44]. Details of the axi-symmetric boundary-layer problem and solution algorithms used by the code are presented in the final section of this chapter.
2.1 Catalyst Synthesis

Thermally stable hexaaluminate catalysts and catalyst supports are shown in the literature to be fabricated either by coprecipitation [4], hydrolysis of alkoxide precursors [50], sol-gel methods [51], or the novel process of the alumoxane method [52, 53]. This work utilizes two of these methods. Initially, the alumoxane method was employed by TDA Research Inc (Wheat Ridge, CO) to synthesize strontium-based-hexaaluminate catalysts and catalyst supports for steam reforming methane. Other hexaaluminate-based catalysts in this work were synthesized using the method of co-precipitation.

2.1.1 Alumoxane Method

The alumoxane method, as developed by Kareiva et al. [52, 53], has several advantages over the traditional methods of synthesizing hexaaluminates. These advantages include atomic scale mixing of the metals leading to indefinitely stable materials in both solid and solution, evenly substituted materials, and processibility (e.g. materials are inexpensive when compared to materials required for the other processes such as alkoxide precursors). TDA Research (Wheat Ridge, CO) has shown that a wide range of metals can be substituted under very mild conditions using this process [52, 53]. Early research experimented with substituting Rh metal into the crystal lattice in an effort to prevent agglomeration of active metal under harsh steam reforming conditions. This has proven to be an effective technique when Ba is the large cation used to prevent sintering and Ni is the active metal [33]. Characterization of these catalysts fabricated in early research showed that the Rh did not substitute into the crystal lattice but rather is dispersed as metal clusters supported by the hexaaluminate structure.

The alumoxane process begins with an alumoxane precursor consisting of carboxylic acids bonded to boehmite particles. The exchange reaction is accomplished by reacting this precursor with the appropriate metal acetylacetonates (acacs), in this case a strontium acac. Al$^{3+}$ cations are eliminated from the structure by replacement with the alkaline earth metal Sr and converted to Al(acac). The Al(acac) is a stable
molecule that provides the driving force for the reaction. Following the exchange, the materials are calcined at 1300 °C, which burns off the organic ligands and allows the nanoparticles to form a hexaaluminate structure.

2.1.2 Co-precipitation Method

Other hexaaluminate catalyst supports in this work are prepared by co-precipitation of appropriate nitrates. The co-precipitation process is inexpensive and widely used for preparation of hexaaluminates [4]. Sr- and Ca-based hexaaluminates are prepared for direct comparison via characterization. The hexaaluminate supports are also compared to other commercial catalyst supports such as γ-alumina, yttria stabilized zirconia, and gadolinium doped ceria. To prepare a strontium hexaaluminate, 3.14 g of Sr(NO₃)₂ (Sigma Aldrich) is added to 61.3 g of Al(NO₃)₃ (Sigma Aldrich) and dissolved in 200 mL of de-ionized water. The resulting mixture is stirred and 5.0 M ammonium hydroxide is added until a pH between 7 and 8 is obtained. This mixture is then dried at 110 °C and calcined at 1300 °C. Similarly, to prepare the calcium hexaaluminate 3.78 g of Ca(NO₃)₂ (Sigma Aldrich) was added to 66 g of aluminum nitrate (Sigma Aldrich) and dissolved in 200 mL of de-ionized water. The resulting mixture was stirred and 5.0 M ammonium hydroxide was added until a pH between 7 and 8 was measured. This mixture is then dried at 110 °C and calcined at 1300 °C. The hexaaluminate supports are crushed by mortar and pestle. The samples are in powder form after this process.

2.1.3 Addition of Catalyst Supports to Substrates

The hexaaluminate support powders were identified by X-Ray diffraction and characterized for surface area in powder form. No additional aging or other processing was done between the fabrication presented in the previous section and the characterization by BET or XRD.

Testing catalyst activity requires not only impregnation with an active phase but also deposition of the supported catalyst onto a substrate. Additional processing steps were required to deposit the catalysts onto different substrates. Crushed foam
monoliths were utilized for CO pulse chemisorption and a custom-molded ceramic substrate was used for stagnation-flow boundary layer measurements. The following sections describe the substrate fabrication and deposition processes used in this work.

**Foam Substrate**

Catalyst support powders were deposited on crushed porous-foam monoliths for initial CO pulse chemisorption tests. The reason to deposit the catalyst onto a porous foam substrate is to create a catalyst coating that is similar in thickness to what is tested within the stagnation-flow reactor. An image of the foams used in this work is shown in Figure 2.1. Porous foam substrates of 99.5% purity α-Al₂O₃ from Sud Chemie Advanced Hi Tek Ceramics were used. The ceramic foams have 45 pores per inch and a surface area of approximately 65 cm²/g.

To deposit the catalyst support on the foam substrate, a solution consisting of the support powder (0.1g) and 11 ml of aluminum hydroxide gel (Sigma Aldrich)
is created. Porous foams are dipped into the support powder/aluminum hydroxide solution and then calcined at 550 °C. The thickness of the layer deposited onto the surface is estimated by weight gain of foam after the coating process. The aluminum hydroxide gel (Al(OH)₃) has a density of approximately 13 mg/ml. After calcination, the solids in the aluminum hydroxide gel are converted to α-alumina. Thus, 11 ml of solution leaves approximately 0.1 g of solid after calcination of the substrate. Combined with the 0.1 g of added strontium hexaaluminate the resulting mixture on the surface of the substrate is approximately a 50:50 mixture of α-Al₂O₃ and catalyst support powder.

For initial CO pulse chemisorption tests the 45-ppi foam support from Sud Chemie was crushed with a mortar and pestle into smaller particles prior to deposition of the catalyst. The size of the porous foam particles after the crushing was > 420 micron (Mesh 40 sieve).

**Stagnation Surface: Assembly and Coating**

Additional processing steps are also taken to apply the hexaaluminate support powders to a flat ceramic substrate for testing in the stagnation-flow reactor. The flat ceramic substrate is cast from Cotronics Rescor 780. A mold for casting the substrate was designed and fabricated from Cotronics Replicast 101 Rubber Mold Making Compound.

To cast the substrate, 11.5 grams of the Rescor 780 activator is mixed with 50 g of the Rescor 780 base powder to produce a slurry that is poured into the rubber mold. Replicast 101 Mold Release is sprayed into the rubber mold prior to the slurry being poured in. The rubber mold is specifically designed to create a flat ceramic stagnation surface compatible with the other components of the stagnation-flow reactor. The stagnation-flow reactor is described in the next section. The slurry is vibrated in the mold for approximately 5 minutes. Immediately following vibration of the mold, R-type thermocouples (Omega unsheathed fine gauge thermocouples (dia.=0.010")) are embedded in the ceramic substrate using a guide that spaces the three thermocouples exactly 1 inch apart (Figure 2.2). Unsheathed fine gauge thermocouples are threaded into ceramic sheaths before being embedded in the cast ceramic surface. The cast
Fig. 2.2: Embedding thermocouple sheaths into the cast ceramic substrate (actual fine gauge R-type thermocouples not shown).

ceramic part with embedded thermocouples cures in the mold at room temperature for 16h. After the room-temperature cure, the surface is removed from the mold and then post-cured at 950 °C. A 10.2h ramp to get to 950 °C is used and the part is held at this temperature for 1h before returning to room temperature at the same ramp rate. The post cure prevents any out-gassing of the ceramic part during stagnation-flow reactor experiments.

Following the casting of the ceramic substrate, a thin catalyst layer is added via spray deposition. The hexaaluminate support in powder form (0.1g) is mixed with an aluminum hydroxide gel (11 ml) and sprayed with a paint sprayer (Paasche model no. VL202) onto the surface of the cast ceramic substrate. The coated part is calcined at 550 °C and the process of spraying and calcining is repeated until the desired coating thickness is achieved. Coating thickness is estimated by the amount of weight gain
Fig. 2.3: SEM micrograph showing the coating thickness on the cast ceramic substrate with catalyst coating.

by the substrate following each coating. A density of 1 g/cm$^3$ and a perfectly flat ceramic substrate surface is assumed for estimation of thickness coating.

Figure 2.3 shows an SEM micrograph of a coated surface cross section. The SEM images show a clear division of morphology between the cast substrate and the coating, indicating that the spray-coating method is effective. Estimates of coating thickness based on the weight gain of the cast ceramic substrate are consistent with coating thicknesses observed in SEM micrographs.
2.1.4 Addition of Metal

Rhodium metal is added to the deposited hexaaluminate catalyst supports via incipient wetness impregnation [1]. The Rh metal is added using Rh(NO$_3$)$_3$ from Sigma Aldrich. Rhodium nitrate is mixed with DI water until an exact amount of solution that will wet the catalyst support powder or substrate (foam or cast ceramic substrate) is achieved. The exact amount of solution that will wet the sample is determined from prior tests using plain DI water. This solution is then dripped onto the substrate and the substrate is calcined at 700 °C with a ramp rate from room temperature of 5 °C/min.

Two different methods of metal impregnation were used in this work. The methods are referred to as post-impregnation and pre-impregnation. In the pre-impregnation method, rhodium nitrate was added to the support powder via incipient wetness impregnation and then mixed with the aluminum hydroxide for deposition onto the substrate (foam or cast ceramic stagnation surface). In the post-impregnation method only the hexaaluminate support powder was added to the aluminum hydroxide and deposited onto the surface of the substrate. With the support powder already deposited on the substrate, the metal is added via incipient wetness impregnation using rhodium nitrate. The effect of impregnation method on available catalyst surface area is investigated in Section 3.4.1.

2.2 Catalyst Characterization

A number of diagnostic techniques are used to characterize the catalysts fabricated in this work. One of the objectives of characterization is to confirm the formation of hexaaluminate structures and addition of the active phase, Rh. An additional objective is to evaluate the thermal stability of hexaaluminate-based catalysts as compared to commercially acquired catalysts. The characterization techniques and the aging processes used in this work are described in this section.
2.2.1 X-Ray Diffraction

Powder X-ray diffraction (XRD) is used to identify phases present in the as-fabricated hexaaluminate support powders. The XRD equipment is a Philips X'Pert with an X'Celerator detector. A Cu X-ray source operated at 45 kV and 40 mA is used with a Ni filter. The spectra were scanned between $2\theta = 10^\circ$ and $2\theta = 150^\circ$. For each sample tested the step size is 0.010$\theta$ and the time per step is 0.50s.

2.2.2 BET Surface Area

Surface area for various catalyst supports is determined through the use of a Micromeritics Flowisorb II 2300 BET surface-area analyzer. Supports tested are in powder form for BET surface area measurements. The method used is single-point N$_2$ adsorption.

Sample sizes for the BET surface-area measurement ranged from 0.05g to 2.0g. The sample sizes are chosen in accordance with expected surface areas. Values for the total surface area of similarly produced hexaaluminates have been previously published in the literature [4]. Prior to BET surface-area measurements, the sample is degassed at a temperature of 300 °C for 1h. During the degas process the instrument is calibrated to 1.0 cc of N$_2$ gas. A surface area value ($S$) for 1.0 cc of N$_2$ gas is calculated according to Equation 2.1

$$S = \frac{(v)(273.2K)(P_{atm})(N_A)(A_{N_2})}{(T_{room})(760\text{torr})(22.414E + 03 \text{cc/mole})} \left[1 - \frac{(%N_2)(P_{atm})}{(P_{atm} + 15)}\right] \quad (2.1)$$

In Equation 2.1 $v$ is the volume of N$_2$ injected, $P_{atm}$ is the atmospheric pressure, $N_A$ is Avogadro’s number, $A_{N_2}$ is the area of a single nitrogen molecule, $T_{room}$ is the room temperature and %$N_2$ is the percentage of nitrogen in the gas mixture flowing over the sample.

With the instrument calibrated and the sample degassed, a flow of 30% N$_2$ in He is directed over the catalyst support. The N$_2$-adsorption surface area is obtained
by placing a Dewar flask containing liquid N\(_2\) around the sample tube and measuring the change in N\(_2\) concentration with a thermal conductivity detector. Similarly, the N\(_2\)-desorption surface area is obtained by removing the Dewar flask and recording the surface area. The readings for adsorption and desorption surface areas are typically within 1 m\(^2\) g\(^{-1}\) of each other. The specific surface area is calculated by dividing the surface area reading on the instrument by the sample weight.

### 2.2.3 Scanning Electron Microscopy

A JEOL 7000F microscope operated at 2.0kV with an EDAX EDS system is used to obtain scanning electron micrographs. The secondary electron detector is used to evaluate the morphology in prepared catalyst samples. Backscatter electron detectors and a Philips CM200 transmission electron microscope are used to compare relative metal-particle sizes before and after aging. The catalyst samples are also in powder form for these characterization experiments.

### 2.2.4 CO Pulse Chemisorption

Active metal surface area for the catalysts fabricated in this work is quantified using the CO pulse-chemisorption method. The instrument for performing the CO-pulse chemisorption tests is a modified Micromeritics Flowsorb 2300. The unit is equipped with an eight port sampling valve for the pulsing of the carbon monoxide as well as a thermal conductivity detector for measuring the CO adsorption. A process flow diagram for the CO pulse chemisorption unit is illustrated in Figure 2.4.

The He is provided as both the carrier gas and as a reference for the thermal conductivity detector. The UHP He undergoes several stages of purification, as any amount of oxygen in the carrier gas stream will alter the chemisorption results. The purification includes Agilent oxygen scrubbers, a tube of copper turnings heated to 400 °C, and another catalyst which must be reduced (Mn/SiO\(_2\)). All of these steps plus a liquid-nitrogen cold trap minimize the amount of oxygen present in the carrier gas stream.
The sample, including hexaaluminate support and rhodium, is reduced in a flow of H$_2$ at 400 °C prior to CO pulse chemisorption experiments. During the CO pulse chemisorption experiments, the reduced catalyst sample is exposed to 10 μL pulses of CO at two minute intervals until the active surface is completely covered in chemisorbed CO molecules. An adsorption stoichiometry of 1:1 between CO molecules and Rh surface atoms is assumed [19]. Two characteristics of the synthesized catalysts can be determined by CO pulse chemisorption: the amount of active metal exposed as well as what percent of the metal put on to the support is exposed and available for reaction (dispersion). Further details of the chemisorption measurements and calculations are located in Appendix C.

2.2.5 Aging Process

To evaluate the thermal stability of prepared catalysts, an accelerated-aging process is used. The catalyst-aging process consists of exposing the catalyst to a mixture of 50% Ar, 19% H$_2$ and 31% H$_2$O for 24h at 900 °C. This process has been shown to effectively 'age' the catalysts to the point where the surface areas and dispersions are similar to catalysts that had been subjected to auto-thermal reforming of gasoline for over 100h [4]. The present work creates these conditions within a quartz-tube reactor equipped with mass flow controllers that bubble gases
through a heated water reservoir for steam addition.

2.3 Stagnation-Flow Reactor

This work uses a stagnation-flow reactor (SFR) to test catalyst activity. The stagnation-flow reactor is a useful tool in understanding the underlying gas-phase and surface chemical processes present in heterogeneous catalysis. The stagnation-flow enables measurement and modeling of the gas-phase boundary layer adjacent to the catalytic surface [29, 44]. Such measurements are not available in practical reactor configurations (e.g. channel monoliths or porous foams). This flow configuration has been used to study the underlying chemical processes present in steam reforming [29], dry reforming, and partial oxidation of methane [25, 38].

Figure 2.5 shows an illustration of the stagnation flow reactor used in this work. Details regarding aspects of reactor design can be found in theses by Bridges [54] and Kibler [55]. In the SFR, mass flow controllers meter the reactive gases into the stainless steel reactor where they impinge upon a heated, downward facing, catalytically active stagnation surface. Section 2.1.3 describes in detail the steps taken in the fabrication of the catalyst coated surface. Catalyst surface heating is achieved using a SiC resistive heater (Morgan Advanced Ceramics) that is located directly behind the pre-cast ceramic substrate with catalyst coating (Figure 2.5). R-type thermocouples from Omega Engineering are embedded in the castable-ceramic stagnation-surface to measure the catalyst surface temperature. A feedback-control strategy with Labview is used to maintain a specific catalyst surface temperature (typically between 700 °C and 850 °C during catalytic activity testing). Heated silicon-based oil (approximately 60 °C) circulates through the reactor housing to control wall temperature.

As gases encounter the catalytically active stagnation surface a chemical boundary layer is formed. Reactants such as methane, carbon dioxide, water or oxygen are consumed at the surface. Products of the reforming reactions (H₂ and CO) are produced at the surface. The changes within the chemical boundary layer are sampled by a quartz microprobe that accurately traverses the chemical boundary-layer through the use of a precision stepping motor. Once gases impinge upon the flat
FIG. 2.5: Illustration of the stagnation-flow reactor, with the inset highlighting details around the catalytic surface.
stagnation surface they are directed through an annular space (Fig. 2.5) towards the exhaust port of the reactor. Gases are exhausted from the stagnation-flow reactor through the annular space by a dry scroll vacuum pump. The pump maintains reactor pressure at 300 torr. Slightly sub-atmospheric reactor pressures lend to increased chemical boundary-layer thicknesses that are well resolved through gas sampling. This section describes experimental details regarding assembly, modifications made to the pre-existing reactor, measurement of gas-phase composition, experimental error, and hysteresis effects.

2.3.1 Assembly of the Pedestal

A stainless steel pedestal (labeled 'Support Pedestal' in Figure 2.5) lowers the stagnation surface to the gas inlet. The pedestal also routes thermocouple wires and electrical connections from the catalyst surface to the outside of the reactor chamber through an MKS vacuum CF flange.

An exploded, cut-away view of the stagnation-surface assembly that includes the catalyst coated surface, twist-lock cap, and SiC resistive heater is shown in Figure 2.6. The current pedestal assembly consists of four main components that are assembled prior to stagnation-flow reactor experiments.

1. Stainless steel heater pedestal that lowers the stagnation surface to the gas inlet and routes thermocouple wires and electrical connections through a vacuum CF flange.

2. Ceramic heater housing produced by Ceramco Inc. (Figure 2.7). This item is referred to as the "twist-lock cap"

3. SiC heater (Figure 2.8).

4. Catalyst-coated stagnation surface (Details in Section 2.1.3).

Assembly of the pedestal begins with adhering the catalyst-coated stagnation surface to a twist lock cap (labeled 'Ceramic housing' in Figure 2.5 using Cotronics
989 ceramic adhesive. The twist-lock cap is fabricated by Ceramco Inc. and also houses the SiC resistive heater that is used to heat the catalyst. The cap-heater-surface assembly locks into the stainless steel pedestal through machined keyways. The embedded thermocouples as well as power leads for the heating apparatus are fed through the SiC heater and twist-lock cap, up the pedestal and through a CF flange out of the reactor.

![Diagram of reactor](image.png)

**Fig. 2.6:** Schematic of a) the Stagnation-Flow Reactor; and b) the newly designed heater assembly.

### 2.3.2 Heating the Catalyst Surface

Heating of the catalyst surface was previously accomplished through resistive heating of Ni-Cr wire. Initial experiments under steam-reforming conditions (Chapter 4) utilized this heating system. Complete details of the heating system can be found in works by Bridges and Kibler [54, 55]. In this heating configuration the catalyst is coated onto a castable ceramic (Cotronics Rescor 780) structure that has embedded 24-gauge Ni-Cr resistance heaters. The integrated catalyst-heater structure is bonded into a removable ceramic housing that is similar in design to the presently used twist-lock cap. Two thermocouples embedded in the surface measure
Fig. 27: Dimensions of the twist-lock cap in the stagnation-flow reactor. Dimensions are in inches.
the catalyst surface temperature. A heater controller is used to maintain a specific catalyst surface temperature.

The embedded Ni-Cr heating configuration has several drawbacks. The configuration utilizes K-type OMEGA thermocouples that are not suitable for high-temperature operation. Additionally, the fabrication of stagnation-surface substrates with embedded Ni-Cr wire was time consuming and labor intensive. The fabrication method was also prone to errors that made consistent heating of the surface difficult. The long lead time for surface fabrication also hampered rapid testing of different types of catalysts.

In this effort, the stagnation-flow reactor heating configuration designed by Kibler and Bridges [54, 55] is modified to promote more consistent, and accurate heating of the stagnation surface and also enable more-rapid testing of different catalysts. The embedded Ni-Cr wires were replaced by a prefabricated SiC heating element from Morgan Advanced Ceramics. A cartridge heater is not embedded in the stagnation surface but radiatively heats the backside of the stagnation surface. This approach may require more power to achieve similar heating profiles, but will enable rapid changeover of catalysts on the stagnation surface.

A drawing of the heater provided by Morgan Advanced Ceramics is shown in Figure 2.8. The heater is 0.25" thick and provides a resistance of approximately 1Ω. It is fabricated via chemical vapor deposition and machined by Morgan Advanced Ceramics to CSM supplied specifications. The removable ceramic housing (twist-lock cap) is enlarged to accommodate the SiC heater.

Electrical current is supplied to the SiC heater through two molybdenum threaded rods affixed to the SiC heater by molybdenum nuts and washers (size M2.5). The power supply for the SiC heater is a Control Concepts Inc. Silicon Control Rectifier (SCR) that modulates AC power from an outlet (120VAC 60 Hz). High-temperature R-type thermocouples are embedded into the catalyst-coated stagnation surface to monitor the catalyst surface temperature and also provide feedback to the SCR. The radial distance between embedded R-type thermocouples in this configuration is approximately 1.8 cm. A heater controller is used to maintain the temperature of the
stagnation surface between 700 °C and 850 °C.

Fig. 2.8: Drawing of SiC resistive heater fabricated by Morgan Advanced Ceramics. Dimensions are in inches.

Two-dimensional heat-transfer simulations in COMSOL were carried out to determine the required power for the SiC heater to achieve desired surface temperatures. A characteristic results of such modeling efforts is shown in Figure 2.9. In the COMSOL models used here only the radiative heat transfer between the SiC heater and interior of the ceramic housing was considered. The SiC heater power capacity is specified in accordance with the results of these simulations.

Despite attempts to obtain a uniform surface temperature through heat-transfer modeling in COMSOL, radially distributed thermocouple readings in the stagnation surface indicate a non-uniform surface temperature during experiments. The two-dimensional heat-transfer simulation performed in COMSOL did not account for the convective heat transfer present in the stagnation-flow configuration. Simultaneous experimental measurements of two surface temperatures indicate that the convective heat transfer contribution to the catalyst surface temperature is significant. The difference in temperature between the center of the stagnation surface and the outside
FIG. 2.9: Two dimensional heat transfer modeling of the stagnation-flow reactor. Modeled using COMSOL software. Temperature shown in units of K.

edge varied by as much as 70 °C. For such a case the temperature measurement of the center thermocouple is 630 °C.

Several solutions were proposed to correct this variation, including a thicker substrate, embedding a silver mesh into the cast ceramic substrate, and a combination of the two. The results of these efforts are illustrated in Figure 2.10. As shown, the efforts have corrected the surface temperature uniformity by a small amount. The silver mesh reduces the ΔT to 65 °C and the thicker substrate reduces the ΔT to 52.5 °C for identical conditions. However, additional power to the SiC heater was required for marginal gains in surface temperature uniformity. Initial experiments with the SiC heater showed that excessive power input for extended periods of time can irreversibly damage the electrical connections to the SiC heater. For the methane dry-reforming cases presented in the next chapter, one thermocouple located at the center of the stagnation surface was used to measure and control the catalyst surface temperature. The catalyst is coated onto a ceramic substrate that is 0.25” thick.
Fig. 2.10: Temperature uniformity of the stagnation surface at 630 °C.

2.3.3 Introduction of Gas Reactants

A process flow diagram for the stagnation-flow experiment is illustrated in Figure 2.11. The dry reactants in the stagnation-flow experiments (CH₄, CO₂, Ar, O₂) flow from gas cylinders (General Air) to ALICAT mass flow controllers. The reactant gases are introduced into the stagnation-flow reactor through a porous frit (3.18 cm in diameter), that assures the gases enter the reactor with uniform velocity and temperature. Flow rates are specified by Labview software communicating with the ALICAT mass flow controllers. In experiments where water vapor is a reactant, the water vapor is added to the gas stream with a precision milliGAT micropump that dispenses water in the range of 0-100 μL per minute. The feed gases pass through a heated damping reservoir that is designed to damp out any fluctuations associated with the water pump. Following water-vapor introduction, heating tape is used to maintain all lines at approximately 135 °C. The heated lines assure that all the H₂O remains in the vapor phase as it enters the reactor. The upward-flowing gases impinge onto the heated, catalytically active, stagnation surface. The catalytic surface is 5
cm in diameter, and positioned 1.6 cm above the porous frit. Figure 2.5 has an inset that provides a detailed view of the catalytic surface and porous frit.

2.3.4 Evacuation of the Reactor Chamber

Once the reactants encounter the heated stagnation surface they are evacuated from the chamber through an annular space by a dry scroll pump. The dry scroll pump used in this work is a BOC Edwards EX10 model. The scroll pump introduces ballast to prevent any residual water condensation in the exhaust gas stream from damaging the pump. The scroll pump works with a controlled butterfly valve in a feedback loop that maintains the reactor pressure at 40 kPa (300 torr). The reactor is designed to operate at slightly sub-atmospheric pressures. Reducing pressure tends to increase boundary-layer thickness, which facilitates resolving boundary-layer profiles. Residual water vapor is condensed downstream of the scroll pump before the remaining gases flow to lab exhaust.

2.3.5 Modification to Accommodate Steam Addition

Some experiments in this work incorporate high concentrations of water vapor. During initial experiments under steam reforming conditions high amounts of condensation were observed in the stagnation flow reactor through the viewport located on the front of the reactor. Modifications were made to the existing stagnation-flow experiment initially designed by Kibler [55] to accommodate the water addition. Hot, silicon-based oil (Thermo-Electron Sil 180, approximately 130°C) circulates through the reactor housing to control wall temperature. A NESLAB EX-20 heating bath/pump is used to circulate silicon oil through the walls of the stagnation flow reactor.

2.3.6 Boundary-Layer Measurements

A quartz microprobe with approximately 50 micron tip opening is used to sample gases within the chemical boundary layer during stagnation-flow experiments. The quartz microprobe has the ability to move vertically in order to capture gas-phase
Fig. 2.11: Process flow diagram of the experimental setup.
compositions within the chemical boundary layer. However, care must be taken to position the probe in the proper radial position. Initial experiments with the probe positioned along the centerline of the stagnation surface yielded inaccurate boundary layer thicknesses presumably due to the absence of a radial flow entering the quartz microprobe. The position of the microprobe in relation to the stagnation surface is illustrated in Figure 2.12. The experimental measurements presented in this work are all taken with the microprobe positioned 10 mm off the center axis of the stagnation surface.

![Illustration of the quartz microprobe position in relation to the stagnation surface.](image)

**Fig. 2.12:** Illustration of the quartz microprobe position in relation to the stagnation surface.

The quartz microprobe is first positioned at a distance approximately 0.1 mm from the stagnation surface. Gases are sampled for four minutes at this measurement position. Previous experiments show that four minutes is a sufficient amount of time for the flow field to achieve steady-state operation. Sampled gases are sent to a quadrupole mass spectrometer for analysis. At the end of the four-minute sampling period a precision stepping motor is used to move the quartz microprobe 0.635 mm away from the last measurement point for further gas-phase-composition analysis. A boundary-layer profile typically consists of eight measurement points, spanning approximately 5 mm below the stagnation surface.
2.3.7 Gas Analysis

For gas analysis we use a quadrupole residual gas analyzer from Stanford Research Systems (SRS RGA 200). The residual gas analyzer probe head is enclosed in a high-vacuum chamber that is evacuated by a Pfeiffer turbo molecular pump in series with a rotary vane pump. An ion gauge made by Kurt J. Lesker Vacuum systems monitors the pressure within the mass spectrometer vacuum chamber during experiments. A process flow diagram of the mass spectrometer vacuum system and sample transfer line is shown in Figure 2.13.

![Diagram of mass spectrometer vacuum system](image)

Fig. 2.13: Process flow diagram of the quadrupole mass spectrometer vacuum system. Diagram from Bridges [54]

Sample gases from the quartz microprobe travel through a transfer line that is evacuated by a rotary vane pump. For experiments that have a high water content, the transfer line incorporates drierite dessicant to remove water from the microprobe sample line. A small amount of gas from this sample transfer line is leaked into the high vacuum chamber using a Vacuum Generators LVM-series leak valve. During operation the mass spectrometer vacuum pressure ranges between 3.0E-06 torr and
6E-06 torr. Through the course of a single boundary layer measurement the MS vacuum chamber pressure starts at 3.0E-06 torr with the probe at a distance of 0.1mm from the surface and increases to approximately 6E-06 torr when the probe is at a distance of 5 mm from the stagnation surface. The small variation in MS vacuum chamber pressure is accounted for by normalizing the spectrometer signals for the species of interest by the signal for the inert gas, Ar.

The quadrupole mass spectrometer (consisting of the SRS RGA 200 and vacuum system) is calibrated using independently mixed gases with known concentrations of CH₄, CO₂, CO, H₂ and Ar. Results of the calibration are shown in Appendix B. Mass spectrometer signals for the gases of interest (H₂ at 2 amu, CH₄ at 15 amu, CO at 28 amu, O₂ at 32 amu, Ar at 40 amu, and CO₂ at 44 amu) are measured relative to Ar, a chemically inert component of the reactant streams. This serves to eliminate signal changes by instrument instabilities. The only cross sensitivity considered is the CO₂ contribution to the CO signal at 28 amu. Water vapor (H₂O) is not measured in these experiments. For steam-reforming experiments, the water content is back calculated based on the oxygen-atom balance using Ar as an internal standard.

A typical boundary layer measurement is shown in Figure 2.14. In this figure the catalyst surface is at the left edge of the graph with reactant gases flowing from right to left. The experimental conditions used to produce this example result are stoichiometric partial oxidation of methane with a small amount of carbon dioxide addition at a catalyst surface temperature of 800 °C. The inlet velocity was 90 cm s⁻¹, CH₄-to-O₂ ratio was 2 and the CH₄-to-CO₂ ratio was 8. The catalyst is a 10 wt% Rh on Sr-hexaaluminate. The example results here show eight measurement points within the chemical boundary layer. From Figure 2.14 it is evident that the entire chemical boundary layer is captured. That is, the measurements asymptote to the values that would be expected based on the flow rates specified by the mass flow controllers. Subsequent chemical boundary layer measurements in this work use eight measurement points for a given set of experimental conditions.
Fig. 2.14: Sample results for chemical boundary layer showing that the chemical boundary layer for these conditions does not extend beyond 0.5 cm. Eight measurement points are enough to capture the entire chemical boundary layer.

2.3.8 Repeatability in the Experiment and Error Estimates

In this section, the experimental repeatability of experimental boundary layer profile measurements in stagnation flow is investigated. Figure 2.15 shows several reactant species profiles within the chemical boundary layer. Figure 2.16 shows carbon monoxide profiles within the chemical boundary layer. All boundary layer profiles were measured under identical conditions and over the same radial position of the catalyst surface. The conditions are identical to those used in generating the results shown in Figure 2.14. The catalyst is a 10 wt% Rh on Sr-hexaaluminate and the catalyst surface temperature is 800°C. The inlet velocity was 90 cm s\(^{-1}\). A series of four measurements were taken over the period of two days with identical experimental conditions.

Carbon balance for all measurements is maintained within 7%. Figure 2.17 shows the average measurement value for the three separate chemical boundary layer measurements shown in Figures 2.15 and 2.16. Error bars in the horizontal direction
**Fig. 2.15:** Repeatability of chemical boundary layer measurements at a surface temperature of 800°C (Reactants).

**Fig. 2.16:** Repeatability of chemical boundary layer measurements at a surface temperature of 800°C (Products).
Table 2.1: Average values and error estimates for repeated experiments

<table>
<thead>
<tr>
<th>Species</th>
<th>Avg. value at surface</th>
<th>St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>0.052</td>
<td>0.004</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>CO</td>
<td>0.054</td>
<td>0.005</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.018</td>
<td>0.002</td>
</tr>
</tbody>
</table>

represent microprobe positioning and sample volume error [54]. The size of the sample volume is also larger than the distance between the surface and the microprobe at the first measurement point. This tends to bias the first measurement point away from the surface, resulting in non-linear profiles near the stagnation surface.

Error bars in the vertical direction represent one standard deviation in the data during the repeated experiments. The standard deviation in the vertical direction increases as the quartz microprobe moves closer to the surface. Specific values for the average and standard deviations at the surface are shown in Table 2.1. The mole fraction profiles for the reactant species show reasonable precision far from the surface.

![Graph showing mole fraction of CH$_4$, CO, and O$_2$ vs. distance from surface]

**Fig. 2.17:** Error in chemical boundary layer measurements at a surface temperature of 800 °C.
2.3.9 Hysteresis

This section investigates the effects of hysteresis on the boundary layer measurements. Figure 2.18 shows the results of two chemical boundary layer measurements measured in opposite directions. The experimental conditions here are partial oxidation of methane with carbon dioxide addition at a catalyst surface temperature of 800 °C. The inlet velocity was 90 cm s\(^{-1}\). The first boundary layer was measured in the method described previously. That is, the first gas phase composition in the boundary layer measurement was taken with the microprobe at the catalyst surface and subsequent measurements were taken at increasing distances from the catalyst surface.

The second boundary layer in Fig. 2.18 is measured with the quartz microprobe initially positioned at a distance of 5mm from the stagnation surface. Subsequent data points in the second chemical boundary layer are taken at decreasing distances from the catalyst surface. In Figure 2.18 the second boundary layer is indicated by the cross symbols. The two chemical boundary layer measurements were taken one after another (approx 30 minutes measurement time) under identical experimental conditions. The results show that there is no significant effect of hysteresis on the chemical boundary layer measurement.

2.3.10 Reforming on Non-Catalytic Substrates

This section investigates the possibility of reforming on a bare stagnation surface with no catalyst coating. Gas-phase compositions within the chemical boundary layer for this section were measured under dry-reforming conditions. In the first boundary layer (Figure 2.19) the inlet conditions are a CO\(_2\)-to-methane ratio of two with oxygen addition and a surface temperature of 800 °C. In the presence of a substrate with a catalyst coating these conditions have shown measurable catalytic activity. In the second chemical boundary layer (Figure 2.20) the inlet conditions are a CO\(_2\)-to-methane ratio of 1.15 with 1% oxygen addition at a catalyst surface temperature of 900 °C. Boundary-layer results in the following two figures show minimal change in composition from inlet to surface of the substrate. This result indicates that the
pre-cast ceramic substrates do not contribute significantly to the catalytic activity that is observed within the stagnation-flow boundary-layer during experimentation.

2.4 Computational Modeling

To validate and develop previously existing chemical reaction mechanisms, numerical simulations that incorporate elementary reaction mechanisms are conducted in concert with the stagnation-flow experiments. With good experiment to model agreement, the model outputs can be probed for a deeper understanding of the fundamental processes taking place on the catalyst surface during methane reforming.

The modeling results in this work are computed using the SPIN application of the CHEMKIN (CHEMKIN-III Version 5.23) software package [48, 49, 44]. This software is widely used to simulate chemically reacting stagnation flows [56, 57, 46, 47, 25]. Stagnation flows are commonly used in the semiconductor processing industry to produce uniform material growth across large wafers. Such flow configurations are also
Fig. 2.19: Dry reforming on a stagnation substrate with no catalyst coating. Surface temperature 800 °C.

Fig. 2.20: Dry reforming on a stagnation substrate with no catalyst coating. Surface temperature 900 °C.
used in combustion research to analyze flames and develop combustion mechanisms. The chemical information that can be derived from the experiments studying heterogeneous catalysis can be applied via modeling to practical reactor configurations such as channel monoliths [45], ceramic-foam supported catalysts [26], or packed beds.

2.4.1 Governing Equations

The model is formulated as an axisymmetric stagnation-flow boundary-layer problem. A simplified illustration of the stagnation-flow configuration is shown in Figure 2.21. The stagnation-flow similarity creates a one-dimensional flow-field where temperature and species profiles within the boundary layer do not vary with radial position. The axial profiles measured and simulated within the chemical boundary layer can then be used to infer reaction rates. The method of inferring reaction rates from stagnation-flow data has been previously published [25]. In essence, the diffusive flux of gas phase species is balanced by the net molar production rate via surface reactions.

The SPIN application of the CHEMKIN software package solves the boundary-layer problem problem efficiently, accounting for fluid flow, molecular transport, and complex multi-step heterogeneous catalytic chemistry. The one-dimensional nature also enables rapid numerical modeling and evaluation of existing reaction mechanisms [38].

The governing equations for the stagnation-flow boundary-layer problem are

Conservation of Mass:

\[
\frac{1}{\rho} \frac{\partial \rho}{\partial t} = - \frac{\partial u}{\partial z} - 2V = \frac{u \partial \rho}{\rho \partial z} = 0, \tag{2.2}
\]

Conservation of radial momentum:

\[
\rho \frac{\partial V}{\partial t} = \frac{\partial}{\partial z} \left( \frac{\mu}{\partial z} \right) - \rho u \frac{\partial V}{\partial z} - \rho (V^2) - \frac{1}{r} \frac{dp_m}{dr} = 0 \tag{2.3}
\]
FIG. 2.21: Stagnation-flow configuration.
Conservation of energy:

\[
\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left( \lambda \frac{\partial T}{\partial z} \right) - \rho c_p u \frac{\partial T}{\partial z} - \sum_{k=1}^{K_g} \left( c_{pk} \rho Y_k V_k \frac{\partial T}{\partial z} + \dot{\omega}_k h_k \right) = 0
\]  
(2.4)

Conservation of species:

\[
\rho \frac{\partial Y_k}{\partial t} = \frac{\partial \rho Y_k V_k}{\partial z} - \rho u \frac{\partial Y_k}{\partial z} + M_k \dot{\omega}_k = 0 \quad (k = 1, \ldots, K_g),
\]  
(2.5)

Perfect gas law:

\[
P = \frac{\rho R T}{M},
\]  
(2.6)

Conservation of surface species:

\[
\frac{dZ_k}{dt} = \frac{\dot{s}_k}{\Lambda_r} = 0 \quad (k = 1, \ldots, K_g)
\]  
(2.7)

SPIN solves the steady-state boundary-layer problem; thus all time dependent partial derivatives in the above equations go to zero. In these equations the independent variable is the axial coordinate \(z\). The dependent variables are the axial velocity \(u\), the scaled radial velocity \(V = v/r\) (\(v\) is the radial velocity and \(r\) is the radial coordinate), the temperature \(T\), the gas-phase mass fractions \(Y_k\), and the surface-species site fraction \(Z_k\). The term \(\Lambda_r\) describing the pressure gradient is taken to be a constant and is computed as an eigenvalue of the problem.

\[
\Lambda_r = \frac{1}{r} \frac{dp}{dr}
\]  
(2.8)
A perfect-gas equation of state relates the pressure $p$, density $\rho$, temperature, and mass fractions, with $R$ and $\overline{M}$ being the gas constant and average molecular weight, respectively. Other variables include the mixture specific heat $c_p = \sum_{k=1}^{K} Y_k c_{pk}$, where $c_{pk}$ is the specific heat for species $k$, dynamic viscosity $\mu$, thermal conductivity $\lambda$, surface site density $\Lambda_n$ where $n$ is the site type, and molecular weight of species $k$, $M_k$.

The variable $\dot{\omega}_k$ is the molar production rate of species $k$ via gas-phase kinetics and $h_k$ is the enthalpy of species $k$. A gas-phase reaction-mechanism is a required input for SPIN. The gas-phase reaction-mechanism used here is a modified version of GRI-Mech3.0 that excludes all nitrogen-containing species. Simulations that incorporate gas-phase chemistry (GRI-Mech 3.0 [58]) show that the effects of gas-phase chemistry are negligible for methane reforming at temperatures below 900°C, thus they are excluded from the simulations presented in this work. As a limiting case, simulations were also performed with the water-gas-shift reaction at equilibrium. Similarly, there is a negligible effect on the boundary-layer species profiles presented here.

The species-diffusion velocities are evaluated at the multicomponent level by Equation 2.9

$$V_k = \frac{1}{X_k \overline{M}} \sum_{j \neq k}^{K} M_j D_{kj} \frac{dX_j}{dz} - \frac{D_k^T}{\rho Y_k} \frac{1}{T} \frac{dT}{dz}, \quad (2.9)$$

where $X_j$ are mole fractions, $D_{kj}$ are the ordinary multicomponent diffusion coefficients, and $D_k^T$ are thermal diffusion coefficients. SPIN accounts for both ordinary diffusion and thermal diffusion. Thermal diffusion (Soret effect) is important to consider in such applications as chemical vapor deposition and in the present work due to the presence of large temperature gradients. With large temperature gradients high molecular weight species in a low molecular weight carrier diffuse rapidly towards the low temperature region. While such effects are included in these simulations, their impact is not expected to be significant. All transport properties in the current effort are calculated using the TRANSPORT application of the CHEMKIN software package.

Boundary conditions at the inlet (i.e., the porous frit shown in Fig. 2.5) are

$$u = U_{in}, \quad V = 0, \quad T = T_{in}, \quad Y_k = Y_{k, in}. \quad (2.10)$$
Boundary conditions at the catalytic stagnation surface are

\[ u = 0, \quad V = 0, \quad T = T_s, \quad \rho Y_k V_k = F_{\text{cat,geo}} \dot{s}_k W_k. \]  \hspace{1cm} (2.11)

The last condition above means that the diffusive flux of gas-phase species \( k \) at the surface is balanced by the net molar production rate of that species via catalytic kinetics (Table 4.2). Furthermore, the net production rate of surface-adsorbed species must vanish (i.e., \( \dot{s}_k = 0, \quad (k = 1, K_s) \), where \( K_s \) is the number of surface species).

Because of stagnation-flow similarity the problem is mathematically an ordinary-differential-equation boundary-value problem. The \textsc{Twopnt} software of the \textsc{Chemkin} package implements a hybrid Newton/time-step algorithm to solve the problem [59]. Following finite-volume discretization, \textsc{Twopnt} solves the problem initially on a coarse grid. Additional grid points are added in regions where there are large gradients and an interpolation of the initial solution is used as the initial guess for the solution on the finer mesh. This procedure of finding a solution, adding grid points and finding another solution on a finer mesh is repeated to a degree specified by the user.

The modeling results depend upon knowing the effective catalyst area. Because the catalyst is dispersed as small particles in the porous support, the active catalyst area is typically much greater than geometric surface area. The area ratio may defined as

\[ F_{\text{cat,geo}} = \frac{A_{\text{catalyst}}}{A_{\text{geometric}}}. \]  \hspace{1cm} (2.12)

Because the effective area has not been measured directly on the substrate in the stagnation-flow reactor, the effective area is taken as a parameter that is adjusted once to achieve agreement with the baseline measurements.

Modeling the experimental results in \textsc{Spin} also requires a user-defined surface reaction mechanism and gas-phase reaction mechanism. Details of the surface reaction mechanism used in the current work are presented in Section 4.1.2.
2.5 Summary of Experimental Methodology

In this work thermally stable hexaaluminate catalyst supports are fabricated using two different methods. A number of diagnostic techniques are used to characterize the catalysts and evaluate the thermal stability under simulated reforming conditions. The diagnostic techniques used here are BET surface area, x-ray diffraction, scanning and transmission electron microscopy, and CO pulse chemisorption.

A stagnation-flow reactor is used to test catalyst activity. The stagnation-flow reactor developed in a previous work [54, 55] is modified to accommodate steam addition and facilitate rapid changeover of different catalyst surfaces. Species profiles within the chemical boundary layer adjacent to the catalyst surface are measured using microprobe mass spectrometry. The experimental results are used in concert with modeled results in SPIN to further develop elementary reaction mechanisms. Once reasonable model-to-experimental results are achieved the model output files are probed for a deeper understanding of physical processes underway on the catalyst surface.
Chapter 3

PHYSICAL CHARACTERIZATION OF HEXAALUMINATE CATALYSTS

Hexaaluminates are a thermally stable support for reforming catalysts operating at high temperatures. This chapter presents the results of the diagnostic techniques used to characterize hexaaluminate-supported reforming catalysts. In the first section of this chapter, surface areas of the hexaaluminates and control supports are measured using single-point N₂ adsorption. Measurements before and after an accelerated-aging process show the thermal stability of the hexaaluminate catalyst supports fabricated in this work. In the second section, powder X-ray diffraction is used to confirm the presence of hexaaluminate crystal structure in samples made by both TDA Research and CSM using different fabrication methods. In the third section, scanning electron microscopy (SEM) is used to characterize the morphology of the hexaaluminates that were fabricated using different techniques. The hexaaluminate-support samples as well as commercial supports are examined before and after the accelerated-aging process. SEM and transmission electron microscopy (TEM) are also used to characterize Rh metal-particle sizes on the loaded supports. In the final section, the results of metal-dispersion measurements using CO pulse chemisorption are presented. The effects of processing technique, loading, support and aging condition on the available metal surface area are investigated.

3.1 Surface Area Analysis by BET Adsorption

One of the major components of any catalyst system is the total available surface area of the support on which the metal can be deposited. High-surface-area supports are often correlated with highly active catalysts because the metal can be
Table 3.1: BET surface-area measurements.

<table>
<thead>
<tr>
<th>Material</th>
<th>Source</th>
<th>Area (m²/g)</th>
<th>% Decrease</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaAl₂O₁₉</td>
<td>CSM</td>
<td>7.0</td>
<td>5.7</td>
</tr>
<tr>
<td>CaAl₂O₁₉, aged</td>
<td></td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>SrAl₂O₁₉</td>
<td>CSM</td>
<td>14.3</td>
<td>9.8</td>
</tr>
<tr>
<td>SrAl₂O₁₉, aged</td>
<td></td>
<td>12.9</td>
<td></td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>Sigma Aldrich</td>
<td>79.2</td>
<td>47.6</td>
</tr>
<tr>
<td>γ-Al₂O₃, aged</td>
<td></td>
<td>41.5</td>
<td></td>
</tr>
<tr>
<td>8 mol% Y₂O₃-ZrO₂</td>
<td>Tosoh Co.</td>
<td>12.8</td>
<td>7.8</td>
</tr>
<tr>
<td>8 mol% Y₂O₃-ZrO₂, aged</td>
<td></td>
<td>11.8</td>
<td></td>
</tr>
<tr>
<td>Gd₀.₁Ce₀.₅O₂</td>
<td>Praxair</td>
<td>9.3</td>
<td>35.4</td>
</tr>
<tr>
<td>Gd₀.₁Ce₀.₅O₂, aged</td>
<td></td>
<td>6.0</td>
<td></td>
</tr>
</tbody>
</table>

well dispersed and offers many sites for reaction. The ability of the catalyst support to maintain this surface area under harsh operating conditions is one of the indicators of a quality catalyst. This section investigates several catalyst supports, including hexaaluminates fabricated as described in the previous section, and their ability to retain surface area under harsh operating conditions. The surface areas are measured by the BET single-point N₂-adsorption method discussed in the previous chapter. BET surface areas are measured before and after an accelerated-aging process meant to mimic time on stream. The aging process used here is described in Section 2.2.5 and was originally presented by Ferrandon and Krause [4]. The catalyst-aging process consists of exposing the catalyst to a mixture of 50% Ar, 19% H₂ and 31% H₂O for 24h at 900 °C.

Table 3.1 compares the BET surface areas before and after aging for hexaaluminate supports (calcium and strontium substitutions) and other commercially acquired Rh catalyst supports. The commercially acquired supports examined in this work include γ-Al₂O₃, yttria-stabilized ZrO₂, and Gd-doped ceria. As expected the γ-Al₂O₃ has the highest initial surface area at almost 80 m²/g. However, the γ-Al₂O₃ loses over 50% of this surface area as a result of the accelerated-aging process. Of the remaining supports examined, the percentage of surface area retained decreases in order of CaAl₂O₁₉ > 8 mol% YSZ > SrAl₂O₁₉ > Gd₀.₁Ce₀.₅O₂. The Gd₀.₁Ce₀.₅O₂ appears to have lost the most surface area at around 35%, while the other three supports lost only 5-10% by the aging process. The Sr-based hexaaluminate has the greatest initial
and final surface areas of these three. Sr-based hexaaluminates are used in this work as the support for catalytic activity tests.

3.2 Phase Analysis by X-Ray Diffraction

X-ray diffraction (XRD) analysis provides insight into the phases present in the fabricated hexaaluminate samples. The primary objective of x-ray diffraction as used in this work is identification of hexaaluminate phases formed using the fabrication methods described in the previous chapter. XRD is performed on the hexaaluminate powders that are fabricated by the alumoxane process developed by TDA Research Inc. Figure 3.1 shows the XRD pattern for the material that was intended to be Sr-substituted hexaaluminate. The results confirms Sr substitution for the SrAl\textsubscript{12}O\textsubscript{19} sample. The peaks associated with representative hexaaluminates are consistent with those found in the database (ICDD). The XRD results also indicate the presence of the α-Al\textsubscript{2}O\textsubscript{3} phase in the sample. Since these samples were fabricated with an alumoxane gel, any alumoxane gel that did not participate in the hexaaluminate-forming reaction is converted to α-Al\textsubscript{2}O\textsubscript{3} as soon as the calcination step in the process is performed. Calcination of the alumoxane-process-fabricated hexaaluminates occurs at 1300 °C.

Other cation substitutions were attempted via the alumoxane process of fabricating hexaaluminate supports. Initial screening indicated that Rh on a Zr-substituted hexaaluminate showed good conversion activity. However, the Zr-based catalyst support structures were found to be considerably less stable than the Sr-substituted hexaaluminate. Figure 3.2 shows the XRD pattern for the material that was intended to be a Zr-substituted hexaaluminate. While diffraction patterns for the Sr-hexaaluminate sample matched reference patterns for Sr-hexaaluminates (SrAl\textsubscript{12}O\textsubscript{19}), the current pattern for the material intended to be Zr-substituted hexaaluminate shows clear diffraction patterns associated with zirconia (ZrO\textsubscript{2}). Fig. 3.2 shows no evidence for Zr substitution.

Therefore, based upon XRD analysis of samples fabricated by the alumoxane method, it appears that the Sr substitution is achieved and SrAl\textsubscript{12}O\textsubscript{19} support is formed, but that the Zr substitution is not achieved and the resulting formulation is
Fig. 3.1: a) XRD pattern for TDA-produced strontium hexaaluminate. b) XRD pattern for SrAl$_{12}$O$_{19}$ from ICDD database. c) XRD pattern for Al$_2$O$_3$ from ICDD database.
FIG. 3.2: a) XRD pattern for TDA-produced strontium hexaaluminate. b) XRD pattern for $\text{Al}_2\text{O}_3$ from ICDD database. c) XRD pattern for $\text{ZrO}_2$ from ICDD database.
ZrO$_2$/$\alpha$-Al$_2$O$_3$. In both cases (Figs. 3.1 and 3.2), the XRD shows alumina (Al$_2$O$_3$) content, which is formed from residual boehmite that is used in the hexaaluminate synthesis.

Hexaaluminate supports in this work were also fabricated by co-precipitation at CSM. In this method, appropriate nitrates were co-precipitated and then calcined at 1300 °C to produce the hexaaluminate phase. See Section 2.1.2 for details of fabrication.

Figure 3.3 shows powder x-ray diffraction results for the Sr-substituted hexaaluminates fabricated by co-precipitation. The peaks associated with Sr hexaaluminates are consistent with those found in the database thus confirming the large-cation substitution into the lattice structure. As in the samples fabricated by the alumoxane process, the peaks associated with $\alpha$-Al$_2$O$_3$ are also present in the XRD patterns shown in Figures 3.3 and 3.4.

Figure 3.4 shows powder XRD results for the CSM-fabricated calcium hexaaluminates. The peaks associated with Ca hexaaluminates are consistent with those found in the database thus confirming the substitution for the hexaaluminate fabricated using the method of co-precipitation.

3.3 Morphology by Scanning Electron Microscope

Scanning electron microscopy is used to examine the morphology of the freshly synthesized hexaaluminate support powders as well as hexaaluminate support powders after Rh impregnation.

3.3.1 Hexaaluminate-Support Morphology

A secondary electron detector is used in the SEM to examine catalyst-support morphology. As shown in Figure 3.5, the Sr-substituted hexaaluminate fabricated by TDA using the alumoxane technique has the expected plate-like structure that
Fig. 3.3: X-ray diffraction pattern for Sr-substituted hexaaluminate fabricated by coprecipitation.

Fig. 3.4: X-ray diffraction pattern for Ca-substituted hexaaluminate fabricated by coprecipitation.
Fig. 3.5: Typical scanning electron micrograph of a Sr-based hexaaluminate sample fabricated by the alumoxane method.

indicates the presence of the hexaaluminate phase [60]. This morphology, which is caused by the large-cation substitution in the mirror planes of the hexaaluminate (Fig. 1.1), contributes greatly to the stability.

SEM micrographs of hexaaluminate-support powders fabricated by coprecipitation also show the desired plate-like structures indicative of the large-cation substitution. An example (Ca-based hexaaluminate) is shown in Figure 3.6.

3.3.2 Addition of Rh to Hexaaluminate Supports

Rhodium metal is added to the hexaaluminate-support powders via incipient-wetness impregnation (Section 2.1.4). Due to their high atomic number, the Rh-rich
particles, typically 0.1-1.0 μm in size, are readily observed in the SEM by their bright appearance relative to the hexaaluminate (Fig. 3.7). Observing the Rh particles in the SEM necessitates the use of the backscatter detector on the scanning electron microscope. The backscatter detector of the SEM offers greater-atomic-number contrast as opposed to the secondary electron detector which is used to characterize sample morphology. Figure 3.7 shows an SEM micrograph of a Sr-based hexaaluminate impregnated with 10 wt% rhodium.

Transmission electron microscopy (TEM) is used to confirm Rh impregnation. In the TEM the Rh particles appear darker relative to the support due to their high atomic number. A representative TEM micrograph that shows a Rh particle is shown in Figure 3.8a. Comparison of SEM and TEM images reveals Rh particles of consistent size.
Energy dispersive x-ray spectroscopy (EDS) in the TEM is used to confirm the Rh enrichment in the dark particles on the surfaces of the hexaaluminate support plates. Figure 3.8 shows the EDS spectra for one of the darker particles observed in the TEM. In addition to the high Rh peak, peaks are observed for the elements incorporated into the hexaaluminate support (Sr, Al, and O). The Cu peak observed is due to the copper grid used to support the TEM sample.

It is clear from Figure 3.7 that the Rh particles observed in the SEM and TEM are very large in size (0.1-1.0 μm). However, the chemisorption data to be presented in Section 3.4 suggests that smaller particles may also be present but not observable by the SEM or TEM microscopes.
FIG. 3.8: a) Representative TEM micrograph of Rh impregnated catalyst sample and b) Energy dispersive x-ray spectrum (EDS) from the dark, Rh-rich particles on the surface of the plate-like support.
3.3.3 Effect of Aging Process on Support Morphology

Fabricated hexaaluminate supports and commercially acquired supports are characterized via scanning electron microscope before and after the accelerated aging condition to evaluate thermal stability.

Gadolinium doped ceria (GDC) is often used a catalyst support due to its oxygen-storage capabilities [61]. The formulation for GDC catalyst is Gd$_{0.1}$Ce$_{0.9}$O$_2$. Figure 3.9 shows SEM images of a commercially acquired GDC catalyst support from Praxair both before (a) and after (b) exposure to the aging process described in Section 2.2.5. The figure shows that there is little observable change in the morphology of the support after the accelerated-aging process. BET surface-area measurements show a 35% decrease in surface area after the aging process.

Figure 3.10 shows SEM images of a commercially acquired yttria stabilized zirconia (YSZ) support under the scanning electron microscope both before (a) and after (b) the accelerated aging process. The commercial YSZ is acquired from the TOSOH corporation and is 8 mol% Yttria. Similar to the aged-GDC support, the YSZ shows little change in morphology following the aging process. This result is consistent with the BET surface area results that indicate an 7.8% decrease in surface area.

TDA Research (Wheat Ridge, Colorado) also provided several samples of fresh-produced hexaaluminate that had been aged in slightly harsher conditions. Here, the aging process consisted of exposing the catalyst samples to 10% steam in air for 5h at various temperatures ranging from 700 °C to 1000 °C. Figure 3.11 shows the SEM images of catalysts exposed to this aging process. From the figure, it is evident that the aging has not diminished the plate-like structures that appear after fabrication. It appears that even more plate-like structures are present in the sample at the higher aging temperatures. This result and the BET surface-area measurements confirm the high temperature stability of the hexaaluminate samples.
Fig. 3.9: SEM micrograph of gadolinium-doped ceria a) before the aging condition and b) after the aging condition.

Fig. 3.10: SEM micrograph of yttria-stabilized zirconia a) before the aging condition and b) after the aging condition.
Fig. 3.11: Sr-based hexaaluminates fabricated by the alumoxane method with 5 wt% Rh loading examined under the scanning electron microscope at various aging conditions: a) fresh, as produced, b) 10% H₂O in air at 700 °C for 5h, c) 10% H₂O in air at 850 °C for 5h, d) 10% H₂O in air at 1000 °C for 5h.
3.3.4 Effect of Aging on Metal Particle Size

This section investigates the ability of the catalyst supports to stabilize metal particle sizes under accelerated aging conditions. Mark and Maier [19] as well as Wei and Iglesia [18] both concluded that the role of the support in methane reforming over Rh has no direct effect on reaction rate. However, the researchers report that the support has an indirect effect on activity by determining how well the metal is dispersed and stabilized under operating conditions.

Using the backscatter detector on the scanning electron microscope enables characterization of the Rh particle size before and after an accelerated-aging process. Initial experimental results indicated the hexaaluminate-based supports may be better at stabilizing Rh particle size, and thus activity, at harsh operating conditions [29].

To confirm the expected higher stability of the plate-like hexaaluminate catalyst supports, the Sr-substituted hexaaluminate and ZrO₂/α-Al₂O₃ samples (both impregnated with 10% Rh) were aged in a 10% steam-in-air environment at 1300 °C for 5 hours. Such an aggressive environment will significantly degrade traditional catalysts. Figure 3.12 shows SEM and TEM images of the Sr-hexaaluminate supports with 10 wt% Rh impregnation before and after aging. The SEM on Fig. 3.12a shows the Rh particles clearly. The particles range in size from a fraction of a micron to around 1 micron. Figure 3.12b is a TEM image of a sample that has been aged. The Rh particles on the Sr-hexaaluminate supports show relatively little sintering and loss of surface area.

Figure 3.13 shows SEM images of a Rh particle on a ZrO₂/α-Al₂O₃ support, before and after aging. In contrast to the Sr-hexaaluminate support, the Rh particles grow significantly during the aggressive aging process. The coarsening leads to a significantly greater loss of active catalyst area and activity for the ZrO₂/α-Al₂O₃ samples. Metal particle size and stability can be investigated quantitatively using CO pulse chemisorption.
Fig. 3.12: SEM and TEM images of Rh particles on Sr-hexaaluminate a) prior to aging and b) after aging.

3.4 Dispersion and Active-Metal Surface Area by CO Chemisorption

Rhodium dispersion is measured by CO pulse chemisorption. This section investigates the effects of processing method, aging, loading and support on the active available area.

3.4.1 Effect of Processing Method

The Sr-based hexaaluminate catalyst supports fabricated by co-precipitation are loaded with the active phase Rh by two different methods. These methods are referred
Fig. 3.13: SEM images of Rh particles on ZrO$_2$/α-Al$_2$O$_3$ a) prior to aging and b) after aging.

to as post-impregnation and pre-impregnation. Details of the impregnation method are described in Section 2.1.4. The major difference between the two methods is the order in which the active phase Rh is added to the support (before or after deposition of the support onto carrier particles).

Table 3.2 shows the results of CO pulse chemisorption experiments on samples utilizing the two different processing techniques. Also shown in Table 3.2 are the effects of metal loading on the dispersion over a hexaaluminate support. The dispersion is defined as the fraction of metal atoms exposed to the surface.
Table 3.2: Chemisorption measurements: Effect of processing method and loading.

<table>
<thead>
<tr>
<th>Material</th>
<th>CO uptake (µL CO/g\textsubscript{cat})</th>
<th>Dispersion(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 wt% Rh/SrAl\textsubscript{12}O\textsubscript{19}, pre</td>
<td>288 ± 41</td>
<td>10.8 ± 1.50</td>
</tr>
<tr>
<td>5.0 wt% Rh/SrAl\textsubscript{12}O\textsubscript{19}, pre</td>
<td>1046 ± 21</td>
<td>7.8 ± 0.04</td>
</tr>
<tr>
<td>5.0 wt% Rh/SrAl\textsubscript{12}O\textsubscript{19}, post</td>
<td>1168 ± 93</td>
<td>8.5 ± 1.10</td>
</tr>
<tr>
<td>10.0 wt% Rh/SrAl\textsubscript{12}O\textsubscript{19}, pre</td>
<td>1075 ± 98</td>
<td>3.9 ± 0.60</td>
</tr>
<tr>
<td>10.0 wt% Rh/SrAl\textsubscript{12}O\textsubscript{19}, post</td>
<td>1679 ± 97</td>
<td>6.3 ± 0.20</td>
</tr>
</tbody>
</table>

\[ D = \frac{N_S}{N_T} \]  

(3.1)

Where \(N_S\) is the number of surface atoms and \(N_T\) is the total number of atoms of a given kind. The CO pulse chemisorption results show that the dispersion decreases with increased metal loading. This is the result of a larger average particle diameter for the Rh with much of the Rh atoms being trapped inside of these larger particles and not available on the surface for reaction. The decrease in dispersion with increased metal loading is consistent with previous studies [18].

In addition, the CO pulse chemisorption results show that the post impregnation method of adding metal to the catalyst supports yields a higher average metal surface area when compared to similarly loaded samples fabricated by the pre-impregnation processing method. During processing, an aluminum-hydroxide gel is used to deposit the support on to the substrate. When the aluminum-hydroxide gel calcines it becomes \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} (see XRD results in Section 3.2) and may cover some of the previously exposed metal on the samples fabricated by pre-impregnation. Because of this improvement in dispersion, post-impregnation methods are used in the fabrication of catalysts used in the stagnation-flow reactor.

3.4.2 Effects of Aging on Rh Dispersion

Active metal surface areas are measured before and after an accelerated aging process. The aging process used in this section is the same as that used in the section measuring overall BET surface areas.
Table 3.3: Chemisorption measurements: Effect of aging and catalyst support.

<table>
<thead>
<tr>
<th>Material</th>
<th>CO uptake (μL CO/g_{cat})</th>
<th>Dispersion(%)</th>
<th>% Decrease</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0 wt% Rh/SrAl_{12}O_{19}</td>
<td>780 ± 50</td>
<td>13.5 ± 0.85</td>
<td></td>
</tr>
<tr>
<td>2.0 wt% Rh/SrAl_{12}O_{19}, aged</td>
<td>459 ± 6</td>
<td>7.9 ± 0.11</td>
<td>41%</td>
</tr>
<tr>
<td>2.0 wt% Rh/CaAl_{12}O_{19}</td>
<td>440 ± 66</td>
<td>7.6 ± 1.15</td>
<td></td>
</tr>
<tr>
<td>2.0 wt% Rh/CaAl_{12}O_{19}, aged</td>
<td>322 ± 52</td>
<td>5.6 ± 0.89</td>
<td>26%</td>
</tr>
<tr>
<td>2.0 wt% Rh/Al_{2}O_{3}</td>
<td>1057 ± 49</td>
<td>18.2 ± 0.84</td>
<td></td>
</tr>
<tr>
<td>2.0 wt% Rh/Al_{2}O_{3}, aged</td>
<td>754 ± 4</td>
<td>13.0 ± 0.06</td>
<td>26%</td>
</tr>
</tbody>
</table>

Table 3.3 shows the results of CO pulse chemisorption on 2wt% Rh catalysts on a variety of catalyst supports before and after the aging conditions. Uncertainty in the measurement is taken as the standard deviation from a series of three repeated chemisorption tests. The results show that there is clear loss of metal surface area after the aging condition for all catalysts. This is consistent with the BET results that show clear loss of overall surface area after the aging condition. The dispersion numbers for the calcium-based hexaaluminates before and after the aging condition are consistent with those found in the literature [4]. The aging condition seems to have affected the Sr-based hexaaluminate catalyst similarly but the magnitude of the active surface areas are greater than that of the Ca-based hexaaluminate.

It is interesting to consider the dispersion numbers for the 2 wt% Rh/Al_{2}O_{3} catalysts. As expected, the pre-aged dispersion numbers are greater than the dispersions for the hexaaluminate supported catalysts. This result is consistent with the measured BET surface areas. The aged catalyst lost some metal surface area but not to the extent of the loss in overall surface area (Table 3.1).

3.5 Summary of Physical Characterization Results and Conclusion

The physical characterization techniques performed in this work have provided insight into the nature of hexaaluminates as catalyst supports and how they respond to harsh operating conditions. Based on the results of the characterization study, several relationships have been observed.
Both the alumoxane [52, 53] and co-precipitation methods are adequate in producing desired hexaaluminate phases. This is evident by analyzing the samples by powder x-ray diffraction as well as observing the plate-like structures that arise after calcination. A Zr substitution was attempted but was not successful as evident by XRD and SEM results. However, calcium and strontium substitutions were successful.

The plate-like structures of the hexaaluminate samples are also resistant to loss of surface area under high-temperature aging conditions. The surface-area retention is observed in the BET results for fresh samples as well as aged samples. The BET surface areas of other supports are also measured. As expected, the γ-Al₂O₃ control support had the highest initial surface area. BET surface-area measurements also indicated the stability of YSZ and GDC catalyst supports.

Two different methods are used to impregnate the Rh metal onto the hexaaluminate supports. The methods of post-impregnation and pre-impregnation yield different available metal surface areas as indicated by the CO pulse chemisorption experimental results. The post-impregnation method yields a higher active surface area. This is a result of the aluminum hydroxide binder being converted to α-Al₂O₃ and covering active sites during the coating process. CO pulse chemisorption is also used to investigate the available metal surface before and after an aging process. There is clear loss of metal surface area after the aging condition for all samples, but not as much as expected for the γ-Al₂O₃. However, all results are consistent with the BET surface area loss after the aging condition.

Larger metal particles (0.1-1.0 μm) are observable in the SEM and TEM micrographs. It appears that when compared to a ZrO₂/α-Al₂O₃, the Sr-based hexaaluminate prevents coarsening of the Rh metal particle sizes after an accelerated-aging process. The aging process for these samples was slightly harsher than the aging process used in the BET and CO-pulse chemisorption tests. The Rh particles supported by the Zr support grew by a factor of 10 observable in the TEM while the Rh particles on the Sr based hexaaluminate support retained their size. Dispersions measured by the CO-pulse chemisorption tests on the Sr-based hexaaluminate supports decreased by a factor of two. The decrease suggests that there are smaller metal particles
present in both samples that are not readily observable by SEM. These smaller metal particles may be agglomerating due to the aging process resulting in a decrease in dispersion.

The hexaaluminate supports provide a thermally stable carrier for methane-reforming catalysts. However, given the processing that is required, the hexaaluminates may be more appropriate in a catalytic-combustion or catalytic-partial-oxidation setting where operating temperatures are much higher. Under the aging conditions used here, significant loss of surface area was observed for $\gamma$-Al$_2$O$_3$ supports. Other supports including commercially acquired YSZ and GDC show thermal stability, however these supports are more expensive than the materials required to fabricate hexaaluminates.
Chapter 4

METHANE REFORMING IN A STAGNATION-FLOW REACTOR

A stagnation-flow reactor is used to study methane reforming at various experimental conditions for the purposes of providing fundamental data that will assist in elementary chemical-kinetic mechanism development. The experimental setup used in this work is specifically designed to enable rapid computational modeling. Such modeling is valuable for quickly evaluating the validity of previously published elementary mechanisms. This chapter investigates the stagnation-flow reactor results of dry reforming and steam reforming. Mixed reactant mixtures (autothermal reforming) are also investigated. For all stagnation-flow tests a Rh/Sr-hexaaluminate catalyst is used. The catalyst consists of Rh clusters supported on Sr-substituted hexaaluminate. A previous publication shows this catalyst system stabilizes surface area and metal-particle size under accelerated-aging conditions [29].

The first section of this chapter investigates methane-dry-reforming results in a stagnation-flow reactor. Gas-phase compositions are measured within the stagnation flow chemical boundary layer under dry reforming conditions. Experimental results over a range of conditions are used to develop rate constants in a previously published reaction mechanism [43]. The results in this section are also simulated numerically using the SPIN application of the CHEMKIN software. The model predictions which utilize the modified elementary reaction mechanism are shown to have reasonable agreement with the experimentally measured results. In the second section, steam is introduced as the co-reactant in methane-steam-reforming tests. The results are simulated using the developed mechanism from the dry-reforming section as well as an earlier version of that mechanism designed specifically for partial-oxidation of methane over Rh catalysts [62]. Contrasts in the results between the two mechanisms are discussed.
The focus of this chapter is providing new experimental data for computational model development. Because the elementary mechanisms utilized in this work have not been previously validated against experimental conditions incorporating large fractions of CO₂, the data presented here has value for developing models that encompass a wider range of process conditions.

4.1 Dry Reforming on Rh-Hexaaluminate Catalysts

Dry reforming of methane on a Rh-hexaaluminate catalyst is investigated using the stagnation-flow reactor presented in Chapter 2. This section presents experimental data which aids the development of a previously published elementary reaction mechanism [43]. Even though the mechanism includes elementary steps covering dry-reforming, it has not explicitly been evaluated for dry-reforming operation, which leads to questions regarding accuracy of the model for predicting dry-reforming processes. Model fidelity is tested by varying parameters such as CO₂/CH₄ ratio, addition of oxygen, and also catalyst temperature. A total of sixteen dry-reforming experiments were conducted with various operating parameters. Simulations for each of the sixteen experiments are performed in parallel to evaluate the fidelity of the model. The experimentally measured and computationally predicted results are compared for each parameter variation. It should be noted that the mechanism [43] was originally developed for Rh coated alumina washcoats and the present study uses Rh on Sr-doped hexaaluminate. Previous studies indicate that the identity of the support has little effect on the dry-reforming reaction rate over Rh catalysts [18, 19].

4.1.1 Dry Reforming: Baseline Case

Consider first a baseline dry-reforming case. The catalyst formulation on the stagnation surface is 10% Rh on Sr-hexaaluminate. The inlet composition is 10% CH₄ and 15% CO₂ (balance Ar). Slightly greater-than-stoichiometric inlet compositions are used because initial experiments at stoichiometric conditions showed deactivation presumably due to carbon deposition. At stoichiometric ratios there is often the possibility for carbon formation on the catalyst surface [13]. The total inlet flow rate
is 19.5 slm, the gas inlet temperature is 35 °C, and reactor pressure is maintained at 300 torr. These conditions result in an inlet velocity of $U_{in}=90$ cm s$^{-1}$. For the initial baseline case, surface temperature is maintained at $T_s=800$ °C. The CO$_2$ to CH$_4$ ratio for the baseline case is 1.5.

Figure 4.1 shows the experimentally measured species profiles within the stagnation-flow boundary layer for the baseline experimental conditions. The catalyst surface is at the left edge of the graph ($z = 0$ cm), with gases flowing from right to left as shown in the inset stagnation-flow image. Only the dry products are considered here. Carbon balance for all measurements is maintained within 7%.

Figure 4.1 shows that there is significant reforming activity at these conditions. The methane activity is characterized by 5.5% methane measured at the surface as compared to 10% methane at the inlet. Co-reactant consumption is significant as well, characterized by the CO$_2$ at inlet measuring 15% while at the surface it measures nearly 8.5%. In addition to the reactants being consumed there is measurable formation of synthesis gas at the surface of the catalyst. Carbon monoxide is measured at almost 9.5% at the surface while hydrogen is measured at greater than 2%
Fig. 4.2: Experimentally measured boundary-layer mole-fraction profiles for a CO$_2$ to methane ratio of 1.5 and surface temperature of 800 °C (baseline case). Also shown is the approximate size and location of the quartz sampling microprobe.

of the total flow.

Because the gas-phase chemistry is negligible at these temperatures, the boundary-layer profiles must be linear near the surface. The non-linearity of the experimental measurements at close proximity to the surface is due to the sample volume associated with the quartz microprobe. Since the sample volume is larger than the distance between the surface and the tip of the microprobe, the measurement point closest to the surface tends to bias away from the surface. This behavior is exaggerated in species profiles that have steeper gradients such as CO$_2$ and CO. Figure 4.2 shows the boundary layer species measurements with the approximate location and size of the quartz microprobe included.

Assuming a global reaction (CH$_4$ + CO$_2$ → 2CO + 2H$_2$) and equal levels of CH$_4$ and CO$_2$, the dry-reforming process should produce equal levels of H$_2$ and CO. Here, because excess CO$_2$ is used, the products should have relatively more CO. This behavior is observed in the results shown in Figure 4.1. With excess CO$_2$ available, the reverse water-gas-shift process (H$_2$ + CO$_2$ → CO + H$_2$O), tends to convert H$_2$ to CO.
The excess CO$_2$ in the present experimental conditions may be contributing to the increased CO/H$_2$ ratio at the surface.

4.1.2 Elementary Heterogeneous Reaction Mechanism

The gas-phase compositions within the chemical boundary layer are simulated in this work using the SPIN application of the CHEMIKIN chemically reacting flow software. Brief details of the model formulation are found in Chapter 2. As discussed previously, to effectively model experimental results from the stagnation-flow reactor an elementary heterogeneous reaction mechanism is required.

Several different versions of a methane-on-Rh reaction mechanism from the Deutschmann group at the Karlsruhe Institute of Technology are considered. Complete details about the reaction-mechanism development and validation studies are found in journal papers by the Deutschmann group at the University of Karlsruhe [62, 34, 41, 43]. Figure 4.3 shows the experimentally obtained methane mole fraction profile for the baseline dry-reforming case as well as the model predictions from SPIN using five separate heterogeneous reaction mechanisms.

Some of the mechanisms tested [62, 34, 43] are not initially active for CO$_2$/CH$_4$ mixtures. This result is consistent with recent findings in the literature [37]. More recent versions of the reaction mechanism [41] include more reactions which are apparently crucial to modeling dry reforming. The added reactions involve the surface adsorbed species, HCO$^*$. Yan et al. first suggested that these species play a crucial role in reforming reactions [63]. Schadel et al. added the reactions in the published elementary mechanism for steam reforming methane [41]. The reaction mechanism is based upon the previous works of the Deutschmann group [62, 34]. The added reactions to the mechanisms are listed below.

\[ \text{CO}^* + \text{H}^* \rightarrow \text{HCO}^* + \text{Rh}^* \]  \hspace{1cm} (4.1)
Fig. 4.3: Results of SPIN modeling in the baseline dry reforming case using several different versions of a methane-on-Rh elementary reaction mechanism.

\[
\begin{align*}
\text{HCO}^* + \text{Rh}^* &\rightarrow \text{CO}^* + \text{H}^* \\
\text{HCO}^* + \text{Rh}^* &\rightarrow \text{CH}^* + \text{O}^* \\
\text{CH}^* + \text{O}^* &\rightarrow \text{HCO}^* + \text{Rh}^*
\end{align*}
\]  

(4.2)  
(4.3)  
(4.4)

A recently published elementary mechanism initially developed for modeling partial oxidation of iso-octane [43] includes these reactions and is used to model the dry-reforming surface chemistry in this work. Hartmann et al. report that such reactions are crucial in modeling the water-gas-shift reaction. In the unmodified state, the Hartmann et al. mechanism [43] is inactive for the baseline dry-reforming conditions presented above. That is, baseline dry-reforming simulations which utilize the unmodified elementary mechanism result in complete coverage of the catalyst surface by atomic carbon, and no methane conversion. Modification is required and sensitivity analysis provides direction for modification.

In this work, we modify the Hartmann et al. mechanism in two ways. Firstly, the pre-exponential factors of three adsorption and desorption steps are adjusted. The desorption rate of methane (R12) is increased to speed the removal of atomic
Table 4.1: Pre-exponential factors modified in the current work.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Published A</th>
<th>Current A</th>
</tr>
</thead>
<tbody>
<tr>
<td>5. ( \text{CO}_2^+ \rightarrow \text{CO}_2 )</td>
<td>1.0E-05</td>
<td>4.8E-02</td>
</tr>
<tr>
<td>11. ( \text{CO}_2 \rightarrow \text{CO}_2^+ )</td>
<td>1.0E+13</td>
<td>4.1E+11</td>
</tr>
<tr>
<td>12. ( \text{CH}_4^+ \rightarrow \text{CH}_4 )</td>
<td>1.0E+13</td>
<td>1.9E+14</td>
</tr>
</tbody>
</table>

carbon from the catalyst surface. The sticking coefficient of \( \text{CO}_2 \) (R5) is increased and the desorption rate of \( \text{CO}_2 \) (R11) is decreased to maintain sufficient coverage of the catalyst surface by an oxidizing species. In addition, the activation energy of the \( \text{CO}_2 \) desorption step is decreased from 21.7 kJ mol\(^{-1}\) to 18.0 kJ mol\(^{-1}\). The complete mechanism used in this work is listed in Table 4.2. Table 4.1 shows the pre-exponential factors as published by Hartmann et al. [43] and the pre-exponential factors used in the present work.

Additionally we have reduced the Hartmann et al. mechanism [43] to a \( \text{C}_1 \) mechanism consisting of 42 irreversible elementary reactions involving 12 surface-adsorbed species and 6 gas-phase species. The results of the modifications are indicated as McGuire 2010 in Figure 4.3. Model predictions using this modified mechanism display reasonable agreement with experimental data for methane conversion.

Effectively modeling experimental results from the stagnation flow reactor also requires an effective area \( (F_{\text{cat,geo}}) \). This parameter is a ratio of the catalytically active area to the geometric surface area and is typically taken as a parameter in the model that can be adjusted that is adjusted to achieve agreement with the baseline measurements. This value is then left unchanged in modeling conditions that differ from the baseline case.

An estimation of the effective area on the catalyst-coated stagnation surface can be made using data from CO pulse chemisorption experiments. The CO pulse chemisorption experiments indicate how many exposed Rh atoms are present per gram of catalyst. This value is multiplied by the mass of the catalyst deposited on the stagnation surface to get a rough estimate of how many exposed Rh atoms are on the catalyst surface. The effective area is determined by dividing this estimate by the number of Rh atoms that would be exposed if the geometric surface area of the stagnation surface were a plain Rh crystal with a site density of 2.72E-09 mol/cm\(^2\).
Fig. 4.4: Boundary-layer mole-fraction profiles for a CO$_2$ to methane ratio of 1.5 and surface temperature of 800 °C (baseline case). Shown are the experimental results (symbols) and results of SPIN modeling with modified elementary reaction mechanism (lines).

The site density is a property of Rh and is based on the crystal lattice spacing. The CO pulse chemisorption measurements found $F_{\text{cat, geo}} = 56$.

The results shown in Fig. 4.3 use $F_{\text{cat, geo}} = 90$ and all subsequent modeling results use this factor. This factor is arrived at by tuning the model to best match experimental results, as shown in Figure 4.4. It is in reasonable agreement with the CO pulse chemisorption measurements on catalysts that were fabricated with similar loadings and processing techniques.

Figure 4.4 shows the experimentally measured (points) and predicted (lines) species profiles within the stagnation-flow boundary layer for the above listed baseline experimental conditions. The results show that in addition to a reasonable agreement between the modified model predictions and the experimentally measured methane profiles shown in Figure 4.3, the other species measured also show good agreement. The agreement is particularly strong for hydrogen containing species but is weak for oxygen containing species near the surface.
Table 4.2: Surface reaction mechanism. Subset of mechanism from Hartmann et al. [43].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A^b$</th>
<th>$E^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\text{H}_2 + \text{Rh}^* \rightarrow \text{H}^* + \text{H}^*$</td>
<td>1.0E-02$^a$</td>
<td>0.00</td>
</tr>
<tr>
<td>2. $\text{O}_2 + \text{Rh}^* \rightarrow \text{O}^* + \text{O}^*$</td>
<td>1.0E-02$^a$</td>
<td>0.00</td>
</tr>
<tr>
<td>3. $\text{CH}_4 + \text{Rh}^* \rightarrow \text{CH}_3^*$</td>
<td>8.0E-03$^a$</td>
<td>0.00</td>
</tr>
<tr>
<td>4. $\text{H}_2\text{O} + \text{Rh}^* \rightarrow \text{H}_2\text{O}^*$</td>
<td>1.0E-01$^a$</td>
<td>0.00</td>
</tr>
<tr>
<td>5. $\text{CO}_2 + \text{Rh}^* \rightarrow \text{CO}_2^*$</td>
<td>6.0E-03$^a$</td>
<td>0.00</td>
</tr>
<tr>
<td>6. $\text{CO} + \text{Rh}^* \rightarrow \text{CO}^*$</td>
<td>5.0E-01$^a$</td>
<td>0.00</td>
</tr>
<tr>
<td>7. $\text{H}^* + \text{H}^* \rightarrow \text{H}_2 + \text{Rh}^* + \text{Rh}^*$</td>
<td>3.0E-21</td>
<td>77.80</td>
</tr>
<tr>
<td>8. $\text{O}^* + \text{O}^* \rightarrow \text{O}_2 + \text{Rh}^* + \text{Rh}^*$</td>
<td>1.3E-22</td>
<td>335.20</td>
</tr>
<tr>
<td>$\theta_{\text{O}}$</td>
<td>-280.0$^b$</td>
<td></td>
</tr>
<tr>
<td>9. $\text{H}_2\text{O}^* \rightarrow \text{H}_2\text{O} + \text{Rh}^*$</td>
<td>3.0E+13</td>
<td>45.00</td>
</tr>
<tr>
<td>10. $\text{CO}^* \rightarrow \text{CO} + \text{Rh}^*$</td>
<td>1.0E+13$^c$</td>
<td>133.40</td>
</tr>
<tr>
<td>$\theta_{\text{CO}^*}$</td>
<td>-15.0$^b$</td>
<td></td>
</tr>
<tr>
<td>11. $\text{CO}_2^* \rightarrow \text{CO}_2 + \text{Rh}^*$</td>
<td>1.0E+11$^c$</td>
<td>21.70</td>
</tr>
<tr>
<td>12. $\text{CH}_4^* \rightarrow \text{CH}_4 + \text{Rh}^*$</td>
<td>1.0E+14$^c$</td>
<td>25.10</td>
</tr>
<tr>
<td>13. $\text{H}^* + \text{O}^* \rightarrow \text{OH}^* + \text{Rh}^*$</td>
<td>5.0E-22</td>
<td>83.70</td>
</tr>
<tr>
<td>14. $\text{OH}^* + \text{Rh}^* \rightarrow \text{H}^* + \text{O}^*$</td>
<td>3.0E-20</td>
<td>37.70</td>
</tr>
<tr>
<td>15. $\text{H}^* + \text{OH}^* \rightarrow \text{H}_2\text{O}^* + \text{Rh}^*$</td>
<td>3.0E-20</td>
<td>33.50</td>
</tr>
<tr>
<td>16. $\text{H}_2\text{O}^* + \text{Rh}^* \rightarrow \text{H}^* + \text{OH}^*$</td>
<td>5.0E-22</td>
<td>106.40</td>
</tr>
<tr>
<td>17. $\text{OH}^* + \text{OH}^* \rightarrow \text{H}_2\text{O}^* + \text{O}^*$</td>
<td>3.0E-21</td>
<td>100.80</td>
</tr>
<tr>
<td>18. $\text{H}_2\text{O}^* + \text{O}^* \rightarrow \text{OH}^* + \text{OH}^*$</td>
<td>3.0E-21</td>
<td>171.8</td>
</tr>
<tr>
<td>19. $\text{C}^* + \text{O}^* \rightarrow \text{CO}^* + \text{Rh}^*$</td>
<td>5.2E-23</td>
<td>97.90</td>
</tr>
<tr>
<td>20. $\text{CO}^* + \text{Rh}^* \rightarrow \text{C}^* + \text{O}^*$</td>
<td>2.5E-21</td>
<td>169.00</td>
</tr>
<tr>
<td>21. $\text{CO}^* + \text{O}^* \rightarrow \text{CO}_2^* + \text{Rh}^*$</td>
<td>5.5E+18</td>
<td>121.60</td>
</tr>
<tr>
<td>22. $\text{CO}_2^* + \text{Rh}^* \rightarrow \text{CO}_2 + \text{Rh}^*$</td>
<td>3.0E+21</td>
<td>171.8</td>
</tr>
<tr>
<td>23. $\text{CO}_2 + \text{H}^* \rightarrow \text{HCO}^* + \text{Rh}^*$</td>
<td>5.0E+19</td>
<td>108.90</td>
</tr>
<tr>
<td>24. $\text{HCO}^* + \text{Rh}^* \rightarrow \text{CH}^* + \text{O}^*$</td>
<td>3.7E+24</td>
<td>+50.0$^b$</td>
</tr>
<tr>
<td>25. $\text{HCO}^* + \text{Rh}^* \rightarrow \text{CH}^* + \text{O}^*$</td>
<td>3.7E+21</td>
<td>59.50</td>
</tr>
<tr>
<td>26. $\text{CH}_2^* + \text{O}^* \rightarrow \text{HCO}^* + \text{Rh}^*$</td>
<td>3.7E+21</td>
<td>167.50</td>
</tr>
<tr>
<td>27. $\text{CH}_2^* + \text{Rh}^* \rightarrow \text{CH}_3^* + \text{H}^*$</td>
<td>3.7E+21</td>
<td>61.00</td>
</tr>
<tr>
<td>28. $\text{CH}_2^* + \text{H}^* \rightarrow \text{CH}_2^* + \text{Rh}^*$</td>
<td>3.7E+21</td>
<td>51.00</td>
</tr>
<tr>
<td>29. $\text{CH}_3^* + \text{Rh}^* \rightarrow \text{CH}_3^* + \text{H}^*$</td>
<td>3.7E+21</td>
<td>103.00</td>
</tr>
<tr>
<td>30. $\text{CH}_3^* + \text{H}^* \rightarrow \text{CH}_3^* + \text{Rh}^*$</td>
<td>3.7E+21</td>
<td>44.10</td>
</tr>
<tr>
<td>31. $\text{CH}_3^* + \text{Rh}^* \rightarrow \text{CH}_3^* + \text{H}^*$</td>
<td>3.7E+21</td>
<td>100.00</td>
</tr>
<tr>
<td>32. $\text{CH}_3^* + \text{H}^* \rightarrow \text{CH}_3 + \text{Rh}^*$</td>
<td>3.7E+21</td>
<td>68.00</td>
</tr>
<tr>
<td>33. $\text{CH}_3^* + \text{Rh}^* \rightarrow \text{CH}_3 + \text{H}^*$</td>
<td>3.7E+21</td>
<td>21.00</td>
</tr>
<tr>
<td>34. $\text{C}^* + \text{H}^* \rightarrow \text{CH}^* + \text{Rh}^*$</td>
<td>3.7E+21</td>
<td>172.80</td>
</tr>
<tr>
<td>35. $\text{CH}_3^* + \text{O}^* \rightarrow \text{CH}_2^* + \text{OH}^*$</td>
<td>1.7E+24</td>
<td>80.34</td>
</tr>
<tr>
<td>36. $\text{CH}_3^* + \text{OH}^* \rightarrow \text{CH}_2^* + \text{O}^*$</td>
<td>3.7E+21</td>
<td>24.27</td>
</tr>
<tr>
<td>37. $\text{CH}_2^* + \text{O}^* \rightarrow \text{CH}_2^* + \text{OH}^*$</td>
<td>3.7E+24</td>
<td>120.31</td>
</tr>
<tr>
<td>38. $\text{CH}_2^* + \text{OH}^* \rightarrow \text{CH}_2^* + \text{O}^*$</td>
<td>3.7E+21</td>
<td>15.06</td>
</tr>
<tr>
<td>39. $\text{CH}_2^* + \text{O}^* \rightarrow \text{CH}_2^* + \text{OH}^*$</td>
<td>3.7E+24</td>
<td>114.50</td>
</tr>
<tr>
<td>40. $\text{CH}_3^* + \text{OH}^* \rightarrow \text{CH}_2^* + \text{O}^*$</td>
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<td>36.82</td>
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<tr>
<td>41. $\text{CH}_3^* + \text{O}^* \rightarrow \text{CH}_3^* + \text{OH}^*$</td>
<td>3.7E+21</td>
<td>30.13</td>
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<tr>
<td>42. $\text{C}_2^* + \text{O}^* \rightarrow \text{CH}_2^* + \text{O}^*$</td>
<td>3.7E+21</td>
<td>136.00</td>
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</table>

$^a$ Arrhenius parameters for the rate constants written in the form: $k = A \exp(-E/RT)$. The units of $A$ are given in terms of moles, centimeters, and seconds. $E$ is in kJ/mol.

$^b$ Sticking coefficient.

$^c$ Coverage dependent activation energy.

$^d$ Detailed definition may be found in Kee et al. [44].

$^e$ Modified rate parameter.

$^f$ Total available surface site density is $\Gamma = 2.72 \times 10^{-9}$ mol/cm$^2$. 
4.1.3 Dry Reforming: Reaction Pathway

The model incorporates a previously published and validated elementary reaction mechanism to represent methane reforming on Rh. Moreover, when the mechanism is incorporated into a stagnation-flow simulation, the results are in good agreement with the measured boundary-layer profiles for the baseline case. Thus it is reasonable to assume that the reaction mechanism provides a good representation of the underpinning chemical processes. The computational simulation can be interrogated to analyze details of the reaction pathways that are responsible for the observed reforming performance. Reaction-path diagrams are created to assist in understanding methane-conversion pathways. Figure 4.5 shows the reaction-path diagram for our baseline dry-reforming case.

The net rates of production for each surface species have contributions from several different reactions. Only the dominant reactions to both produce and consume a particular surface species are considered here. Gas-phase reactants and products are shown on the left- and right-hand sides respectively while surface species (designated by an asterisk) occupy the space in between. Open surface sites are designated by single asterisks. Lines in the reaction path diagram indicate elementary reactions; the line thicknesses indicate the magnitudes of the rates of progress for the reaction (because the rates-of-progress vary greatly, from $5.3 \times 10^{-7}$ mol/cm²s to $1.2 \times 10^{-3}$ mol/cm²s, the line thicknesses are proportional to the logarithm of the rates of progress). A species associated with a line indicates a reactant in that particular elementary reaction.

The reaction pathway shown in Figure 4.5 for the baseline dry reforming case indicates that methane is adsorbed onto the surface, decomposed to surface-adsorbed atomic carbon (C*) (Reactions 27, 29, 31, 33) and then oxidized to CO* by surface-adsorbed atomic oxygen (O*) (Reaction 19). The surface-adsorbed atomic oxygen is created by the dissociation of HCO* to CH* and O* (Reaction 25) as well as the dissociation of CO₂ to CO* and O* (Reaction 22). The elementary step in the pathway where surface adsorbed carbon is oxidized by surface adsorbed oxygen is in agreement with mechanisms previously published in the literature [18, 42]. However, it is important to consider the origin of surface adsorbed oxygen. In this mechanism
Fig. 4.5: Reaction pathway for a CO$_2$ to CH$_4$ ratio of 1.5. Surface temperature is 800 °C.

The majority of the surface adsorbed atomic oxygen is created from the dissociation of HCO* to CH* and O*. This is in contrast to findings in the literature listing O* as coming from CO$_2$* dissociating to CO* and O*. While this reaction pathway is also included in this elementary mechanism, it is not the primary pathway to O* production.

There are other opinions in the literature regarding which species oxidizes the surface-adsorbed carbon. Maestri and co-workers recently proposed a C1 microkinetic model for reforming methane and carried out reaction-path analyses using this model. They report that the oxidation of surface-adsorbed carbon occurs by OH* species rather than O*. While this reaction is also included in the currently used mechanism, it is not the dominant pathway to C* oxidation under dry-reforming conditions.

After validating the model for the baseline conditions, we explore the fidelity of the mechanism by varying the experimental conditions and comparing the measured
results to predictions made using the modified elementary reaction model. In the following series of experiments, the reactor pressure is maintained at 300 torr and the total inlet flow rate is constant at 19.5 SLM.

4.1.4 Dry Reforming: Effect of CO$_2$/CH$_4$ Ratio

Carbon dioxide-to-methane ratios are often increased to avoid carbon formation [13]. The primary objective of this section is to investigate the effect on dry reforming activity in a stagnation-flow reactor when the CO$_2$/CH$_4$ ratio has been increased from 1.5 to 2.0 and to examine the fidelity of the model in predicting these effects. The catalyst formulation on the stagnation surface is 10% Rh on Sr-hexaaluminate, the same as that in the previous two sections. The inlet composition is 10% CH$_4$ and 20% CO$_2$ (balance Ar). As in the initial baseline case, surface temperature is maintained at $T_s=800$ °C.

Figure 4.6 shows the experimentally measured (points) and computationally pre-
dicted (lines) species profiles within the stagnation-flow boundary layer for the above listed experimental conditions. Figure 4.6 continues to show strong agreement between the experimentally measured results and predictions of the modified kinetic model that utilizes the developed elementary reaction mechanism shown in Table 4.2 for hydrogen containing species. However, for oxygen containing species the predictions continue to deviate from the measurements. The non-linearity of measurements close to the surface is apparent in Figure 4.6.

At higher CO₂/CH₄ ratios, the reaction-path diagram is qualitatively similar to the case with CO₂/CH₄ = 1.5 (Figure 4.5). The rates of production of surface H₂O increase slightly, presumably due to the marginal increase in surface oxygen.

4.1.5 Dry Reforming: Effect of Temperature

Because most catalytic processes depend strongly upon temperature, it is important to measure and model temperature-dependent performance. The experiments presented in this section are conducted with surface temperatures ranging from Tₛ=750°C to Tₛ=850°C. The previous experiments were performed at the baseline catalyst surface temperature of Tₛ=800 °C. Complete boundary layer profiles are measured for a range of temperatures to observe temperature dependencies of dry reforming in the stagnation flow reactor. Reasonable agreement between experimentally measured results and computational predictions is achieved for boundary layers through a range of temperatures for major species.

Figure 4.7 shows boundary layer methane mole fraction profiles for a range of surface temperatures (Tₛ=750 °C to Tₛ=850 °C). The inlet compositions are identical to the baseline case. As expected, methane conversion increases as a function of increasing temperature, and the model is in reasonable agreement with the measurements. Both the magnitude and slope of the measurements are well captured by the model.

Figure 4.8 shows boundary layer carbon dioxide mole fraction profiles through the range of temperatures Tₛ=750 °C to Tₛ=850 °C. Similar to the boundary layer methane mole fraction profiles, carbon-dioxide conversion increases as a function
Fig. 4.7: Boundary-layer methane mole-fraction profile with an inlet composition of $\text{CO}_2/\text{CH}_4=1.5$ and surface temperatures of 750 °C, 800 °C, 850 °C. Experimental measurements are represented as symbols and computational predictions are represented as lines.

Fig. 4.8: Boundary-layer carbon dioxide mole-fraction profile with an inlet composition of $\text{CO}_2/\text{CH}_4=1.5$ and surface temperatures of 750 °C, 800 °C, 850 °C. Experimental measurements are represented as symbols and computational predictions are represented as lines.
of increasing temperature. However the modeled temperature dependence appears stronger for the carbon dioxide species than the experimentally measured results.

Figure 4.9 shows boundary layer carbon monoxide mole fraction profiles through the range of temperatures $T_s=750 \, ^\circ\text{C}$ to $T_b=850 \, ^\circ\text{C}$. In both the measured and modeled cases, carbon monoxide production increases as a function of increasing temperature. Again, the modeled temperature dependence is greater than that of experimentally measured results.

Figure 4.10 shows boundary layer hydrogen mole fraction profiles through the range of temperatures 750 °C to 850 °C. Similar to the boundary layer carbon monoxide mole fraction profiles, hydrogen production increases as a function of increasing temperature. Again, low levels of hydrogen are measured because the excess CO$_2$ being used to mitigate carbon formation is converting hydrogen to carbon monoxide via the reverse water-gas-shift reaction. The model incorporating the modified elementary reaction mechanism captures this behavior.

As a criterion to evaluate performance in a stagnation-flow reactor, Taylor, et al. defined an effective conversion [38] using the mole fraction of methane at the surface. For methane, the conversion is defined as

$$\eta_{\text{CH}_4} = \frac{X_{\text{CH}_4,\text{inlet}} - X_{\text{CH}_4,\text{surf}}}{X_{\text{CH}_4,\text{inlet}}}, \quad (4.5)$$

where $X_{\text{CH}_4,\text{inlet}}$ and $X_{\text{CH}_4,\text{surf}}$ are the methane mole fractions at the inlet (i.e., unreacted feed stream) and at the surface respectively. The present effort applies this concept, but substitutes the value for $X_{\text{CH}_4,\text{surf}}$ at a distance of $z = 0.075 \, \text{cm}$ rather than at the surface due to the measurement error at the catalyst surface.

Figure 4.11 shows an Arrhenius plot for dry reforming in the stagnation flow reactor. Results show that the net activation energy predicted by the model is slightly greater than measured. This is in agreement with the complete boundary layers shown in Figures 4.8 and 4.9.
Fig. 4.9: Boundary-layer CO mole-fraction profiles for three different surface temperatures under dry-reforming methane. Experimental measurements are represented as symbols and computational predictions are represented as lines.

Fig. 4.10: Boundary-layer H₂ mole-fraction profiles for three different surface temperatures under dry-reforming methane. Experimental measurements are represented as symbols and computational predictions are represented as lines.
Fig. 4.11: Arrhenius plots for measurements and predictions based on effective methane conversion, $\eta_{CH_4}$.

4.1.6 Dry Reforming: Effect of $O_2$ Enrichment

Ashcroft and coworkers showed successful combination of the dry reforming and partial oxidation processes as an energy efficient approach to methane reforming [2]. Up to 90% methane conversion was achieved at stoichiometric dry reforming with a 1% oxygen addition over an irridium catalyst at 1050K. In a recent work, Choudhary and coworkers showed that a small addition of oxygen to the dry-reforming system increases the amount of $CH_4$ conversion [3]. Donazzi et al [5] showed a similar result, noting that the increase in conversion cannot be simply explained by the additional reaction of $CH_4$ with co-fed oxygen given the little amount. Donazzi et al. added 0.1% oxygen to $CH_4/CO_2$ mixtures aiming to perturb the surface amount of hydroxyl radicals. They proposed that in the $CO_2$ reforming system, $H_2O$ produced by reverse water gas shift (RWGS) was the effective co-reactant. Making more $H_2O$ by oxidation reactions upon the addition of oxygen weakens the steam-reforming dependence on RWGS and thus produces greater conversions. However, for $CO_2/CH_4$ ratios greater than 1, the addition of oxygen had negligible effect.
The primary objective of this section is to analyze similar conditions in the stagnation-flow reactor by adding a small amount of oxygen to the feed stream. The results are simulated numerically using the developed reaction mechanism.

The catalyst formulation on the stagnation surface is the same as the previous section. The inlet composition is 10% CH$_4$, 20% CO$_2$, 1% O$_2$ (balance Ar). All other experimental parameters are identical to the baseline case (total flow rate, surface temperature, and reactor pressure). One-percent oxygen displaces 1% argon so that the inlet mole fractions of the other reactants (CH$_4$ and CO$_2$) are constant between experiments.

Figure 4.12 shows the experimentally measured (points) and model predicted (lines) species profiles within the stagnation-flow boundary layer for the above listed experimental conditions. The results continue to show strong agreement for hydrogen containing species between the experimentally measured results and predictions using the modified kinetic model for the dry-reforming case with oxygen addition. The model weakness in predicting oxygen containing species (CO and CO$_2$) near the surface remains.
The previous experiments were performed at the baseline catalyst surface temperature of 800 °C. Similar cases are conducted for a CO\textsubscript{2}/CH\textsubscript{4} ratio of 1.5 with and without oxygen addition over a range of surface temperatures. The effective conversion concept is used here to evaluate the effects of oxygen addition on methane and CO\textsubscript{2} conversion.

Figure 4.13 shows effective methane conversions at CO\textsubscript{2}/CH\textsubscript{4}=1.5 for the cases with and without 1 % oxygen addition in the temperature range 700 to 850 °C. The addition of oxygen at this carbon dioxide-to-methane ratio does not appear to have any effect on the effective methane conversion over the range of temperatures tested. A small increase is seen for most of the temperatures but all of the increases observed are within the resolution of the experiment.

Similar effects of oxygen enrichment are observed at an increased CO\textsubscript{2}/CH\textsubscript{4} ratio. Figure 4.14 shows effective methane conversions at CO\textsubscript{2}/CH\textsubscript{4}=2.0 for the cases with and without 1 % oxygen addition in the surface temperature range $T_s=700$ to $T_s=850$ °C. Similar to the case where the inlet CO\textsubscript{2}-to-methane ratio was 1.5, the addition of oxygen does little to increase activity of the methane mole fraction at the surface. Similar results are reported by Donazzi et al. [5]. The negligible effect of oxygen addition may be due to the already-high oxygen coverages on the surface of the catalyst resulting from the increased CO\textsubscript{2}/CH\textsubscript{4} ratio.

An investigation into the reaction pathways for the modeled case with oxygen addition may reveal some clues as to the lack of increased activity upon the addition of oxygen. The reaction pathways shown in Figure 4.15 that there is an increased rate of production of surface-adsorbed oxygen from the dissociative adsorption of the O\textsubscript{2} species. It appears that rather than getting surface oxygen from the CO\textsubscript{2}, the surface is being saturated by surface oxygen from the gaseous O\textsubscript{2} species. The result is a measurable decrease in CO\textsubscript{2} effective conversion for all cases. This decrease in CO\textsubscript{2} adsorption is observable experimentally and also capture by the model incorporating the developed heterogeneous reaction mechanism.

Figure 4.16 shows effective carbon dioxide conversions at CO\textsubscript{2}/CH\textsubscript{4}=1.5 for the cases with and without 1 % oxygen addition in the temperature range $T_s=700$ to
Fig. 4.13: Effective methane conversions for CO$_2$/CH$_4$ = 1.5. Experimental measurements are represented as symbols and computational predictions are represented as lines.

Fig. 4.14: Effective methane conversions for CO$_2$/CH$_4$ = 2.0. Experimental measurements are represented as symbols and computational predictions are represented as lines.
Fig. 4.15: Reaction pathway for a CO₂ to CH₄ ratio of 2.0. Surface temperature is 800 °C and 1% oxygen is added to reactant stream.

$T_s=850$ °C. As in the plots for effective methane conversion, there is an increase in effective conversion at higher temperatures. The addition of oxygen results in a decrease in effective carbon dioxide conversion. This experimentally measured result is also captured by the model prediction over the range of temperatures tested.

Similar to the case where the inlet carbon dioxide-to-methane ratio is 1.5, the addition of oxygen slightly decreases the effective carbon dioxide conversion when the CO₂ to methane ratio is increased to 2. Figure 4.17 shows the effective carbon dioxide conversions for the above experimental conditions over the temperature range from $T_s=700$ °C to $T_s=850$ °C. Again, the temperature dependence on the CO₂ conversion is apparently greater for the the model predictions than it is for the experimentally measured results.
**Fig. 4.16:** Effective carbon dioxide conversions for $\text{CO}_2/\text{CH}_4 = 1.5$.

**Fig. 4.17:** Effective carbon dioxide conversions for $\text{CO}_2/\text{CH}_4 = 2.0$. 
4.1.7 Numerical Experiments

With the numerical model validated across a range of conditions, it is reasonable to assume that the modified heterogeneous reaction mechanism is a good representation of the underlying chemical processes. In this section we investigate the effect of oxygen enrichment on dry reforming where the $\text{CO}_2/\text{CH}_4$ ratio is 1.

Figure 4.18 shows effective methane conversions with and without oxygen addition over the temperature range from $T_s=700$ °C to $T_s=850$ °C. The model results show that at the lower end of the temperature scale, the addition of oxygen significantly increases methane conversion. In contrast, at the higher end of the scale (800 °C and 850 °C) the effect of oxygen enrichment on effective methane conversion is reduced.
4.1.8 Conclusion

In this section we established a baseline case for dry reforming methane in a stagnation flow reactor. The results of this baseline case are used to develop rate constants in an elementary heterogeneous reaction mechanism that has not been explicitly tested for CO$_2$ reactant mixtures. Experimental measurements were then obtained for a range of conditions across different inlet compositions and temperatures to test the fidelity of the modified reaction mechanism. The results show that reasonable agreement between the experimentally obtained results and model predictions is valid across a range of temperatures. Further development may be needed for the activation energies of the CO$_2$ chemistry. The next section investigates steam-reforming methane within a stagnation flow reactor.

The measurements presented here provide new data that aid in developing the CO$_2$ aspects of a published elementary reaction mechanism. The kinetic data regarding CO$_2$ chemistry need further development. The data show a net activation energy for dry reforming in a stagnation flow configuration that is slightly lower than the model predictions. Further development on this aspect of the current mechanism, supported by experiments focused on the net activation energies, is required.

4.2 Steam Reforming on Rh-hexaaluminate Catalysts

Steam reforming is a process that is ideal for producing large volumes of hydrogen because of the high ratio of hydrogen to carbon monoxide found in the product syngas. In this section gas-phase compositions within the stagnation-flow chemical boundary layer are measured under steam-reforming conditions. The experimentally measured boundary layers are compared to those predicted by SPIN using two different elementary reaction mechanisms. The catalyst used in this section is 1wt% Rh/SrAl$_{12}$O$_{19}$ catalyst that is fabricated by TDA Research.
FIG. 4.19: Boundary-layer mole-fraction profiles measured in the stagnation-flow reactor under steam reforming conditions. Steam-to-carbon ratio is 1.4 and surface temperature is approximately 740 °C.

4.2.1 Steam Reforming: Baseline Case

Consider first a baseline steam-reforming case (globally, $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$). The inlet composition is 4.3% $\text{CH}_4$ and 5.9% $\text{H}_2\text{O}$ (balance Ar), which is a steam-to-carbon ratio of 1.4. The inlet temperature is 135 °C. The total inlet flow rate is 16.4 slm, resulting in an inlet velocity at the porous-frit face of $U_m=130$ cm/s. The baseline catalyst surface temperature is maintained at $T_s=740$ °C. Reactor pressure is maintained at $p=40$ kPa (300 torr).

Figure 4.19 shows measured (points) species profiles within the stagnation-flow boundary layer. It is clear from Fig. 4.19 that there is significant reforming activity at the catalyst surface. It is also evident that under the steam-reforming conditions listed above, the complete chemical boundary layer has been adequately resolved. Approximately 45% of the methane supplied in the reactant stream is reformed, with a selectivity to hydrogen of 69%. As expected, the product composition for steam
reforming has a greater selectivity to hydrogen when compared to the dry reforming results in the previous section.

4.2.2 Catalytic Reaction Mechanism

In this work, we use two different versions of a elementary heterogeneous reaction mechanism and compare the results of the numerical simulations to the experimentally obtained steam reforming results. Initially, an unmodified catalytic reaction mechanism published by Deutschmann in 2001 [62] is used to model the results. The results of these experiments and predictions using this mechanism have recently been published [29]. The mechanism used is listed in Table 4.3.

Figure 4.20 shows measured (points) and predicted (lines) species profiles within the stagnation-flow boundary layer using the unmodified Deutschmann mechanism [62]. There is reasonable agreement between model-predicted and experimentally measured results across all species for the baseline steam-reforming conditions.

The steam-reforming experiments are also simulated using the newly developed mechanism presented in the previous section (Table 4.2). Effective-area factors are different due to the fact that a different catalyst was used in the dry reforming experiments versus the steam reforming experiments. Figure 4.21 shows the same experimentally measured mole fraction profiles within the stagnation flow boundary layer as presented in Figures 4.19 and 4.20. The modeled results presented in Figure 4.21 are computed using the elementary reaction mechanism listed in Table 4.2.

The major difference between the two mechanisms used to simulate the experimental steam reforming results is the presence of the HCO surface species mentioned previously (Section 4.1.2). It is interesting to consider that while these reactions are crucial to modeling dry reforming systems, it does not appear that they are as important to modeling steam-reforming systems. Both of the mechanisms used in this section are able to model steam and methane mixtures in a chemically-reacting stagnation-flow configuration. However, the prediction for oxygen containing species (CO and CO₂) is still weak when compared to the experimental measurements. The CO is slightly over predicted and the mole-fraction boundary-layer profile is flat.
Table 4.3: Surface reaction mechanism for CH₄ on Rh [62].

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\(^1\) Arrhenius parameters for the rate constants written in the form: 
\(k = A \exp(-E/RT)\). The units of \(A\) are given in terms of moles, centimeters, and seconds. \(E\) is in kJ/mol.

\(^a\) Sticking coefficient.

Total available surface site density is \(\Gamma = 2.72 \times 10^{-9}\) mol/cm².
Fig. 4.20: Boundary-layer mole-fraction profiles measured in the stagnation-flow reactor under steam reforming conditions. Steam to carbon ratio is 1.4 and surface temperature is approximately 740 °C. Modeled results here are obtained using the 2001 version of methane on Rh mechanism [62].

Fig. 4.21: Boundary-layer mole-fraction profiles measured in the stagnation-flow reactor under steam reforming conditions. Steam to carbon ratio is 1.4 and surface temperature is approximately 740 °C. Modeled results here are obtained using the 2010 version of methane on Rh mechanism [43].
Fig. 4.22: Boundary-layer mole-fraction profiles measured in the stagnation-flow reactor under steam reforming conditions. Steam-to-carbon ratio is 5 and surface temperature is approximately 740 °C. Modeled results here are obtained using the 2010 version of methane on Rh mechanism [43].

4.2.3 Steam Reforming: Effect of Steam-to-Carbon Ratio

As in the case of dry reforming, the ratio of co-reactant to methane is often increased to avoid carbon deposits. This section investigates the results of increasing the steam-to-carbon ratio on methane-reforming results within the stagnation flow reactor. Figure 4.22 shows mole-fraction profiles for a case in which steam-to-carbon ratio is increased from 1.4 to 5. The inlet composition for this case is 1.7% CH₄ and 8.6% H₂O (balance Ar). All other parameters are the same as the baseline steam-reforming case.

As in the baseline case, the model predictions agree reasonably well with the measured profiles. Compared with the baseline case, methane conversion is decreased to 35%. Because of the extra steam, the hydrogen selectivity is increased to 76%. The increased H₂O also promotes water-gas-shift processes that increase the relative levels of CO₂ compared to CO. Predictions for this case are simulated using the modified
2010 version of the methane-on-Rh mechanism (Table 4.2).

4.2.4 Steam Reforming: Effect of Temperature

This section investigates the temperature dependence of steam reforming in the stagnation flow reactor. Because steam-reforming is typically carried out for the purposes of hydrogen generation, only the hydrogen boundary-layer mole-fraction profiles are considered here. Figure 4.23 illustrates hydrogen profiles for three different catalytic surface temperatures as well as simulated hydrogen profiles for the three surface temperatures using the 2001 version of the mechanism [62]. The inlet compositions are similar to the base case, but do vary somewhat. For the 665 °C case, inlet composition is 4.6% CH₄ and 7.4% H₂O (balance Ar). For the 740 °C case, inlet composition is 4.4% CH₄ and 7.4% H₂O, and for the 802 °C case, inlet composition is 4.1% CH₄ and 7.4% H₂O. As expected, methane conversion and hydrogen production increase as functions of increasing temperature. Again, the model is in reasonable agreement with the measurements. However, it appears that the modeled temperature dependence is weaker than that measured. This suggests that the model reaction mechanism could be improved, presumably by increasing activation energies for rate-limiting steps.

Figure 4.24 illustrates the same experimentally observed hydrogen profiles as in Figure 4.23 but the simulated hydrogen profiles are obtained using the latest developed version of the Deutschmann mechanism presented in Table 4.2. Here, the model developed in this work is once again is in agreement with the experimental results. The strength of the model continues to be in predicting hydrogen containing species (CH₄ and H₂) and weaknesses lie in predicting oxygen containing species (H₂O, CO₂, CO).

4.2.5 Steam Reforming: Reaction Pathways

Similar to Section 4.1.3, the computational simulation is interrogated to analyze details of the reaction pathways that are responsible for the observed reforming performance. Figure 4.25 is a reaction path diagram extracted from the modeled so-
FIG. 4.23: Boundary-layer $\text{H}_2$ mole-fraction profiles for three different surface temperatures. Modeled results here are obtained using the 2001 version of methane on Rh mechanism [62].

FIG. 4.24: Boundary-layer $\text{H}_2$ mole-fraction profiles for three different surface temperatures. Modeled results here are obtained using the 2010 version of methane on Rh mechanism [43].
Fig. 4.25: Reaction pathway for the baseline steam reforming case. Steam-to-carbon ratio is 1.4 and surface temperature is approximately 740 °C.

olution to the baseline steam-reforming case (steam-carbon ratio of 1.4). The catalysis process begins with gas-phase CH₄ and H₂O being competitively adsorbed onto the catalyst surface (adsorbates represented as CH₄* and H₂O*). The adsorbed methane undergoes a series of reactions that sequentially strip atomic hydrogen, producing adsorbed methyl, methylene, etc. Each such reaction also produces an adsorbed atomic hydrogen H*. The adsorbed H* can recombine, providing the primary route to gas-phase H₂ production.

The adsorbed H₂O* dissociates to produce adsorbed H* and hydroxyl OH*. The hydroxyl further dissociates to produce more adsorbed atomic hydrogen and atomic oxygen O*. The atomic oxygen is the primary link to the carbon-containing species, producing adsorbed carbon monoxide CO*. The adsorbed CO* can react with O* to produce CO₂. Both the adsorbed CO* and CO₂ can desorb, producing gas-phase products CO and CO₂.

At higher steam-to-carbon ratios, the reaction-path diagram is qualitatively simi-
lar to the low steam-to-carbon cases. However, the level of steam adsorption increases relative to methane. The higher steam levels lead to increased surface coverage of hydroxyl and oxygen. The increased oxygen promotes the increased conversion of CO to CO₂. Methane conversion is decreased and hydrogen production is increased.

Maestri et al examined reaction pathways in their publication of a C1 microkinetic model for modeling reforming of methane [39]. In their work, the atomic adsorbed carbon is oxidized by adsorbed hydroxyl radicals which originate from the dissociation of water to OH* and H*. As in the case of dry-reforming methane, that pathway is included in the current mechanism. However, it is not the primary path to surface carbon oxidation found in this study.

4.3 Conclusions

Rhodium supported on Sr-substituted hexaaluminate is found to perform well for the reforming of methane. The reforming activity in this work is studied using a stagnation-flow reactor. Microprobe mass spectrometry is used to measure species profiles in the boundary layer adjacent to the catalyst surface. The stagnation-flow configuration provides diagnostics access that would be extraordinarily difficult, if not impossible, in technologically viable catalyst configurations such as porous foams or channel monoliths. Moreover, the stagnation-flow similarity enables efficient mathematical modeling of the chemical boundary layers.

The primary objective of this work is to provide fundamental data that can assist in extending previously published reaction mechanisms for catalytic dry-reforming of methane. The specific catalyst considered is Rh, supported on Sr-doped hexaaluminate. Reaction mechanisms originally developed for Rh/Al₂O₃ washcoats are validated by comparing measurements with model predictions. The model results are then used to assist interpretation of the fundamental reaction pathways, providing quantitative insight about the overall reforming processes.

By analyzing boundary-layer measurements taken in the stagnation-flow reactor at various experimental conditions, rate constants are developed that extend a
previously published elementary mechanism to modeling dry reforming of methane on Rh. With these new parameters, reasonable agreement is obtained between simulated and experimental results. The model appears to accurately predict mole-fraction boundary-layer profiles for hydrogen containing species, but slightly overpredicts conversion to products such as CO.

Although the modified mechanism presented in this chapter was developed for dry reforming, it has also been tested against published data for steam-reforming conditions. The agreement for hydrogen containing species between measurements and computational predictions under steam reforming remains strong. However, for oxygen containing species, the model continues to overpredict mole-fractions near the catalyst surface.

The measurements presented here provide new data that aid in developing the CO\(_2\) aspects of the elementary reaction mechanism. However, the kinetic data regarding CO\(_2\) chemistry may need further development. The data show a net activation energy that is lower from the model results. Further development on these aspects of the current mechanism, supported by additional experiments focusing on the activation energies, is needed.
Chapter 5

CONCLUSIONS

In this work we have fabricated thermally stable hexaaluminate catalysts supports. Supports are loaded with the active phase, Rh and then characterized and tested under simulated reforming conditions to evaluate thermal stability. Hexaaluminate catalyst supports are shown to retain surface area and stabilize metal particles under the harsh aging conditions.

In the second part of this work we have utilized a stagnation-flow reactor to collect data under different conditions for converting methane to synthesis gas. The majority of the data are collected under dry-reforming conditions. The data presented here have been used to develop a previously published mechanism that has not been explicitly tested for CO$_2$ reactant mixtures. New rate constants are proposed for the elementary mechanism that will enable simulation of dry-reforming processes. With these new parameters reasonable agreement is obtained between simulated and experimental results. A study of the model’s output shows reaction pathways responsible for the observed dry reforming activity.

5.1 Physical Characterization of Hexaaluminate Catalysts

The characterization techniques performed in this work have provided insight into the nature of hexaaluminates as catalyst supports and how they respond to harsh operating conditions. Based on the results of the characterization study, several relationships have been observed. Here, two methods of hexaaluminate synthesis are used. The alumoxane and co-precipitation methods are adequate in producing desired hexaaluminate phases. This is evident by analyzing freshly synthesized samples
by powder x-ray diffraction. The peaks associated with representative hexaaluminates are consistent with those found in the ICDD database for Sr- and Ca-based hexaaluminates. A Zr substitution was attempted but not successful as evident by XRD results. XRD patterns for Zr-based samples showed the presence of only ZrO$_2$ and $\alpha$-Al$_2$O$_3$ indicating that Zr-hexaoaluminate was not formed.

The high-temperature stability is attributable to the morphology of the hexaaluminate samples. The large-cation substitution in the mirror plane of the hexaaluminate structure prevents sintering in the [0 0 1] direction. Plate-like structures form as a result of exposure to the high temperatures of the calcination process and are readily observable by scanning electron microscope. The plate-like structures are resistant to loss of surface area under high-temperature aging conditions. The aging condition used in this work is adapted from Ferrandon and Krause [4]. Ferrandon and Krause have shown that their aging technique is effective at reproducing surface areas and dispersion measured on catalysts that have been exposed to autothermal reforming conditions for over 200h.

The surface area retention is evident in the BET measurements for powder hexaaluminate samples aged in the same manner. For comparison, the total surface areas of several other commercially acquired catalyst supports are measured. As expected, the $\gamma$-Al$_2$O$_3$ control support had the highest initial surface area. Other tested supports showed comparable thermal stability to the CSM-fabricated hexaaluminate samples.

The active phase of the catalyst, Rh, was deposited by incipient wetness impregnation. The Rh impregnation was confirmed by SEM/EDS. Two different methods are used to impregnate the Rh metal onto the hexaaluminate supports. The methods of post-impregnation and pre-impregnation yield different available metal surface areas as indicated by the CO pulse chemisorption experimental results. The post impregnation method yields a higher active surface area due to the action of the aluminum-hydroxide gel used during the coating process. CO pulse chemisorption is also used to investigate the available metal surface before and after an aging process. There is clear loss of metal surface area after the aging condition for all samples but not as much as expected for the $\gamma$-Al$_2$O$_3$ samples. However, all the results are
consistent with the BET surface area lost after the aging condition.

The hexaaluminate supports provide a thermally stable support for methane reforming catalysts. However, the hexaaluminates may be more appropriate in a catalytic combustion or catalytic partial oxidation setting where reforming temperatures are much higher. It appears at the lower temperatures of reforming investigated here the use of hexaaluminate may not be necessary.

5.2 Reforming Results in a Stagnation-Flow Reactor

The stagnation-flow reactor used in this work provides a means to measure gas-phase composition profiles immediately adjacent to the catalyst surface. Such measurements are not available in practical reactor configurations (e.g. channel monoliths or porous foams). Moreover, the stagnation-flow similarity enables efficient mathematical modeling of the chemical boundary layers adjacent to the catalyst surface. Reaction mechanisms originally developed for Rh/Al₂O₃ washcoats are validated by comparing measurements with model predictions. The model results are then used to assist interpretation of the fundamental reaction pathways, providing quantitative insight about the overall reforming processes.

By analyzing boundary-layer measurements taken in the stagnation-flow reactor at various experimental conditions, rate constants are developed that extend a previously published elementary mechanism [43] to modeling dry reforming of methane on Rh. With these new rate parameters, reasonable agreement is obtained between simulated and experimental results. The model appears to accurately predict mole-fraction boundary-layer profiles for hydrogen containing species, but slightly overpredicts conversion to products such as CO.

A study of the model’s output shows possible reaction pathways responsible for the observed dry reforming activity. The major difference between our reaction pathway and those found in the literature is the origin of the O* species that oxidizes C*. Here, the majority of surface oxygen originates from the dissociation of HCO*. The HCO* species is formed by the reaction of CO* and surface adsorbed atomic
hydrogen (H*). Others have proposed that the majority of surface oxygen is created by the dissociation of CO$_2$*.

The mechanism developed here for dry reforming is also tested against previously published data from a stagnation flow reactor. The previously published data was collected under steam-reforming conditions. Steam-reforming simulations incorporating the newly developed mechanism continue to show good agreement with measured results. Predicted and measured mole fraction profiles line up well for hydrogen containing species but the agreement for oxygen containing species remains a weakness.

5.3 Suggestions for Future Work

Hexaaluminate-based catalysts are thermally stable catalysts that show reasonable reforming activity. However, the accelerated-aging processes studied in this work did not sufficiently degrade control catalysts to an extent where the hexaaluminate approach would be advantageous from a thermal stability standpoint. Further research on this aspect of hexaaluminate catalysts is needed. The research may be facilitated through experiments by exposing fabricated catalysts to actual time on stream as opposed to the simulated aging conditions used here. Alternately, harsher aging conditions could be postulated.

The stagnation-flow measurements presented here provide new data that aid in developing the CO$_2$ aspects of a published elementary reaction mechanism. The kinetic data regarding CO$_2$ chemistry appears to need further development. The data show a net activation energy for dry reforming in a stagnation flow configuration that is slightly lower than the model predictions. Further development on this aspect of the current mechanism, supported by experiments focused on the net activation energies, is required.
5.4 Summary

This work reports new data on hexaaluminate-supported catalysts and the effects of aging, loading, and fabrication on overall surface area and metal surface area available for reaction. In addition, we have modified a stagnation-flow reactor for characterization of catalyst activity. The new modifications enable rapid changeover of catalysts and also introduction of steam as a co-reactant. Dry reforming results from the stagnation-flow reactor are used to develop a previously published reaction mechanism in aspects regarding CO₂ chemistry. Model predictions incorporating the newly developed mechanism are compared to experimental results across a range of steam- and dry-reforming conditions with reasonable agreement observed.
REFERENCES


[58] Gregory P. Smith, David M. Golden, Michael Frenklach, Nigel W. Moriarty, Boris Eiteneer, Mikhail Goldenberg, C. Thomas Bowman, Ronald K. Hanson, Soonho Song, William C. Gardiner Jr., Vitali V. Lissianski, and Zhiwei Qin. Gri-mech 3.0. [http://www.me.berkeley.edu/gri_mech/](http://www.me.berkeley.edu/gri_mech/).


APPENDIX A

PROCEDURES

Procedures were developed to prevent damage to the apparatus and injury to the operator.

A.1 Stagnation-Flow Reactor

System Startup

1. Open argon cylinder and valves to mass flow controllers.
2. Turn on power supply and exhaust components.
3. Start BOC Edwards scroll pump to evacuate SFR chamber.
5. If temperature and pressure data are to be written to a file, set two booleans on left side of "StagnationFlowReactor.vi" to "True".
6. Specify name for file that pressure and temperature data will be written to.
7. Start "Multi MFC Control.vi".
8. Set argon flow rate to 3 SLM.

Power Supply/Heater Startup

1. Set manual control input on "StagnationFlowReactor.vi" to a value of "10".
2. Wait for power supply LED to come on.
3. Once power supply LED is on, set manual control input to "7".
4. Set "Output Low" range on PID parameters to "7".
5. Wait 15 min for surface temperature to reach approximately 150 °C.
6. Set ramp rate to 8 °C/min.
7. Set auto temperature setpoint to current surface temperature +10 °C.
8. Turn auto temp control to "on".
9. Set "Output High" on PID parameters to between 18 and 20 depending on the desired final surface temperature.
10. Once auto temperature control is on, turn the PID control from "Manual" to "Auto".
11. Turn on oil pump when stagnation surface temperature reaches 400 °C.

A.2 Mass Spectrometer Startup

1. Start RGA 3.0 software from Windows Start Menu.
2. Connect to RGA probe via connections menu.
3. Switch to "P vs T" mode.
4. Switch Y axis to units of amps.
5. Open scan parameters.
6. Set "P vs T" mode to monitor following species.
   (a) H₂ at 2 amu.
   (b) CH₄ at 15 amu.
   (c) Water at 18 amu.
   (d) Carbon monoxide at 28 amu.
   (e) Oxygen at 32 amu.
   (f) Argon at 40 amu.
   (g) Carbon dioxide at 44 amu.
7. Turn on Kurt Lesker ion pressure gauge. Wait for mass spectrometer (MS) chamber pressure to read 5.0E-08 torr.
8. Open valves on sample transfer line.
9. Start filament (MS chamber pressure will spike, should return to 5.0E-08 torr).
A.3 Boundary-Layer Measurement

1. Wait for stagnation surface to reach desired temperature.
2. Increase argon flow to desired flow for experiments.
3. Start "Manip.vi".
4. Verify quartz microprobe is close to the catalyst surface by moving the probe to the surface and then backing off 5/1000 inch.
5. Open mass spectrometer leak valve until mass spectrometer chamber pressure is 2.0E-06 torr.
6. Start "P vs T" scan on RGA 3.0 software.
7. Run Ar for 2-3 minutes before turning on reactants.
8. Switch on flow of reactants (CH₄, CO₂, O₂).
9. Verify power output to heater.
10. Verify that all gases are flowing at specified rates.
11. Wait for steady state operation, usually 10 minutes.
12. Move quartz microprobe to next measurement position by holding "send command" on "manip.vi" until stepper motor movement is observed.
13. Record position of probe within boundary layer and time of movement in lab notebook.
14. Repeat steps 11 and 12 for different measurement positions within boundary layer. Hold each position for approximately 3 mins (time to reach steady state).
15. Once boundary layer measurements are complete, stop "P vs T" scan on RGA 3.0 software.
16. Save data as ascii text file.

A.4 Shutdown Procedure

1. Turn off MS filament and disconnect.
2. Close leak valve on MS chamber.
3. Shut off Kurt Lesker ion gauge.
4. Stop flow of all reacting gases.
5. Change flow rate of argon to 7 slm.

6. Move quartz microprobe probe to a distance far from the stagnation surface (\(\approx\)1 cm).

7. Switch PID heater control to manual mode and set heater command signal for power supply to nearest whole number.

8. Turn off oil pump when annulus gases are below 100 °C.

9. Continue to reduce power output until surface temperature is below 300 °C.

10. Set "Low Output" range to zero, then command signal to zero.

11. Stop flow of Ar.

12. Shut off BOC edwards scroll pump.

13. Stop "StagnationFlowReactor.vi".

14. Close all valves.

15. Open switches supplying power to power supply and vacuum pump.
APPENDIX B

MASS SPECTROMETER CALIBRATION

The quadrupole mass spectrometer (consisting of the SRS RGA 200 and vacuum system) is calibrated using independent gas mixtures with known concentrations of CH$_4$, CO$_2$, CO, H$_2$ and Ar. Water vapor (H$_2$O) is not measured in these experiments. For steam reforming experiments, the water content is back calculated based on the oxygen atom balance using Ar as an internal standard. This section describes the mass spectrometer calibration and data processing used to convert mass spectrometer signals to mole fractions.

B.1 SRS RGA 3.0 Software

The SRS RGA 3.0 software is used to read signal intensity from the SRS RGA 200. The software is operated in "P vs T" mode. In "P vs T" mode the signal intensities for several specified mass to charge ratios are measured as a function of time. The signal intensities have units of amps.

B.2 Gas Compositions

Calibration gas compositions are selected based on the maximum mole fractions expected to be observed in the stagnation-flow experiments. For example if a maximum mole fraction of CO$_2$ is expected to be no more than 20 percent, than the maximum gas composition for the CO$_2$ calibration will be approximately 25 percent. All gas compositions are mixed with Ar as the diluent. Ar is also used as the in-
Table B.1: Mass spectrometer sensitivity factors.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Range</th>
<th>$R^2$</th>
<th>Slope</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>0-12%</td>
<td>0.9994</td>
<td>1.7401</td>
<td>-0.0002</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0-22%</td>
<td>0.9993</td>
<td>1.3518</td>
<td>-0.0018</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0-8%</td>
<td>0.9981</td>
<td>2.2935</td>
<td>0.0006</td>
</tr>
<tr>
<td>CO</td>
<td>0-11%</td>
<td>0.9997</td>
<td>1.5673</td>
<td>-0.0072</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0-8%</td>
<td>0.993</td>
<td>0.2327</td>
<td>-0.0012</td>
</tr>
</tbody>
</table>

ternal standard. The gases are calibrated independent of each other. The gases are metered using Alicat mass flow controllers and mixed prior to measurement in the stagnation-flow reactor.

### B.3 Calibration Curves

Calibration curves are created by plotting the Ar normalized signal intensity of gas $k$ ($\frac{s_k}{s_{Ar}}$) by the Ar normalized mole fraction of gas $k$ ($\frac{X_k}{X_{Ar}}$). Mass spectrometer signals for the gases of interest (H$_2$ at 2 amu, CH$_4$ at 15 amu, CO at 28 amu, O$_2$ at 32 amu, Ar at 40 amu, and CO$_2$ at 44 amu) are measured relative to Ar, a chemically inert component of the reactant streams. This serves to eliminate signal changes by instrument instabilities. The only cross sensitivity considered is the CO$_2$ contribution to the CO signal at 28 amu. Mole fractions are estimated based on the mass flow rates of gas $k$ and Ar.

Figure B.1 shows the calibration curves for the gases measured in this work. Extracting the slope and intercept for each of these calibration curves gives the instrument sensitivities to each gas. The sensitivity factors and the mole fraction range over which they are valid is listed in Table B.1.
Fig. B.1: Mass spectrometer calibration curves.
B.4 Conversion to Mole Fraction

This section describes the data processing required to convert the raw mass spectrometer signal intensities to mole fractions. First the signal intensity for each gas being measured is divided by the signal intensity for Ar. This value is then multiplied by the sensitivity factors presented in the previous section which gives a normalized mole fraction. The normalized mole fraction is divided by the sum of all normalized mole fractions.

\[
X_k = \frac{s_k c_k}{\sum_{j \text{All Species}} \frac{s_j}{s_{Ar}} c_j}
\]  \hspace{1cm} (B.1)

In the above equation \(X_k\) is the mole fraction for species \(k\), \(s_k\) is the mass spectrometer signal for species \(k\), \(c_k\) is the sensitivity factor for species \(k\) and \(s_{Ar}\) is the signal intensity for argon.
APPENDIX C

CO-PULSE CHEMISORPTION

This section describes in detail the chemisorption measurements and data processing to convert those measurements to an active surface area.

C.1 Chemisorption Results and Calculation of Active Surface Area

Figure C.1 shows a typical chemisorption result. The sample that produced the results in Fig. C.1 was exposed to 20 separate pulses of carbon monoxide. It is clear from the graph that at least the first 8 pulses completely chemisorbed onto the exposed Rh sites. At the 9th pulse there appears to be a small amount of CO breakthrough as measured by the thermal conductivity detector. Increasingly greater quantities of the carbon monoxide pulses reach the thermal conductivity detector until the Rh surface has been completely saturated with chemisorbed carbon monoxide molecules. Each pulse has a volume of approximately 10 $\mu$L.

The data processing to convert the thermal conductivity detector measurements occurs in several steps. The peak areas are calculated by the Peak simple software. First, an average of the last 2-3 pulses is taken and multiplied by the total number of pulses. The total area of all the pulses measured is subtracted from this value to determine the adsorbed area. Next, the adsorbed area is converted to an adsorbed volume by equating the average area of the last 2-3 pulses to the volume of the sample loop. The adsorbed volume is then normalized by the weight of the catalyst sample.

The adsorbed volume can also be converted to moles of adsorbed CO by the ideal gas law. A 1:1 adsorption stoichiometry between molecules of CO and molecules of
Fig. C.1: Typical CO pulse chemisorption result.

Rh. Therefore, each molecule of adsorbed CO constitutes a single open Rh site available for reaction. The number of exposed Rh atoms is divided by the total number of Rh loading of the catalyst sample

\[ A_{ads} = (N_{pulse,T})(A_{pulse}) - (A_{meas}) \]  \hspace{1cm} (C.1)

\[ V_{ads} = \frac{A_{pulse}}{(V_{sample\ loop})(A_{ads})} \]  \hspace{1cm} (C.2)

\[ CO_{ads} = \frac{(V_{ads})(P_{atm})}{(T_{atm})(R)} \]  \hspace{1cm} (C.3)

In the above set of equations \( A_{ads} \) is the total area adsorbed by the sample, \( N_{pulse,T} \) is the total number of pulses for a given experiment, \( A_{pulse} \) is the average of the last 2-3 pulses of an experiment once the sample surface has been saturated with CO molecules, and \( A_{meas} \) is the total area of all observed pulses according to the thermal conductivity detector. \( V_{ads} \) is the total volume of CO adsorbed by the sample, \( V_{sample\ loop} \) is the volume of a single pulse of CO, and \( CO_{ads} \) is the number of moles of CO adsorbed by the sample.