Catalytic Active Site, Mechanistic and Kinetic Studies of Dry (CO2) Reforming of Methane over Lanthanum Zirconate (La2Zr2O7) Pyrochlores

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CATALYTIC ACTIVE SITE, MECHANISTIC AND KINETIC STUDIES OF DRY (CO₂)
REFORMING OF METHANE OVER LANTHANUM ZIRCONATE (La₂Zr₂O₇)
PYROCHLORES

A Dissertation

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Abstract

Dry (CO₂) reforming of CH₄ (DRM) produces commercially important synthesis gas (H₂ and CO) with H₂/CO ≤ 1, which can be used for synthesis of higher alkanes and oxygenates. DRM is highly endothermic and requires temperatures as high as 800°C-1000°C to attain high equilibrium conversions. A major problem associated with DRM is catalyst deactivation due to carbon deposition. Thus it is imperative that the catalyst used for DRM must resist deactivation due to sintering and carbon deposition.

DRM is well studied in the literature over various catalysts, however, there is no literature, except the Ashcroft (1993) article, for DRM over pyrochlores. Pyrochlores are metal oxides (A₂B₂O₇), with larger rare earth metal occupying the A-site and smaller alkali earth or transition metal occupying the B-site. Ashcroft. et al. studied pyrochlore catalysts composed of rare-earth metals at A-site and catalytically active transition metals like Ru and Ir at B-site (e.g., Nd₂Ru₂O₇, Eu₂Ir₂O₇, and Gd₂Ru₂O₇). These pyrochlores lost their structure under CH₄ and CO₂ above 340°C. Unlike their work, we use La on A-site and Zr on B-site and only partially substitute the B-site with catalytically active Rh, Ru, or Pt. This La-Zr framework provides high thermal stability to the catalysts used in our study as compared to that by Ashcroft. The inherent lattice oxygen reactivity of pyrochlores helps to resist deactivation due to carbon formation.

In this work, Rh, Ru, or Pt substituted lanthanum zirconate pyrochlore catalysts were synthesized, characterized by X-ray diffraction (XRD), temperature programmed reduction (TPR), and X-ray photoelectron spectroscopy (XPS). The catalytic active sites and the mechanistic steps of DRM reaction were studied by means of kinetic rate modeling, isotopic labeling, in-situ Fourier transform infrared spectroscopy (FTIR), in-situ XPS and transient
pulsing of CH₄/CO₂. The rate limiting step in the DRM mechanism over pyrochlores was determined by studying the (CH₄/CD₄) deuterium kinetic isotope effect. A sequence of intermediate reaction steps was proposed based on these experimental results and kinetic rate modeling, to most closely depict the mechanism of DRM over pyrochlore catalysts.
Chapter 1: Introduction

1.1. Research Objective

Primary objective is to isomorphically substitute Rh, Ru, or Pt in the lanthanum zirconate (La$_2$Zr$_2$O$_7$) pyrochlores and study the catalytic active sites and the role these active sites play in kinetics and mechanism of dry reforming of methane (DRM).

1.2. Engineering Relevance of Project

Fossil liquid fuels are a major and extremely vital source of energy [1]. The usage of liquid fuels is expected to rise from 85.7 million barrels per day in 2008 to 112.2 in 2035. The U.S. Energy Information Administration reported that the U.S natural gas production is expected to increase from 23 trillion cubic feet in 2011 to 33.1 trillion cubic feet by 2040 [2]. With the depletion of the fossil liquid fuels and exponential increase in energy demand [3], there is a need to investigate other means to utilize the available abundant resources, like natural gas reserves, to produce fractions of compounds obtained from fossil liquid fuels [4]. One way of utilizing natural gas is by reforming it to synthesis gas which can later be used to synthesize higher hydrocarbons and oxygenated hydrocarbons by Fischer-Tropsch synthesis [5-12].

1.3. Rationale for Selecting La$_2$Zr$_2$O$_7$ Pyrochlore Catalyst

The major problem associated with DRM is catalyst deactivation due to carbon deposition [13-22]. Due to high endothermicity of DRM, the reaction condition requires high temperatures for reaching equilibrium conversions and this may sinter the catalytic sites causing deactivation [9, 23, 24]. Thus there is a need to design a catalyst with high thermal stability and resistance to carbon deposition. Lanthanum zirconate (La$_2$Zr$_2$O$_7$; designated LZ) pyrochlores
have been studied in the literature as thermal barrier coatings for steam turbines and aircraft propulsion systems [25-27]. These materials show high phase stability and low thermal conductivity at elevated temperatures [28, 29]. For obtaining a stable pyrochlore structure it is essential that the ratio of the A-site to B-site ion is between 1.4 and 1.8 [30-33]. The radii ratio of \( \text{La}^{3+} \) (co-ordination no: 8) and \( \text{Zr}^{4+} \) (co-ordination no: 6) is 1.61. Thus the combination of La and Zr provides structural stability and helps in maintaining the \( \text{A}_2\text{B}_2\text{O}_7 \) framework even at temperatures as high as 800-1000°C. Lanthanum zirconate pyrochlores are catalytically inactive but allow partial isomorphic substitution of transition metals like Ni, Rh, Ru, Pt on their Zr-site which adds catalytic activity [32]. Apart from high thermal stability and isomorphic substitution, the lattice oxygen of pyrochlore crystals is believed to be reactive which could act as a secondary oxygen source (\( \text{CO}_2 \) being the primary source) and prove beneficial in limiting carbon formation under DRM conditions [33-38].

For studying the kinetics of DRM it is important to have a structurally stable catalyst with resistance to sintering and thermal decomposition at high reaction temperatures. Carbon deposition is a major impediment in DRM but one way of limiting surface carbon is by increasing the pool of oxygen on the catalyst surface which can oxidize the surface carbon. Since La is basic in nature and \( \text{CO}_2 \) is mildly acidic, the presence of La on \( \text{La}_2\text{Zr}_2\text{O}_7 \) pyrochlores help in increasing \( \text{CO}_2 \) activation rate to form La-oxycarbonates which then oxidizes the surface carbon formed during DRM [9, 39]. Thus due to properties like strong thermal stability, reactive lattice oxygen, isomorphic substitution of catalytically active transition metals, efficient \( \text{CO}_2 \) activation; lanthanum zirconate pyrochlores are a well-suited choice as catalysts for DRM.
1.4. **Rationale for Rh as the Metal of Interest**

DRM is usually accompanied by simultaneous occurrence of reverse water gas shift (RWGS), methane decomposition (MD), and Boudouard reaction (BR). For studying the kinetics of DRM it is important to limit the extent of occurrence of these simultaneous reaction. The most effective way to achieve this is by using noble metals in place of metals like Ni, which are most widely studied for DRM in the literature [7, 16, 40-52]. Noble metals show high reactant conversion at lower temperatures compared to non-noble metals and limits deactivation due to carbon formation [41, 53-61]. Thus, we conducted preliminary activity and characterization studies on Ru, Pt and Rh as metals of interest for studying DRM. The characterization results showed that Ru was unstable in the pyrochlore structure and delocalized from the LZ framework to aggregate on the surface during H$_2$ reduction at 950°C [30]. The Pt and Rh pyrochlores were relatively stable within the pyrochlore structure under strong reducing conditions. The activity results showed that the final H$_2$/CO ratio of Pt pyrochlores was extremely low as compared to that of Rh and Ru pyrochlores and H$_2$-TPR of Pt pyrochlore was very similar to that of LZ suggesting ambiguity in the reducibility of Pt [62].

A study by Ghelamallah, et al [63], showed that Rh was well dispersed over Al$_2$O$_3$ in the presence of La$_2$O$_3$ (0.5%Rh/α-Al$_2$O$_3$-20%La$_2$O$_3$) as compared to without La$_2$O$_3$ (0.5%Rh/α-Al$_2$O$_3$). In that same study they also observed that Rh was much more stable than Pt (in 1%Pt/α-Al$_2$O$_3$-20%La$_2$O$_3$) as there was no significant difference in the dispersion of Rh on spent catalysts compared to fresh ones [63]. Rh was observed to preferentially interact with La$_2$O$_3$ (in 0.5%Rh/α-Al$_2$O$_3$-20%La$_2$O$_3$) and no change was observed upon addition of promoters like BaO (in 0.5%Rh/α-Al$_2$O$_3$-20%La$_2$O$_3$-10%BaO), whereas, Pt (in 1%Pt/α-Al$_2$O$_3$-10%BaO) showed strong interaction with BaO and no change was observed upon addition of La$_2$O$_3$ (in 1%Pt/α-
Al$_2$O$_3$-20%La$_2$O$_3$-10%BaO) to the catalyst [63]. Thus due to Rh-La compatibility, in order to have a stable pyrochlore structure, and optimum reactant conversion at low temperatures we selected Rh substituted pyrochlores to determine its catalytic active sites and to perform detailed kinetic and mechanistic DRM studies.

1.5. Outline of the Dissertation

Chapter 1 describes the background of this project, explains the engineering relevance of DRM and the rationale for studying DRM reaction over pyrochlore catalysts. The rationale for selecting Rh as an active metal as opposed to Ru, Pt or Ni to conduct comprehensive mechanistic study of DRM is also explained in this chapter.

Chapter 2-Chapter 7 are written in scientific journal format since these are either published papers or are under peer-review. These chapters may have the experimental procedures and equipment details repeated but the results are unique.

Chapter 2 is a published critical review paper [64], which comprehensively covers literature on DRM studies over noble (Rh, Ru, Pt, and Pd) metal catalysts. This discusses the effect of synthesis procedure, promoters, reaction temperature, and reactant composition on the performance of the catalyst. This chapter also differentiates between different classes of carbon that are formed during DRM and reviews the ways in which the deactivation due to carbon formation can be minimized.

Chapter 3 is a published paper [30] that presents characterization study of Ru and Pt substituted pyrochlores (LRuZ and LPtZ). The changes in the pyrochlore structure was studied by X-ray diffraction (XRD), H$_2$ and CH$_4$ temperature programmed reduction (TPR), and
temperature programmed surface reaction (TPSR). These results helped in understanding the changes in the structure of La$_2$Zr$_2$O$_7$ pyrochlore crystals as a result of partial Pt or Ru substitution on Zr-site. Chapter 4 is a published paper [62] and covers the activity studies of LRuZ and LPtZ that were characterized in Chapter 3. The difference in the activity of Ru and Pt metal is attributed to the difference in the surface concentration of the active metal (i.e., Ru or Pt). The carbon formed during DRM was characterized by temperature programmed oxidation (TPO).

Chapter 5 has been published in a peer-review journal [31] and presents characterization and activity studies on 2 wt% and 5wt% Rh substituted LRhZ pyrochlore catalysts designated as L2RhZ and L5RhZ, respectively. The freshly calcined pyrochlores were characterized by XRD, H$_2$ TPR, X-ray photoelectron spectroscopy (XPS), and their activity towards DRM was studied at different temperatures. The higher activity of L5RhZ compared to L2RhZ was attributed to the higher Rh surface concentration. The catalyst spent during DRM were characterized by XRD, TPO, and H$_2$ TPR to study the changes in the pyrochlore structure as a result of DRM.

Chapter 6 is a comprehensive study of CH$_4$ activation on Rh substituted pyrochlores which has been submitted for publication and is currently under review. This work determines the active sites and the significance of CH$_4$ activation step in DRM mechanism. This study shows that CH$_4$ is activated on Rh by direct dissociation mechanism to form surface carbon and H$_2$. The Rh sites on L5RhZ are fundamentally different from those on L2RhZ as seen by CH$_4$ TPR and Arrhenius plot. Activation energy, CH$_4$/CD$_4$ isotope effect, and kinetic rate modeling confirmed that activation of CH$_4$ is the rate limiting step in the DRM mechanism over these catalysts. The mechanism of oxidation of the surface carbon was studied by transient pulsing of CH$_4$ and CO$_2$ with Ar tracer and monitoring the pulse response in the product stream.
Chapter 7 is a study of active sites for CO\textsubscript{2} activation and intermediate mechanistic steps in DRM mechanism on L2RhZ and L5RhZ pyrochlores. This work has been submitted for publication and is under review. This chapter shows that the mildly acidic CO\textsubscript{2} is activated on basic La sites to form La-oxycarbonates. These La-oxycarbonates then carry out oxidation of surface carbon and simultaneously reduce itself to CO. Transient pulsing of CH\textsubscript{4} over La-oxycarbonates confirm that the oxidation of surface carbon occurs at Rh-La interfacial sites. Results from Chapter 5-Chapter 7 help in postulating a sequence of kinetically significant intermediate mechanistic steps of DRM and determining the active sites catalyzing these steps.

Chapter 8 presents the important conclusions from Chapter 2-Chapter 7 with some recommendation for future DRM work over pyrochlores.

Appendix A is a published paper [65] where DRM is studied over Ru substituted pyrochlores LSRuZ and Ru/Al\textsubscript{2}O\textsubscript{3} catalysts. This work compares DRM activity and stability of Sr (substituted on A-site) and Ru (on B-site) substituted LSRuZ pyrochlores to conventional supported Ru/Al\textsubscript{2}O\textsubscript{3} catalysts. The H\textsubscript{2} TPR results show fundamental differences in the catalytic active sites over LSRuZ compared to Ru/Al\textsubscript{2}O\textsubscript{3}. This difference in active sites is also responsible for the apparent difference in the reactant conversion and type of carbon formed during DRM at varying temperatures.

1.6. References


Chapter 2 : A Review of Dry (CO₂) Reforming of Methane over Noble Metal Catalysts *

2.1. Introduction

2.1.1. Rational for Studying DRM

Fossil fuels are our major source of energy and have a great impact on human welfare [1, 2]. With the depletion of these fossil fuels due to continuously increasing energy demand, there is a need to investigate ways to utilize the available resources like natural gas reserves to produce fuels and chemicals that are fossil fuel derivatives [2, 3]. Recent findings by the US Energy Information Administration have shown the presence of over 280 million cubic feet of proven natural gas reserves and 850 trillion cubic feet of estimated recoverable resources in the United States. These large reserves will help the global economy by providing affordable clean fuel and a dependable feedstock for chemical production.

Apart from the natural gas reserves, biogas produced from anaerobic decomposition of organic material is also a source of gas with nearly equal concentrations of CH₄ and CO₂ [4]. For example, landfill gas (usually composed of 45–55% CH₄, 30–40% CO₂, 0–5% O₂, balance N₂) constitutes approximately 37–57 million tons of CH₄ which amounted to 13-20% of total US CH₄ production in 2006 [5, 6]. Since CH₄ is the primary component of natural gas obtained from petroleum reserves [7] and landfill gas [5, 6], the conversion of CH₄ to higher value products will become increasingly important for the foreseeable future. Among the most widely studied technologies for conversion of CH₄ to syngas (mixture of H₂ and CO) are various reforming

techniques like steam (H₂O) reforming (SR), dry (CO₂) reforming of methane (DRM), partial oxidation (PO), autothermal reforming (AR) [8, 9]. These reforming techniques differ in the oxidant used, final H₂/CO product ratio [10], and the kinetics and energetics of the reaction. SR yields synthesis gas with the H₂:CO ratio of about 3:1 [11], and can be used directly for synthesis of products which require high H₂/CO ratio, such as the synthesis of methanol and ammonia [12]. Reforming of methane with various combinations with O₂/H₂O/CO₂ is called ‘mixed’ reforming, and is used to control H₂/CO ratio of the product stream simply by changing the ratio of H₂O, CO₂, and O₂. However, in spite of the deactivation issues, Ross, et al [13], conclude that DRM has a 20% lower operating cost compared to the other reforming processes. There are certain disadvantages associated with these reforming processes. For example, SR generally produces CO₂ along with CO and H₂. Purification of this syngas to remove CO₂ is a concern for the petroleum industry [13]. The H₂/CO ratio obtained from SR is too high to be used for methanol or other oxo-alcohol synthesis [14]. Because PO is a highly exothermic reaction, there are safety issues associated with operating at high space velocities [15]. DRM, reforming of CH₄ using CO₂, produces high purity syngas containing little CO₂, with H₂/CO ratio ≤ 1[16, 17] but is highly endothermic. One example of its use in sustainable energy production is in solar-chemical energy transmission systems [18-21], where the heat from the renewable resources like the sun can be used to drive the endothermic reaction forward. DRM utilizes two abundantly available green-house gases to produce industrially important syngas and can reduce net emissions of these gases provided the energy required for carrying out this reaction comes from a non-hydrocarbon source like solar or nuclear [22, 23]. Although Fischer-Tropsch (FT, eqn 1) synthesis requires H₂:CO ~2:1 ratio; synthesis gas with lower H₂/CO ratio (~1) such as that from DRM increases the selectivity of long chain hydrocarbons [10, 13, 18, 19, 24-28].
\[ n \text{ CO} + (2n+1) \text{ H}_2 \rightleftharpoons C_n\text{H}_{2n+2} + n \text{ H}_2\text{O} \] (1)

In this case, an Fe-based catalyst is used to produce the needed hydrogen via water-gas shift (eqn 2) [12, 29, 30].

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad (\Delta H_{298K} = -41.2 \text{ kJ mol}^{-1}) \] (2)

The overall stoichiometry is then the sum of eqn 1 and eqn 2,

\[ 2n \text{ CO} + (n+1) \text{ H}_2 \rightleftharpoons C_n\text{H}_{2n+2} + n \text{ CO}_2 \] (3)

In this case the required H\textsubscript{2}/CO ratio for FT over Fe based catalyst is (n+1):2n, which is always less than 1 for \( n \geq 2 \). This is the feed ratio obtained from DRM with simultaneous occurrence of the reverse WGS reaction and can be a direct feed for FT synthesis for more selective synthesis of higher hydrocarbons. For example, Fujimoto, et al. [31], used a two-reactor system with DRM used to produce syngas which is followed by FT in the second reactor, producing higher alkanes from DRM-derived syngas.

### 2.1.2. Brief Historical Context of CH\textsubscript{4} and Hydrocarbon Reforming

DRM was first studied by Fischer and Tropsch in 1928 over Ni and Co catalysts. They observed severe deactivation due to carbon deposition [32]. The deactivation problem was later addressed for the more general case of steam/CO\textsubscript{2} reforming of hydrocarbons by Reitmeier, et al [33] in 1949. They determined a relationship between reactant composition and carbon deposition that helped identify conditions for reforming without carbon deposition. This relationship helped in determining the reactant composition (CH\textsubscript{4}, CO\textsubscript{2} and H\textsubscript{2}O), equipment type and operating conditions needed to produce syngas of a desired H\textsubscript{2}/CO ratio (in the range of 0.5–3) without significant carbon deposition.
A new approach to hydrocarbon reforming was reported in 1949 by Lewis, et al [34], who used a Cu oxide supported catalyst to selectively oxidize methane to CO and H₂. Lewis used stoichiometric amount of metal oxide in order to supply just enough oxygen to selectively oxidize the hydrocarbon to CO and H₂ and named this method “stoichiometric control”. This process consisted of two stages: in the first one, the hydrocarbon was partially oxidized to CO and H₂ and in the second stage the metal oxide was reoxidized. However, the reaction rates in this approach were low and significant carbon deposition was observed. The synthesis of reforming catalysts for methane and higher vaporizable hydrocarbons was first reported by Rostrup-Nielsen in 1964 [35]. The synthesis procedure proposed co-precipitation of fine sludge containing mixture of aluminum hydroxide, magnesium oxide and nickel hydroxide. Upon calcination at 800-1100°C, the Al and Mg form the spinel framework and some basic Mg remains on the surface, acting as a promoter in activation of CO₂ and promoting oxidation of surface carbon [35]. However, they did not identify the mechanism by which these promoters limited deactivation due to carbon formation. This concept of use of basic promoters to inhibit carbon formation has been used by several later researchers. In 1979, Sodesawa, et al [36] studied Ni/SiO₂ catalysts and observed that this catalyst was more stable than the ones reported in the literature prior to 1979 and showed higher selectivity towards CO formation as opposed to carbon deposition. In 1988, Gadalla, et al [10, 12] reported a detailed study on Ni/Al₂O₃ catalysts and reported that carbon formation can be inhibited by increasing the CO₂:CH₄ inlet gas ratio. They first showed that for every CO₂:CH₄ ratio there is an optimum temperature range for uninterrupted DRM operation, below which carbon formation occurs and above that Ni carbide is formed.
2.2. Reaction Thermodynamics

DRM (eqn 4) is an extremely endothermic reaction:

\[
\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2 \quad (\Delta H_{298K}^\circ = +247 \text{ kJ mol}^{-1}) \quad (4)
\]

\[
\Delta G^\circ = 61770 - 67.32 T
\]

Thus it requires extremely high temperatures to attain high equilibrium conversions to syngas [37, 38]. Tomishige, et al [39], suggested adding an oxidant like O\textsubscript{2} to partially or completely oxidize the methane and use the exothermicity of the reaction (eqns 5, 6) to supply the necessary heat directly to the DRM reactant mixture. The \text{CO}_2 and \text{H}_2\text{O} produced in eqn 6 act as co-reactants to further carry out SR and DR of \text{CH}_4 [39-41]. To avoid high temperature gradients, Tomishige, et al. propose to use fluidized bed reactors which would improve heat transfer and stability of the catalyst. A combination of combustion and reforming would make the overall process thermo-neutral and help in limiting carbon formation [4].

\[
\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO} + 2\text{H}_2 \quad (\Delta H_{298K}^\circ = -36 \text{ kJ mol}^{-1}) \quad (5)
\]

\[
\text{CH}_4 + 2\text{O}_2 \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{O} \quad (\Delta H_{298K}^\circ = -803 \text{ kJ mol}^{-1}) \quad (6)
\]

\[
\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \quad (\Delta H_{298K}^\circ = 41.2 \text{ kJ mol}^{-1}) \quad (7)
\]

\[
\Delta G^\circ = -8545 + 7.84 T \quad (K)
\]

Since the metallic state of Pt is much more stable than that of Ni, for reaction with O\textsubscript{2} and \text{CO}_2 as oxidants, noble metals like Pt are preferred. Using membrane reactors can also prove beneficial to overcome the thermodynamic limitations of the reaction; e.g., Pd-Ag membranes have been shown to catalyze DRM and can remove hydrogen selectively from the product, driving the reaction toward hydrogen and CO formation [42, 43]. Eqn (4) shows that DRM produces a syngas with a H\textsubscript{2}/CO ratio close to 1:1, but the simultaneous occurrence of reverse water gas shift (RWGS) (eqn 7) reaction causes a decrease in the H\textsubscript{2}/CO ratio to values <1 [18,
Apart from RWGS, other side reactions may occur simultaneously with DRM depending on the operating temperature and reactant partial pressure. These include CH₄ decomposition (eqn 8, MD), where CH₄ dissociates completely to form solid carbon on the catalyst surface and produce H₂, and the Boudouard reaction (eqn 9, BR) where CO disproportionates to form surface carbon and CO₂. The standard free energies can be used to determine the driving force for these side reactions at different temperatures. From these free energy values Wang, et al [38] [Figure 2.1], inferred that DRM proceeds in the forward direction above 640°C.

\[
\begin{align*}
\text{CH}_4 & \rightleftharpoons C(s) + 2\text{H}_2 & (\Delta H_{298K} = +75 \text{ kJ mol}^{-1}) \\
\Delta G^\circ &= 2190 - 26.45 \text{ T} \\
2\text{CO} & \rightleftharpoons C(s) + \text{CO}_2 & (\Delta H_{298K} = -171 \text{ kJ mol}^{-1}) \\
\Delta G^\circ &= -39810 + 40.87 \text{ T}
\end{align*}
\]

Figure 2.1. Temperature curve for carbon formation at different total pressures below which carbon formation is inevitable irrespective of the CO₂/CH₄ feed ratio. (Reprinted with permission from [38]. Copyright 1996 American Chemical Society)
Similarly, RWGS can occur only up to 820°C and carbon formation can occur due to MD above 557°C and due to BR below 700°C. Thus Wang, et al. suggested that carbon formation can occur due to both MD and BR in 557-700°C range. This is in agreement with the result in Figure 2.1, which suggests that at CO₂/CH₄ ratio of 1, there will be carbon formation below 870°C at 1 atm of total pressure.

The thermodynamic equilibrium plots for DRM as a function of temperature at 1 atm are shown in Figure 2.2. Figure 2.2 (a) shows the DRM equilibrium amount when only H₂, CO, and H₂O are allowed to form. This calculation shows that the H₂/CO ratio at all temperatures after 300°C is between 0.8-1. Formation of H₂O by RWGS is only significant between 400-800°C, which is in agreement with the free energy calculations by Wang, et al [38].

However, this same calculation, when a separate solid phase of carbon is allowed [Figure 2.2 (b)] to accommodate for MD and BR, shows an entirely different equilibrium composition. The H₂/CO ratio is far greater throughout the temperature range when C(s) is allowed. The H₂/CO ratio at temperatures below 900°C is greater than unity because increased carbon formation lowers the amount of CO formed and hence increases the H₂/CO ratio. Above ~900°C, little carbon is present, bringing the H₂/CO ratio close to 1:1. These calculations also show that C(s) formation is thermodynamically inevitable under 900°C, in agreement with Figure 2.1.

Nematollahi, et al [45], conducted the same thermodynamic simulations at various pressures and determined that the conversion of CH₄/CO₂ and the H₂/CO yields both drop significantly with increasing operating pressure. Thus, it is essential to operate at low pressures to attain high conversions and high H₂/CO yields.
Figure 2.2. Thermodynamic equilibrium plots for DRM at 1 atm, from 0-1000°C and at inlet feed ratio of CO$_2$/CH$_4$=1. (a) Assuming no carbon formation occurs, (b) Assuming carbon formation occurs. These plots were created by using Gibbs free energy minimization algorithm on HSC Chemistry 7.1 software. (Reprinted with permission from [46]. Copyright 2013 Elsevier.)
2.3. **Noble Metal Catalysts for DRM**

Thermodynamic analysis shows that DRM requires reaction temperatures as high as 900°C to attain high syngas yields. Even though not thermodynamically favored at high temperatures, the reaction is inevitably accompanied by carbon deposition [19, 47]. At these high temperatures, supported metal catalysts are prone to deactivation due to sintering [20] or irreversible reaction with the support, e.g., forming inactive spinels. Thus, there is a need to develop a thermally stable catalyst that will resist deactivation due to carbon deposition and sintering [19, 27, 48, 49]. The overall activity of the catalyst towards DRM depends on the type of the metal used, nature of the support, surface area of the support, metal particle size, and the interaction between the metal and support [50, 51].

Noble metals like Pt, Rh and Ru are highly active towards DRM and are more resistant to carbon formation than other transition metals [44, 52-55], but are expensive. The high activity of Ru and Rh has also been theoretically proven by first principle calculations, where Ru and Rh had higher activity compared to Ni, Pd, Pt at the same particle size and dispersion [56]. Thus promoting Ni catalysts with noble metals like Rh, Pt, Pd or Ru, adds to the activity of the catalyst and these catalysts appear to be more stable against carbon formation than non-promoted Ni catalysts [57-60]. For example, bimetallic Ni-Pt supported on ZrO₂ have high and stable activity for prolonged period of time as compared to monometallic Ni/ZrO₂, and hence have shown potential industrial application for DRM [61]. In another example, the presence of Rh keeps the Ni in metallic form by hydrogen spill-over, minimizing the formation of Ni oxide, so that there is little activity loss [58]. This approach where a noble metal helps to keep Ni in an active, metallic form was also studied by XANES [62], where noble metal promoters increase the reducibility of Ni by hydrogen spillover, resulting in higher activity of Rh-Ni/Al₂O₃ catalysts than Ni/Al₂O₃.
A similar effect was observed where Co/TiO₂ catalyst deactivated due to oxidation of metallic Co by CO₂. However, promotion with Pt and Ru helped maintain Co [Figure 2.3] in metallic (Co⁰) form and increased activity and stability of the catalyst [63, 64].

Figure 2.3. Conversion of CH₄ vs time on stream for (a) Co/Pt and (b) Co/Ru catalysts at CH₄/CO₂=1, 750°C, 2MPa, SV=12000 ml g⁻¹ h⁻¹. (□) Pt or Ru: Co=0.05; (◊) Co only. (Reprinted with permission from [63]. Copyright 2004 Elsevier.)
In another example, the activity and stability of bimetallic Ni-Pd catalysts was much greater than monometallic Ni catalyst [60], consistent with the hypothesis that Pd helps prevent oxidation of Ni. In this case, the Ni: Pd ratio of 4:1 was optimum and any other ratio either had lower activity or deactivated with time [60].

The pre-treatment reduction temperature also has an important effect on the activity and stability of these catalysts, with lower reduction temperatures generally being preferred. Pt/ZrO$_2$ catalysts reduced at 200°C showed higher activity (CH$_4$ and CO$_2$ conversion) than the catalyst reduced at 500°C [65]. Ru/La$_2$O$_3$-SiO$_2$ reduced at 400°C showed higher activity than the same catalyst reduced at 550°C [66]. Different reduction temperatures could change the particle size (or dispersion) of the metal, resulting in a change in the observed activity of the catalyst [66, 67].

### 2.3.1. Role of Support on Catalyst Activity

DRM has been studied over a series of supported Pt, Pd, Rh, and Ru catalysts [68-72] and other supported transition metals like Co and Fe [73, 74]. The most widely used metal for this reaction is Ni [75-78], but many Ni-based catalysts undergo severe deactivation due to carbon deposition and subsequent loss of activity over time [21, 79]. A number of supports for these active metals have also been investigated, including SiO$_2$, La$_2$O$_3$, ZrO$_2$, TiO$_2$, CeO$_2$, Al$_2$O$_3$, and MgO.

The activity, kinetics and mechanistic steps over these various catalysts have been studied in order to minimize carbon formation [80-82] and other mechanisms of deactivation. There is a strong agreement in the literature that the mechanism of DRM is bi-functional: CH$_4$ is activated on the metal and CO$_2$ activates on an acidic/basic supports. For catalysts supported on relatively inert materials like SiO$_2$, the mechanism is thought to follow a mono-functional pathway, where both reactants are activated by the metal alone. On acidic supports CO$_2$ activates
by formation of formates with the surface hydroxyls and on basic supports by forming oxy-
carbonates [83, 84]. However, on inert supports, once carbon formation occurs by
dehydrogenation of methane, subsequent activation of CO₂ and reaction with carbon is limited,
leading to deactivation [83, 84]. Thus catalysts based on inert supports like SiO₂ have relatively
weak metal-support interaction and are less stable and less active compared to the mildly acidic
(Al₂O₃) or basic (La₂O₃, CeO₂) supports [85-87].

This weaker interaction between metal and inert supports has an advantage over
acidic/basic supports and is reported to improve the metal-metal interaction in case of bimetallic
catalysts. For example, a combination of Rh-Ni supported on boron nitride (BN) has shown
higher DRM activity (CH₄ and CO₂ conversion) as well as stability to deactivation compared to
Rh-Ni on γ-Al₂O₃ [88] [Figure 2.4]. The stability of these bimetallic catalysts is attributed to the
negligible metals-support interaction due to the inert nature of BN, which allows the metal
clusters to migrate freely and form Rh-Ni clusters. This atomically close proximity of Rh to Ni
decreases carbon formation on Ni without compromising its inherent activity [88]. However, this
stability due to metal mobility was not observed for Rh-Ni/γ-Al₂O₃. The strong interaction of
these metals with γ-Al₂O₃ did not allow Rh-Ni bimetallic cluster formation, suggesting that the
support plays an important role in the DRM mechanism. However, the effect of metal mobility
on dispersion or agglomeration of the active metal particles was not addressed in this [88] study.
The nature of the support also depends on the type of the active metal used. Formation of
bimetallic Rh-Ni clusters may not have been assisted by γ-Al₂O₃ as seen in by Wu, et al [88], but
the same γ-Al₂O₃ showed bimetallic formation when Pt (in place of Rh) was used with Ni
catalyst. Miguel, et al [89], observed formation of Pt-Ni bimetallic cluster which increased the
reducibility of Ni, resulting in higher and more stable activity for over 6500 min.
Figure 2.4. Comparison of the CH$_4$ conversion observed over Rh$_{0.1}$Ni$_{10}$/BN and Rh$_{0.1}$Ni$_{10}$/γ-Al$_2$O$_3$ at 700°C and 1 atm. (Reprinted with permission from [88]. Copyright 2009 Elsevier.)

Apart from catalysts based on single oxide supports, catalysts based on mixed oxide supports like ZrO$_2$-SiO$_2$ have also been studied. For example, Reddy, et al [90], prepared Pt/ZrO$_2$-SiO$_2$ by deposition-precipitation. In this method ZrO$_2$ is precipitated in colloidal silica solution in the presence of ammonia. This precipitated Zr and Si complex is dried/calcined and is followed by deposition of Pt. This novel approach was used for the synthesis of highly stable Pt catalysts and the activity of the final catalyst was a strong function of the ZrO$_2$:SiO$_2$ ratio [90]. For ZrO$_2$: SiO$_2$ = 4:1, the activity and stability was the highest followed by pure ZrO$_2$ > 3:1 > 2:1 > pure SiO$_2$. ZrO$_2$ improved the activation of CO$_2$ as compared to pure SiO$_2$, and the presence
of small proportion of SiO\textsubscript{2} was important in increasing the Pt-ZrO\textsubscript{2} interfacial area. The Pt-ZrO\textsubscript{2} interfacial sites are active for oxidation of the surface carbon and thus minimize deactivation of the catalyst for DRM [90]. This suggests that not only the nature of the support is important but the complex interfacial site chemistry and the particular active metal-support combination is very crucial for catalysis of DRM [91].

Other than being directly involved in the reactant activation process on its acidic or basic sites, the supports also play an indirect role in the reaction mechanism by affecting the metal particle size or metal dispersion [87, 92, 93]. Tsipouriari, et al [93], reported a study of 0.5% Rh supported on SiO\textsubscript{2}, TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, MgO, CeO\textsubscript{2}, YSZ and observed that the activity and deactivation characteristics of the catalysts were a strong function of the support. Supported Rh was also studied by Yokota, et al [94], where they supported 0.5% Rh on various materials and observed the changes in the Rh dispersion and activity as a result of change in the support. The EXAFS [Figure 2.5 (a)] show a feature at 0.24 nm confirming the intensity of Rh-Rh neighbor interaction. The Rh atoms in Rh foil have the highest amount of nearest Rh neighbors and is highly coordinated with Rh atoms. In case of Rh-oxide, the Rh-Rh coordination would be less than that of Rh foil. Thus a decrease in Rh-Rh coordination would mean increase in Rh dispersion. Keeping in view that the metal content, metal precursor and the synthesis procedure [of catalysts in Figure 2.5 (a)] is exactly the same; a decrease in the Rh-Rh coordination suggests that Rh dispersion is increasing in the order TiO\textsubscript{2} < MgO < SiO\textsubscript{2} < MCM-41 < γAl\textsubscript{2}O\textsubscript{3}. Thus Rh dispersion is a strong function of support alone. The Rh dispersion as determined by CO chemisorption increases in the order TiO\textsubscript{2} < La\textsubscript{2}O\textsubscript{3} < CeO\textsubscript{2} < ZrO\textsubscript{2} < MgO < SiO\textsubscript{2} < MCM-41 < γ-Al\textsubscript{2}O\textsubscript{3}, in agreement with EXAFS.
Figure 2.5. (a) EXAFS: Rh K-edge Fourier Transform for Rh catalysts with varying supports. (b) XANES: Rh K-edge spectra for Rh/supported catalysts. (Reprinted with permission from [94]. Copyright 2002 Springer.)
The XANES results [Figure 2.5 (B)] show that Rh/TiO₂ spectrum is very similar to Rh foil suggesting that Rh is metallic in nature on TiO₂. Whereas, the spectrum (or the white line) for Rh/γ-Al₂O₃ more closely resembles that of Rh₂O₃, suggesting that Rh in Rh/γ-Al₂O₃ has more cationic character. This shows that the properties of the support have a profound effect on the electronic structure of the metals, which affects its dispersion/activity of the catalyst for DRM [94].

Although presence of TiO₂ maintains the metallic nature of Rh it has certain disadvantages like, TiO₂ is reducible support and is believed to mask the catalytically active metal by being partially reduced to TiOₓ, which then forms a layer over Rh in an Rh/TiO₂ catalyst. The reduction of TiO₂ to TiOₓ generates vacancies which enhances surface diffusion of TiOₓ and the migration of TiOₓ to the Rh surface, which decreases the surface energy of the system [95, 96].

2.3.2. Role of Promoters and Synthesis Procedure

Sigl, et al [97], showed that using V₂O₅ as a promoter forms an over-layer of VOₓ on Rh/SiO₂ which breaks down the larger ensembles into smaller Rh particles. This increases the dispersion of Rh and thus increases the number of sites for activation of CH₄, and the activity compared to the non-promoted Rh/SiO₂ catalyst. Increased Rh dispersion creates interfacial sites which also decreases carbon formation [98].

Promoters like V₂O₅ on Rh/SiO₂ catalysts can increase the activity of the catalyst 15-20 fold compared to non-promoted catalysts [97], primarily by increasing Rh dispersion and TOF for CO formation as a result of V₂O₅ promotion of Rh/SiO₂ catalyst [Figure 2.6]. Stagg, et al [99], observed that Sn-promoted Pt/ZrO₂ and Pt/SiO₂ had lower activity and deactivated more
rapidly than non-promoted Pt/ZrO₂ and Pt/SiO₂. This was attributed to Sn-Pt alloy formation. They observed that when catalysts were prepared by co-impregnation of Sn and Pt on ZrO₂, the catalyst deactivated but when it was prepared by surface reductive deposition, the Sn-promoted catalyst showed increased activity and greater deactivation resistance than the non-promoted monometallic and co-impregnated bimetallic catalyst [99]. This illustrates that the synthesis procedure in which the promoter is added plays an important role in determining the effect of promoter on the catalyst activity.

![Graph showing TOF for CO formation at 450°C vs WHSV for Rh/SiO₂ and Rh/VOₓ/SiO₂ as measured at 0.1 MPa, CH₄:CO₂=1:1. (Reprinted with permission from [97]. Copyright 1999 Springer.)](image)

The effect of sequential versus co-impregnation of promoter Ce on Pt/ZrO₂ catalyst was reported by Ozkara-Aydinoglu, et al [100]. They observed from X-ray photoelectron spectroscopy (XPS) that co-impregnation of Ce adds to the cationic character of Pt which
increases the oxygen transfer properties of the support. Co-impregnation, as opposed to sequential impregnation, creates closer interaction between Pt and Ce which increases the oxygen storing properties of the catalysts, making it more resistant to carbon deposition [100]. SEM-EDX results showed that the interaction between Ce and Pt was significantly lower for the sequentially impregnated Ce-Pt/ZrO₂ catalysts, explaining why the co-impregnated catalysts have high activity and resistance against carbon formation than the sequentially-impregnated catalyst.

The impregnation procedure is extremely important in designing an active and stable catalyst for DRM. For example, the activity of co-impregnated 0.4%Pt-4%Ni/Al₂O₃ catalyst was compared to the same catalyst synthesized by reverse microemulsion (RME). In RME, two reverse micelle solutions were used, one with the reducing agent (N₂H₂) and the other with the metal (Ni and Pt) precursors as reported by Garcia, et al [101]. They observed that since RME involves liquid phase synthesis, the catalysts had higher metal dispersion and thus greater activity than the impregnated catalysts. The highly dispersed and smaller Pt and Ni particles obtained from RME compared to impregnation was confirmed by XRD and TEM [101].

The ratio of promoter to the active metal is also as crucial as the synthesis procedure in the stable operation of the DRM catalyst. Ballarini, et al [102], studied Na, K and Mg promoted catalysts for 0.02%Pt/Al₂O₃, 0.1%Pt/Al₂O₃, and 0.5%Pt/Al₂O₃. They observed that 0.02%Pt/Al₂O₃ promoted with K or Na showed no observable difference in activity, while promotion with Mg showed CH₄/CO₂ conversion greater than for K- or Na-promoted 0.02%Pt/Al₂O₃. Similarly, 0.1%Pt promoted with Mg showed higher activity than the same catalyst promoted with K and Na, although all three catalysts showed deactivation. However, when the Pt loading was increased to 0.5%Pt, the K-promoted catalyst showed higher activity
than the same 0.5%Pt promoted with Mg or Na. There was no deactivation observed for any 0.5%Pt catalysts. This suggests that the promotion effect of the promoter is a strong function of the promoter to active metal ratio [102].

2.3.3. Crystalline Oxide Catalysts

In addition to the conventional supported catalysts, a class of catalysts that have rarely been studied in the literature for DRM are crystalline oxides. Though they are typically inactive as bulk materials, catalytically active metals can be isomorphically substituted into the structure to produce a catalyst that is active for DRM and other reforming reactions. In these materials, the active metal is bound within the structure, producing a catalyst that is thermally stable at high temperatures required for DRM and related reactions. In addition, some of these materials have inherent oxygen mobility that can be enhanced by the substitution of active metals in the lattice, helping to minimize the inevitable effects of carbon deposition. A number of these materials have been investigated for various reforming reactions, including perovskites, pyrochlores, fluorites and hexaaluminates [103-109].

Pyrochlores are highly crystalline mixed metal oxides with the general formula: $A_2B_2O_7$ [Figure 2.7]. The A-site of these materials is usually occupied by the large rare-earth trivalent metal such as La and the B-site is occupied by a smaller tetravalent transition metal such as Zr. These materials were first used to study DRM by Ashcroft, et al [110-112]. They prepared and tested a range of pyrochlores such as $Eu_2Ir_2O_7$ but observed that these materials could not retain the pyrochlore structure above 340°C (under DRM gases) and disintegrated into amorphous $Eu_2O_3$ and metallic Ir. They studied different combinations of rare-earth metals (e.g., Nd, Sm, Gd, Eu) and catalytically active transition metals (like Ru, Ir). However, no catalyst retained the crystalline structure under DRM conditions. A modified approach was used by Pakhare, et al.
in which a metal such as Rh, Ru or Pt was only partially substituted at a low level (2-5 wt %) on the B-site of the La$_2$Zr$_2$O$_7$ pyrochlore. Among other constraints, this sort of substitution is limited to metals meeting the criterion that the pyrochlore structure is stable only if the ionic radii ratio of A-site to B-site metal ion is in the range of 1.4-1.8 [46, 115, 116]. If the ratio exceeds 1.8, a perovskite phase is formed and if the ratio is below 1.4, a fluorite structure is formed. Pakhare, et al [107, 113, 114] observed that the pyrochlore structure and the catalytic activity for DRM were retained at temperatures as high as 900°C for their Rh-, Ru- and Pt-substituted pyrochlores. These materials also have inherent lattice oxygen conductivity which limits carbon formation [details in section 2.6].

Figure 2.7. Pictorial representation of the pyrochlore structure showing the arrangement of the A, B and O sites in the lattice. (Reprinted with permission from [107]. Copyright 2008 Elsevier.)

Apart from the Ashcroft and Pakhare studies, we are aware of no other reports of pyrochlores used as catalysts for the DRM reaction. Since the lattice oxygen is reactive towards surface carbon, as a recommendation for future study on these materials it would be interesting to see what role does lattice oxygen play during DRM in the presence of CO$_2$. Performing labelled O studies with C$^{18}$O$_2$ would suggest if the lattice oxygen is interchangeable with the O
from CO₂ during DRM. It would also be interesting to study the temperature dependence of the interchangeability of lattice oxygen. A detailed study like this would help in designing a highly deactivation resistant catalyst for DRM.

Another class of materials called the perovskite (ABO₃, A and B site metals are similar to those of pyrochlores) have been used to study DRM [18, 19, 25]. Pyrochlores and perovskites can be synthesized by the Pechini sol-gel synthesis method [25, 117]. In this method, the metal precursors are mixed with complexing agents like ethylene glycol and citric acid. The polymerization reaction results in formation of amorphous resin which are precursors of the perovskites or pyrochlores. These precursors are then calcined at 800-1000°C to oxidize all the carbon and form the highly crystalline ABO₃ or A₂B₂O₇ phase [107-109]. Gurav, et al [106], studied B-site substitution of Ru in SrTiO₃ perovskites and observed that the activity of the catalyst towards DRM does not increase in direct proportion to Ru content. From the three levels of Ru substitution i.e., 7.9, 15.6, and 31 wt%, the 15.6% catalyst showed higher conversion than the other two catalysts. There appears to be an optimum level of metal substitution to attain highest activity [106], below the optimum level Ru is well dispersed on both the surface of the catalyst and in the bulk. Beyond this optimum level the excess of Ru starts to sinter to form larger clusters or separate out as a different phase. In both pyrochlores and perovskites, the majority of the active metal is substituted within the bulk of the crystal structure and only a small proportion of this active metal is at the surface.

De Arauj, et al [18], compared perovskites for DRM with the B-site composed of Ru and Ni. They observed that the activity and carbon formation decreased with the substitution of Ru in the perovskite structure. Similar technique was used by Pietraszek, et al [118], where they impregnated Ni on Rh and Ru substituted Ce₀.₆Zr₀.₄O₂ (designated: CeZrRh or CeZrRu) fluorite
structures. They observed that substitution of Rh/Ru in the fluorite structure increased the activity towards DRM and enhance its resistance to deactivation. Thus crystalline oxide with ordered crystal lattice are structurally stable catalysts that can withstand high DRM temperature. With the right proportion of the active metal, these structures also avoid sintering at these high temperatures (800-1000°C) unlike conventional supported catalysts.

2.3.4. **Mesoporous Catalysts and Membrane Reactors for DRM**

Unconventional support materials like silicate structured mesoporous catalysts with ordered pore structures have opened new pathways of catalyst design [119]. These materials are synthesized by hydrothermal synthesis using a surfactant solution as a solvent for mixing sodium silicate and performing hydrothermal synthesis [119]. These silicate mesoporous structures have very uniform parallel pores (minimum tortuosity and hence minimum mass transfer resistance). The pore dimensions of these materials can be altered simply by changing the length of the surfactant during the synthesis. Active metals can be then incorporated in the silicate structure by adding the metal precursor solution to the surfactant solution before carrying out hydrothermal synthesis. Such mesoporous, protonic large pore BEA and FAU type zeolites have been studied for DRM and it is reported that these silica-aluminate structures have high thermal stability that is in direct correlation with the Si/Al ratio of the catalyst [120]. Steam dealumination of these catalysts can help in increasing the pore volume and the Si/Al ratio (hence the thermal stability), which increases the contact time of the reactants with the active metals like Pt and Ni [120] resulting in higher conversion and lower carbon deposition.

Apart from powdered catalysts (used in fixed bed reactors), membranes with Pd, Ru, Ag have also been used to study DRM reaction [42, 43, 121, 122]. Membranes allow permeation of products away from the catalyst bed which drives the reaction towards formation of CO and H₂
[123], leading to higher conversions at lower temperatures and limiting the occurrence of simultaneous (RWGS and BR) reactions [87]. In addition, an ultrapure hydrogen rich stream can be obtained by using the Pd-Ag membrane which has high permeability and selectivity for H₂ [123]. A brief account of Pd and Pd-Ag composite membrane synthesis and its activity towards DRM is reported by Bosko, et al [124]. They found that Pd membranes showed lower light off temperature and higher conversions compared to composite Pd-Ag membrane and that the activity of the Pd membrane is similar to that of Rh/La₂O₃ powder catalyst. The membrane showed stability for about 570 h at 500°C, which is much longer than any supported catalyst at that temperature.

A summary of some important DRM results obtained over different noble metal catalysts is shown in Table 2.1.

Table 2.1. Summary of some important results for noble metal catalysts used for DRM.

<table>
<thead>
<tr>
<th>Catalyst used</th>
<th>Key results</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi₁₋yRu₂O₃₋δ</td>
<td>• Increasing Ru substitution decreases C formation and increases the activity.</td>
<td>[18]</td>
</tr>
<tr>
<td>Pt/ZrO₂, Pt/Al₂O₃, Pt/TiO₂</td>
<td>• ZrO₂ helps in activation of CO₂ and promotes activity of DRM</td>
<td>[125]</td>
</tr>
<tr>
<td>Rh-Ni/BN, Rh-Ni/γ-Al₂O₃</td>
<td>• BN showed lower carbon formation as compared to γ-Al₂O₃ and attribute this to Rh-Ni cluster formation on BN which was not possible on Al₂O₃ due to strong metal support interaction.</td>
<td>[88]</td>
</tr>
<tr>
<td>Rh-Ni/MgAlO</td>
<td>• Mg-Al hydrotalcites are very good reforming catalysts as they resist carbon formation by their basic properties, high surface area and thermal stability</td>
<td>[62]</td>
</tr>
<tr>
<td>Pt/CeₓZr₁₋ₓO₂</td>
<td>• When Ce/Zr=1, the catalyst has highest CO₂ activation. Promoters like Pr, increases the thermal stability of the catalyst.</td>
<td>[126]</td>
</tr>
</tbody>
</table>
| Pt/ZrO₂ and Pt/Al₂O₃         | • After 10 min of exposure to CH₄/He; the reactivity of coke towards TPH was greater for Pt/Al₂O₃ than Pt/ZrO₂.  
• But after the same treatment in CH₄/He, when the catalysts were oxidized in CO₂, the reactivity of ZrO₂ was greater than Al₂O₃.  
• This is attributed to more efficient activation of CO₂ by ZrO₂ (due to the presence of O defects) than by Al₂O₃. | [127]|
<table>
<thead>
<tr>
<th>Catalyst used</th>
<th>Key results</th>
<th>Ref</th>
</tr>
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</table>
| Pd and Pd-Ag composite membranes                                        | • The activity of the Pd membrane was greater than the Pd-Ag composite membrane.  
• The CH\textsubscript{4} conversion for Pd membrane was greater than that at equilibrium at 500°C.  
• The carbon balance was about 98% which suggests no carbon deposition.                                                                                                                                                                                                                                           | [124] |
| 0.5\%Pt/ Al\textsubscript{2}O\textsubscript{3}, 10\%Ni/ Al\textsubscript{2}O\textsubscript{3}, 0.5\%Pt-10\% Ni/ Al\textsubscript{2}O\textsubscript{3} | • The monometallic Pt catalyst had lower activity than Ni catalyst but this could be due to lower metal content.  
• However, the bimetallic catalyst showed better activity than either monometallics and gave stable conversion for over 6500 min without significant deactivation.                                                                                                                                                                                                 | [89]  |
| 0.4\%Pt/ Al\textsubscript{2}O\textsubscript{3} (N), 0.4\%Pt/ Al\textsubscript{2}O\textsubscript{3} (C), 0.4\%Pt-4\%Ni/ Al\textsubscript{2}O\textsubscript{3} (N), | • The catalysts prepared using nanofibrous Al\textsubscript{2}O\textsubscript{3} (N) showed a higher surface area and improved metal dispersion as compared to commercial Al\textsubscript{2}O\textsubscript{3} (C).    
• Promotion of Pt added to the stability of the Ni catalyst against carbon deposition.                                                                                                                                                                                                                                                                          | [128] |
| 1\%Pt-1\%Ce/Zr\textsubscript{2}O\textsubscript{2} | • This catalyst was prepared by two methods, (a) co-impregnation, and (b) sequential impregnation.  
• It was reported that the co-impregnated catalyst had higher stability and activity compared to the sequentially impregnated catalyst.  
• This higher activity was attributed to the increased Pt-Ce interaction which is a result of simultaneous heat treatment (calcination) of Pt and Ce precursors as compared to sequential heat treatment.                                                                                                                                                                                                 | [100] |
| 1\%Pt/Zr\textsubscript{2}O\textsubscript{2}/Si\textsubscript{2}O\textsubscript{2} | • Varying ratios of Zr\textsubscript{2}O\textsubscript{2}:Si\textsubscript{2}O\textsubscript{2} were tested and the observed activity and stability for 16 h were in the order 4:1>pure Zr\textsubscript{2}O\textsubscript{2}>3:1>2:1.                                                                                                                                                                                                 | [90]  |
| (0.3\%Pt-10\%Ni)/ Al\textsubscript{2}O\textsubscript{3}; (0.2\%Pt-15\%Ni)/ Al\textsubscript{2}O\textsubscript{3} | • Addition of Pt increased the activity of the catalyst compared to Ni/ Al\textsubscript{2}O\textsubscript{3}.  
• Highest activity was observed when the Pt/Ni ratio was the lowest.  
• Also higher dispersion and least carbon deposition was observed for lowest Pt/Ni ratio.                                                                                                                                                                                                                                                                  | [129, 130] |
| Co/Ti\textsubscript{2}O\textsubscript{2}, Pt-Co/Ti\textsubscript{2}O\textsubscript{2}, Ru-Co/Ti\textsubscript{2}O\textsubscript{2} | • Addition of Pt and Ru improved the dispersion and reducibility of Co.  
• During the reaction metallic form of Co was maintained for the Pt and Ru promoted catalyst which improved the stability and activity.                                                                                                                                                                                                                                         | [63]  |
(Table 2.1 continued)

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<th>Catalyst used</th>
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| 0.3%Pt/Al₂O₃, 0.3% and 1%Na- Al₂O₃, 0.3% and 0.5%K-Al₂O₃, and ZrO₂ | • The order of activity and stability was Na-Al₂O₃> K-Al₂O₃> ZrO₂> Al₂O₃.  
• The presence of Na and K adds to the basicity of the catalyst which helps in activation of CO₂ to form O species which oxidizes carbon to CO, thus increasing resistance to deactivation.  
• Low concentration (0.3%) of Na and K showed better stability than higher concentrations. | [50] |
| Pt/ZrO₂, Pt/Ce-ZrO₂, Pt/Ce-La-ZrO₂ | • Pt/La-ZrO₂ had the highest activity, surface area, and CO₂ adsorption capacity.  
• Addition of promoters inhibits particle growth during reaction at 800°C.  
• This also increases the metal-support interfacial area which helps in gasification of the carbon formed during reaction. | [65] |
| 2%Ru/TiO₂, 2%Ru/SiO₂, 2% Ru/Al₂O₃, 2%Ru/MgO | • At 0.1 MPa operating pressure, the Ru/MgO resulted in highest activity and least carbon formation due to high basicity which facilitates carbonate formation.  
• At 2 MPa, all catalysts showed almost the same activity and was close to equilibrium values which suggests the possibility of mass transfer effects and reverse reaction. | [131] |

2.4. Activation Mechanism of CH₄

The most kinetically significant and important step in DRM in the absence of transport limitations is the adsorption or activation of CH₄. This requires metals like Rh, Pt, Ni on which methane dissociates directly to form carbon, CHₓ or formyl intermediates. Bitter, et al [16], observed that for Pt/ZrO₂, after certain amount of metal loading there was no increase in the DRM rate with increasing metal content. This suggests that CH₄ activation occurs at the Pt-ZrO₂ interfacial sites and not Pt alone. DRM is typically first order in CH₄ [72, 132, 133] and thus an active catalyst should have a low activation energy for CH₄ dissociation to CHₓ species. Dissociation of CH₄ is thermodynamically most favorable over Rh compared to other transition metals and is observed to dissociate CH₄ starting as low as 150°C [134]. The process of activation of CH₄ is structure sensitive on supported Rh, Ru, and Pt clusters [20, 86, 135, 136],

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with a direct correlation between Rh dispersion and TOF of the catalyst, in agreement with Wei and Yamaguchi et al. [135, 136], who also demonstrated that the rate of DRM over Rh/Al$_2$O$_3$ is first order in CH$_4$ and is independent of CO$_2$ concentration i.e., $r_{CH_4} = kP_{CH_4}$[132, 133]. However, Erdohelyi et al [134], observed that the rate of CH$_4$ dissociation, CO and H$_2$ formation has finite positive order dependence on both CH$_4$ and CO$_2$ over Rh/SiO$_2$, Rh/TiO$_2$, Rh/MgO suggesting significant importance of CO$_2$ activation in the kinetics of DRM. Munera, et al [71], reported that the rate of DRM could have zero order dependence in CO$_2$ on supports like Al$_2$O$_3$ as reported by Wei et al. [135], but with La$_2$O$_3$ as a support the dependence of CO$_2$ is observed to be 0.34 in order. Isotopic studies performed on Rh/Al$_2$O$_3$ by Wang, et al [137], showed that the conversion of CH$_4$ was greater than the conversion of CD$_4$ suggesting that the dissociation of the C-H bond is the rate-determining step in the reforming reaction. Schuurman, et al [138] studied the H/D isotope effect for CH$_4$/CD$_4$ pulsing experiment over Ni/SiO$_2$ and Ru/SiO$_2$ and measured the ratio of CH$_4$ converted to isotopically scrambled methane (CH$_3$D, CH$_2$D$_2$, CHD$_3$) to the amount of CH$_4$ converted to CO. That ratio was about 0.1, suggesting that a significant amount of CH$_4$ is converted to CO and that CH$_4$ dissociates irreversibly to form CO.

There are two mechanisms for dissociation of CH$_4$ on a metal surface as studied by quantum models and by experiments; (1) by direct dissociation [139], and (2) indirect dissociation or by means of formation of an intermediate, like the CH$_x$ or a formyl group [140-142] with the oxygen coming from the support or the oxidant i.e., CO$_2$ in case of DRM. It is believed that CH$_4$ activates to form intermediates at lower temperatures (<550°C) and begins to dissociate directly at high temperatures [143]. Bitter, et al [16], proposed that during DRM, CH$_4$ is activated on the metal while CO$_2$ is activated on the support. However, Zhang et al [27], studied the role of support in the activation process of CH$_4$ and showed that the conversion of
CH$_4$ was greater for Ni/Al$_2$O$_3$ as compared to Ni/La$_2$O$_3$, which suggests that acidic sites on Al$_2$O$_3$ assist in the activation of CH$_4$. However, these acidic sites on Al$_2$O$_3$ have been observed to result in deactivation by carbon formation more rapidly than basic supports. Figure 2.8 shows that Ni/Al$_2$O$_3$ showed higher initial reaction rate compared to Ni/La$_2$O$_3$ up to 100 min suggesting acidic sites on Al$_2$O$_3$ assisted in activation of CH$_4$ initially. However, there was significant drop in activity of Ni/Al$_2$O$_3$ as a result of carbon formation. However, a higher steady state reaction rate was observed for Ni/La$_2$O$_3$ and is attributed to the basic sites on La$_2$O$_3$ which assisted in activation of CO$_2$ and oxidation of surface carbon, increasing the resistance to deactivation and prolonged activity of the La$_2$O$_3$ based catalyst.

![Graph](image)

Figure 2.8. Rate of reaction vs time on stream for 17% Ni/La$_2$O$_3$ and 17% Ni/Al$_2$O$_3$ at 750°C, CH$_4$:CO$_2$=1:1, 1 atm. (Reprinted with permission from [27]. Copyright 1996 Springer.)

Both reactive oxide supports or the presence of O from CO$_2$ help in the dissociation of CH$_4$ [144]. Lisi, et al [145], observed that the lattice oxygen species on the surface help activate CH$_4$ on perovskite catalysts. Similar results are reported by Pakhare, et al. [113, 114], who
observed by means of CH₄ TPR that the lattice oxygen of pyrochlore catalysts reacts with CH₄ to form CO. Ferriera-Aparicio, et al [146], reported that the activation of CH₄ requires the presence of oxygen on the surface, which usually comes from the hydroxyls on the acidic supports and carbonates on basic supports. The reactivity of the lattice oxygen of NiO/MgO was studied in detail by means of transient pulsing of isotopic C¹⁸O₂, O¹⁸₂, C¹³₂, and CH₄ [147]. It was observed that there were two types of O species on the catalyst; an adsorbed O species which reacts rapidly (or at low temperatures) with the C species and the other which are lattice O species that react slow (or at high temperatures) with the C that is formed. They proposed a dynamic redox type mechanism where CO₂ oxidizes some portion of Ni⁰ to Ni⁺δ which causes reduction of CO₂ to CO, and that this Ni⁺δ is reduced to Ni⁰ by the C species formed from CH₄ [147].

Stagg, et al [99], used C¹³ pulses to study the reactivity of the ZrO₂ in Pt/ZrO₂ and observed formation of H₂ and C¹³CO. They attributed this C¹³CO formation to the reaction of the C¹³ from C¹³CH₄ with the O in proximity of the Pt-Zr interface. This created O deficiencies which helped in dissociation of CO₂ in the subsequent pulses [99].

The effect of a reducible support in activation of CH₄ was studied in detail by Bradford, et al [148], who reported the FTIR spectra for H₂ reduction of TiO₂ supported metal catalysts [Figure 2.9]. They observed that the inverted peaks 3660 cm⁻¹ are due to the loss of the hydroxyl species on the TiO₂ that were present during the background collection but reacted with H₂ during the reduction step. The bands in the range 910 and 960 cm⁻¹ are indicative of the Ti-O bond cleavage suggesting formation of TiOₓ species on the support [148]. Formation of TiOₓ species play an important role in the activation of CH₄ to form CHₓO species, suggesting that the active site for DRM over TiO₂ supported catalysts is the metal-support interface. Due to the
formation of this metal-support interfacial site, CO or H\textsubscript{2} chemisorption could not be used to precisely determine the dispersion of the metal on the TiO\textsubscript{2} as the H/metal ratio was no longer known. A similar problem in determining the metal dispersion due to metal-support interaction were reported by other researchers [149-152].

Figure 2.9. FTIR spectra of TiO\textsubscript{2} and TiO\textsubscript{2} supported metals after reduction in H\textsubscript{2}/Ar=5/4 at 773K. (Reprinted with permission from [148]. Copy right 1999 Elsevier.)
The FTIR spectra during reaction of CH$_4$ with TiO$_2$ supported Rh, Pt, Pd and Ni suggest that there was formation of H$_2$C=O species on (Ti$^{+n}$) type sites. For Pt there was also formation of adsorbed CO during CH$_4$ reaction, suggesting that these metals catalyzed the dissociation of CH$_4$ and oxidized it to form adsorbed CO. This feature was not observed for Pd and Ni/TiO$_2$ [148].

Lucredio, et al [62], reported that Rh increased the dispersion of Ni when Mg(Al)O (hydrotalcite-type support) was the support while Rh probably caused aggregation of Ni when γ-Al$_2$O$_3$ was used as a support. These studies show that γ-Al$_2$O$_3$ does not increase catalyst stability when Rh is used in a bimetallic catalyst for DRM reaction. Erdohelyi, et al [134], found a different result when they studied the effect of the support on the dissociation of CH$_4$. They observed that Rh/Al$_2$O$_3$ showed highest reactant conversion (activity) followed by Rh/TiO$_2$, Rh/SiO$_2$ and Rh/MgO. The difference in the results reported by Lucredio et al [62], and Erdohelyi, et al [134] can be explained by the fact that monometallic Rh/Al$_2$O$_3$ may result in a high activity catalyst but Rh may not be as active for bimetallic Rh-Ni supported on Al$_2$O$_3$ catalysts. It is important to acknowledge that the differences in the activity could also be due to the variation in the synthesis procedure and metal dispersion in the mentioned studies. Erdohelyi, et al [134], showed that no CH$_4$ dissociation was observed over the support alone, suggesting that the primary active site is Rh and the support could have some promotional effect. They postulate that the dissociation of CH$_4$ starts by the formation of CH$_3$; this CH$_3$ then dimerizes to form C$_2$H$_6$. The CH$_3$ may also follow a dehydrogenation pathway to ultimately form C(s) and H. The presence of CH$_x$ intermediate species could also be possible but is highly unlikely at temperatures above 500°C [144], where the CH$_x$ species dissociate rapidly to form C(s) and H$_2$ while the degree of dimerization is minimal. Apart from temperature, the metal-support
interaction of the catalyst governs the kinetics of CH₃ dimerization or dehydrogenation [134]. Formation of ethane by dimerization of CH₃ was also observed primarily over Pd/Al₂O₃ and to a small extent on Ru/Al₂O₃ during CH₄ pulsing, however, it is very limited over all catalysts at temperatures greater than 500°C [144].

A novel approach for studying the mechanism was used by Qian, et al [153], where they use magic-angle spinning nuclear magnetic resonance (MAS NMR) of the $^{13}$C and $^1$H atoms to study the mechanism of DRM over 1% Rh/SBA-15 catalyst. They pulsed known amounts of $^{13}$CH₄/$^{12}$CO₂ and monitored for $^{13}$C and $^1$H signal in the gas phase (only) since the adsorbed species are invisible in this NMR equipment [Figure 2.10]. They determined the conversion of $^{13}$CH₄ and the adsorption strengths on Rh/SBA-15. Figure 2.10 shows that there is carbon exchange to form $^{13}$CO₂ from $^{13}$CH₄ above 673K and the reforming reaction starts above 600°C when $^{13}$CO starts to appear.

![Figure 2.10](image.png)
Using similar $^1$H NMR spectra they determined that about $\frac{3}{4}$ of the $^1$H formed from conversion of $^{13}$CH$_4$ was invisible and hence they inferred that a substantial portion of $^{13}$CH$_4$ activated exist in the form of $^{13}$CH$_3^*$. This suggests non-dissociative adsorption of CH$_4$ on 1%Rh/SBA-15, however, some amount of $^{13}$CH$_4$ does undergo dissociation to form combustion products of $^{13}$CO$_2$ above 300°C. This conforms to the fact that CH$_4$ activation proceeds via non-dissociative form at lower temperatures but change to dissociative adsorption at high (above 550°C) temperatures [143]. It is only above 600°C that the reforming reaction becomes significant, forming $^{13}$CO. When they tested $^{13}$CO$_2$/^{12}CH$_4$ pulse, the conversion of $^{13}$CO$_2$ was greater than conversion of $^{13}$CH$_4$ (in pulse 1) suggesting that adsorption of CO$_2$ is faster than that of CH$_4$ and thus activation of CH$_4$ is likely rate-limiting step over these catalysts.

Garcia, et al [48], conducted a transient study of DRM over Pt/Al$_2$O$_3$ by pulsing CH$_4$ and CO$_2$ individually i.e., one CH$_4$ pulse followed by CO$_2$ pulse, to probe the mechanism. They found out that CO was formed during both individual CH$_4$ and CO$_2$ pulse. They inferred that CH$_4$ is activated by two different mechanisms; one in the presence of CO$_2$ and other in its absence. In the absence of CO$_2$, CH$_4$ undergoes thermal cracking to form H$_2$ and surface carbon. This formed H$_2$ was observed in the MS system with a very weak signal of CO. This CO was due to O from support oxidizing the surface carbon formed from CH$_4$ dissociation during the first pulse. During the CO$_2$ pulse following the CH$_4$ pulse, there was a very strong signal of CO observed. This suggests that CO$_2$ favors reforming of CH$_4$ (or oxidation of C(s)) to CO. This is in agreement with the literature that the presence of oxidant (like CO$_2$, H$_2$O or O$_2$) helps in reducing carbon formation on the surface [154] and improves the syngas yield. The final H$_2$/CO ratio and the extent of carbon formation depend on the mechanism by which the methane activates and the ability of the support to activate CO$_2$.  

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2.5. Activation Mechanism of CO₂

During DRM, CO₂ is activated and reduced to CO which helps in the oxidation of the surface carbon formed from CH₄ activation. It is generally believed that this reduction reaction proceeds via formation of carbonate precursors in the presence of basic catalytic sites [144, 155, 156]. Activation of CO₂ occurs on the support (except for inert materials like SiO₂) or the interfacial sites of the catalyst rather than the active metal alone [16, 83, 157]. Van Keulen, et al [125], observed that number of molecules of CO₂ adsorbed was much greater than the number of Pt atoms on the catalyst surface. Assuming that one Pt atom adsorbs one CO₂ molecule, the calculation suggests that the support, i.e., ZrO₂, adsorbs and activates CO₂. They also noticed that conversion of CO₂ was greater for Pt/ZrO₂ compared to Pt/Al₂O₃ for the same wt% of Pt. This varying activity towards CO₂ activation could be attributed to the greater basicity of the ZrO₂ support and the presence of O deficiencies. A similar conclusion was drawn by Mark, et al [70], when they observed that Al₂O₃, which is acidic in nature, does not assist to activate the mildly acidic CO₂. This lack of CO₂ on the surface leads to increased carbon formation over Ru/Al₂O₃. The O deficiencies formed in the catalyst support as a result of reduction pretreatment also helps in activation and dissociation of CO₂ as observed in the case for Pt/ZrO₂ [127] and Pt-Sn/ZrO₂ [99]. A similar conclusion can be drawn from Zhang, et al [27], who observed that the activation of CO₂ over La₂O₃ during DRM was greater than that over Al₂O₃, due to the formation of chemisorbed La₂O₂CO₃ by the reaction of CO₂ with La₂O₃. The formation of La-oxycarbonate was first studied by Turcotte, et al [158], in 1969. They reported that La₂O₂CO₃ are polymeric complexes that are arranged in form of layer-type slabs of La₂O₂²⁺ and CO₃²⁻ ions; La₂O₃ + CO₂ → La₂O₂CO₃. Depending on the positioning of the La₂O₂²⁺ ions the La-oxycarbonate complex can be differentiated into three crystalline polymorph namely, type I, type Ia and type II [42, 122,
The orientation of these types of La oxide and carbonate ions is shown in Figure 2.11.

Type I La-oxycarbonates are square layers of \((\text{La}_2\text{O}_2^{2+})_n\) separated by \(\text{CO}_3^{2-}\) ions which result in a tetragonal crystalline form. Type Ia is a monoclinic distortion of type I [160]. Type II La-oxycarbonate are hexagonal unit cell structures with more than one local coordination of La [159, 161]. Formation of these polymorphs is a function of carbonation temperature, presence of \(\text{H}_2\text{O}\), heating/cooling rates [162], type of active metal and the concentration of the active metal [159].

![Figure 2.11. Reasonable orientation of the carbonate (CO_3^{2-}) ions in the (a) type I, (b) type IA, and (c) type II phases of La-oxide. The corners represent the La atom and the O associated with La is not shown in this figure. (Reprinted with permission from [158]. Copyright 1969 American Chemical Society.)](image-url)
Irusta, et al [159], report details of the experimental procedures for selectively synthesizing one of these types and their characterization by XRD, FTIR, Laser Raman Spectroscopy (LRS), and TPD. At temperatures above 500°C, the type-I transforms to the monoclinic distortion type-Ia and Rh loadings greater than 1% result in transformation of type Ia to type II. La-oxalate, La$_2$(C$_2$O$_4$)$_3$, is another species formed by the adsorption of CO$_2$. High temperature TGA and TG-FTIR of the decomposition of La oxalate shows that it begins to change to La$_2$O$_2$CO$_3$ (La-oxycarbonate) at about 430°C. The concentration of La$_2$O$_2$CO$_3$ increases with temperature until 600°C and then decreases. Above 750°C, all of La$_2$O$_2$CO$_3$ decomposes completely to La$_2$O$_3$, liberating CO$_2$, as seen by TPD and TGA [86, 163]. The formation of La-oxycarbonates by reaction of CO$_2$ with Rh and Pt supported La$_2$O$_3$ catalysts [Figure 2.12] at 500°C.

The bands in the range of 1300-1600 cm$^{-1}$ are attributed to the different types of the La-oxycarbonates. The presence of type-II oxycarbonate is confirmed by the presence of IR bands at 1467, 1087, and 856 cm$^{-1}$ which are signature adsorption bands for La$_2$O$_2$CO$_3$ [161, 163]. The fact that there is a doublet splitting observed at the carbonate peaks suggests presence of multiple type of carbonates chemisorbed. The bands at 1368 cm$^{-1}$ correspond to the absorption bands of the type-Ia La-oxycarbonate [158]. This band of the carbonate ion is usually infra-red inactive for free ions but is active if it is positioned in a crystalline framework. The infra-red active behavior of these bands confirm that the carbonate ions are positioned in the crystalline tetragonal geometry of the type-Ia La-oxycarbonate [160]. These are the major peaks that represent the formation of La-oxycarbonates as a result of activation of CO$_2$ by La-O sites [59, 66, 164, 165]. The presence of hydroxyls also helps in activation of CO$_2$ to form adsorbed CO which is highly ionic in nature [83, 84, 163, 166-170].
Figure 2.12. FTIR spectra showing the absorption bands for adsorbed La$_2$O$_3$CO$_3$ formed after reaction of CO$_2$ on 0.2% Rh/La$_2$O$_3$, 0.6%Rh/La$_2$O$_3$ and 0.93%Pt/La$_2$O$_3$. (Reprinted with permission from [161]. Copyright 2004 Elsevier.)

Tsipouriari, et al [171], studied the carbonaceous species over Ni/La$_2$O$_3$ and Ni/Al$_2$O$_3$ catalysts to understand if their origin is CH$_4$ or CO$_2$. SSITKA experiments using $^{13}$CO$_2$, $^{13}$CH$_4$, C$^{18}$O$_2$ isotopes showed that the carbon balance, i.e. amount of CO formed compared to CH$_4$ or CO$_2$ consumed, was greater for the La$_2$O$_3$ catalyst compared to Al$_2$O$_3$. They attributed this to the higher activation rate of CO$_2$ over La$_2$O$_3$ by La$_2$O$_2$CO$_3$ formation which results in lower carbon deposition on the catalyst [171, 172], thus improving the CO yield and carbon balance.

Reversibly adsorbed CH$_4$ was much greater than reversibly adsorbed CO$_2$ over La$_2$O$_3$ than Al$_2$O$_3$, suggesting that the activation of CO$_2$ over La$_2$O$_3$ is fast compared to CH$_4$ activation.
Wang, et al [95], studied Rh supported on a variety of reducible oxides (CeO$_2$, ZrO$_2$, Nb$_2$O$_5$, Ta$_2$O$_5$, TiO$_2$) and irreducible oxides (La$_2$O$_3$, Al$_2$O$_3$, MgO, Y$_2$O$_3$, SiO$_2$) and observed that Rh/La$_2$O$_3$ and Rh/MgO showed the highest stability and attributed this to the basic sites on the support which enhanced CO$_2$ activation, limiting carbon formation and deactivation. In DRM the oxidation of surface carbon is carried out by O from CO$_2$ and efficient activation of CO$_2$ by MgO and La$_2$O$_3$ helped in achieving uninterrupted syngas production for 100 h [95].

On acidic supports, CO$_2$ activation is weaker than on basic supports but occurs primarily via formation of formates by CO$_2$ reaction with the surface hydroxyls and is dependent on the rate of migration of the hydroxyls within the support or from metal to the support. This was confirmed by Aparicio, et al [84], who treated Ru/Al$_2$O$_3$ with D$_2$O [Figure 2.13] which shows the presence of deuterioxyls at 2786-2667 cm$^{-1}$ as opposed to the hydroxyls at 3769-3598 cm$^{-1}$ [168]. These deuterioxyls then activate CO$_2$ to form formates which then oxidize the surface carbon over a Ru/Al$_2$O$_3$ catalyst. This confirms that on acidic supports, CO$_2$ is activated by reaction with hydroxyls whereas on basic supports, CO$_2$ is activated by formation of carbonates.

In addition to the basicity/acidity of the support, there are other factors that contribute to the activation of CO$_2$, e.g., the presence of H species from CH$_4$ activation, interaction of the support and the metal, the presence of noble metals which catalyzes the reduction of CO$_2$ to CO [144]. There are reports which suggest that activation of CH$_4$ (formation of H species on the catalyst surface) helps in the activation and reduction of CO$_2$ to CO [11, 48, 72, 144, 157]. Bradford, et al [148], showed that the formation of TiO$_x$ species during CO$_2$ treatment of Rh/TiO$_2$ catalysts helps in cleavage of the one C-O bond in CO$_2$ molecule to form CO. This cleavage, however, takes place only in the presence of Rh and not on TiO$_2$ alone. Thus the presence of O defects in the catalyst support act as potential sites for activation of CO$_2$ and
cleavage of the C-O bond, which increases the O pool on the catalyst surface. This O can then oxidize the surface carbon to CO and minimize deactivation due to carbon deposition. Noble metals like Rh readily dissociate H₂, which increases the reducibility of the support by hydrogen spill-over; creating oxygen vacancies for enhanced CO₂ activation [85].

Figure 2.13. IR spectra for Ru/Al₂O₃, (a) treated in H₂O showing the hydroxyl species, (b) treated in D₂O showing the deuteroxyl species at 373K. (Reprinted with permission from [84]. Copyright 1998 Elsevier.)
2.6. Deactivation and Ways to Minimize it

2.6.1. Factors Affecting the Morphology and Reactivity of the Carbon Formed

Carbon deposition is the major disadvantage of DRM [173, 174], suggesting that development of a catalyst that minimizes carbon formation is a key research priority. There are two main reactions that result in carbon formation during DRM on a catalyst, (1) CH₄ decomposition [eqn 8], and (2) CO disproportionation [eqn 9]. When the catalyst is fresh, carbon formation is primarily due to CH₄ dissociation since CO is absent in the reactant feed. For longer time-on-streams, significant levels of CO are present, depending on the temperature (thermodynamics) and operation pressure (because CO disproportionation is favored at high pressures [131]) CO disproportionation forms additional carbon [6]. The balance between the formation of carbon by CH₄ dissociation and/or CO disproportionation, compared to oxidation of surface carbon by CO₂ [175, 176] determines the rate and extent of carbon deposition.

Deactivation in DRM is not only by carbon deposition but also by several other means.

1. Encapsulation of the active metal by reducible supports like ZrO₂ [177],
2. accumulation of inactive adsorbed oxygen groups over Rh/YSZ[26],
3. poisoning by sulfur originating from the support, e.g., MgO [147],
4. sintering of metal particles as observed in Rh/Al₂O₃ [93].

However, carbon deposition is generally the most significant mechanism of catalyst deactivation for DRM. The carbon deposited on the surface of the catalyst differs in morphology [178], location with respect to the active metal [105], concentration of the active metal [59], type of support/promoter and active metal [26, 164], temperature of reaction [114], duration of the reaction and surface area of the support [179].
The carbon formed as a result of DRM may be carbidic, amorphous, polymeric, nanotubes, graphene type, shell-type graphitic, filamentous in morphology [180]. The most reactive form (oxidizing at about 100°C) is the amorphous form which is also called Cα, which is composed of carbon atoms adsorbed and bound to metallic centers, suggesting that their first coordination is only with metals [146]. The polymeric carbon is partially hydrogenated and is in the form of carbon-carbon chains which make it less reactive than amorphous carbon. The oxidation temperature of polymeric carbon increases with decreasing H: C ratio. These are called the “soft” type carbons, which can be oxidized under mild conditions and do not block the active sites [181]. The graphitic form of this type of carbon consists of six-carbon ring compounds (polynuclear aromatics) and hence is the least reactive, requiring high temperature for oxidation [146]. Graphitic and filamentous forms of carbon are also called the “hard” type, which require high temperatures for oxidation and can block the active sites inducing deactivation.

The exact temperature at which these various forms of carbon can be oxidized is difficult to generalize because it is a strong function of the catalyst type under study. Also, transformation of the carbon from active to either inactive or less active forms occur with increasing reaction time and increasing reaction temperature [182]. The reactivity of the carbon is also a function of the location of the carbon with respect to the active metal or the accessibility of the metal. If the carbon is close to the metal then it is more reactive than carbon on the support or far away from the metal [183, 184]. Nagaoka, et al [131] reported that there was carbon formation but no deactivation with time for Ru/Al2O3, SiO2, MgO and TiO2 catalysts for 25 h period. This could be because the type of carbon formed does not block the active sites on Ru. This was later studied by Koubaissy, et al [185], where they observed that Ni-Rh/CeZr and Ni/CeZr showed carbon deposition but the Rh bimetallic catalyst did not show any apparent deactivation, unlike
Ni-Rh/CeZr. They attribute this to formation of carbon nanotubes on monometallic Ni and amorphous carbon on Ni-Rh bimetallic. This shows that a difference in the morphology of the carbon formed can influence the deactivation. Garcia, et al [128], reported that Pt inhibited the formation of carbon nanotubes and nanofibers on Pt/Al₂O₃ (nanofibrous Al₂O₃ are designated with N) but these nanotubes and fibers were present on Ni/Al₂O₃ which are a major cause of blockage of the active site and subsequent deactivation.

Figure 2.14 shows the XPS spectra of the C 1s core level spectra for 0.4%Pt-4%Ni/Al₂O₃(N), and 0.4%Pt/Al₂O₃(N). In the XPS spectra the peak at 279.6 eV corresponds to carbon nanofibers, 282 eV represents filamentous carbon and 284.4 eV is adventitious carbon. Using Rh metal as a promoter for Ni/Al₂O₃ catalysts results in formation of Ni-Rh bimetallic clusters which increase the activation/reduction rate of CO₂ creating a pool of oxygen for efficient gasification of the carbon formed during DRM reaction [20]. On the Rh-Ni/Al₂O₃ bimetallic catalysts carbon was formed but there was no apparent deactivation as measured by CH₄/CO₂ conversion. This was attributed to the fact that carbon could not diffuse through the bimetallic catalyst as it did for the monometallic Ni/Al₂O₃ [58]. A similar conclusion was reported by Wu, et al [88], who observed lower carbon formation over Rh promoted bimetallic Rh-Ni/Boron Nitride (BN) catalysts compared to monometallic Ni/BN catalysts. The presence of noble metals inhibits the formation of carbon nanotubes and nanofibers and hence no deactivation observed for the noble metal catalysts in spite of carbon formation. This is in agreement with the results reported by Koubaissy, et al [185]. Ferreira-Aparicio, et al [146] postulated a mechanism for carbon formation on Rh site of Rh/Al₂O₃ catalysts and stated that carbon oxidation takes place by the hydroxyl groups on the support surface.

\[
C(s) + OH(s) \rightarrow CO + \frac{1}{2} H_2
\]
Carbon oxidation not only depend on the number of interfacial sites but also on the diffusion of the hydroxyls from the support to Rh and/or the migration of carbonaceous species from Rh to the hydroxyls on support. These two types of migration/diffusion and oxidation leave the Rh sites free from carbon and available for continued DRM activity [146].

![Graph](image)

Figure 2.14. C 1s core level spectra for studying the nature of the carbon formed after DRM at 700°C at 6000 h⁻¹. (Reprinted with permission from [128]. Copyright 2010 Elsevier.)

Depending upon time-on-stream, one type of carbon can transform to another form of carbon as seen by Nagaoka, et al [127]. They observed that the carbon formed when Pt/ZrO₂ was exposed to CH₄/He for 10 min was much more reactive (during TPH) than carbon formed after 60 min of exposure to CH₄/He. This suggests that upon longer reaction duration the carbon undergoes dehydrogenation or phase transformation to form a less reactive phase. They proposed that the reactivity of the coke can be related to its crystalline nature. More crystalline carbon is less reactive, and can be oxidized only at higher temperatures [127].
The reactivity of the carbon is also a function of the metal content of the catalyst. For example, the oxidation temperature of carbon decreased with increasing Rh:Cu ratio of Rh-Cu/Al₂O₃ [146]. The TPO results presented by Horvath, et al [178], suggest that there is no direct correlation between the DRM activity of Ce₂Zr₁.₅₁Ni₀.₄₉Rh₀.₀₃O₈ and amount of carbon formed. The oxidation temperature of the carbon formed on sol-gel synthesized catalyst was 400°C while that for the impregnated catalyst was 600°C. This suggests that sol-gel type of synthesis increases the dispersion of the metal or increases the proximity of the metal with CeO₂, which increases the reactivity of the carbon compared to the impregnated catalyst. This observation by Horvath, et al [178] is in agreement with that observed by Verykios, et al [186] and Guczi, et al [182], who observed a change in the carbon formation due to change in metal dispersion as result of the synthesis procedure.

2.6.2. Ways to Control Deactivation

Greater dispersion of active metal on the surface of the support reduces the ensemble size and generally limits carbon deposition [9, 19, 48]. Changes in various factors like the characteristics of the support, type of metal, concentration of metal, promoter, preparation method can result in synthesis of catalysts with increased dispersion and thus greater resistance to deactivation [62]. Crisafulli, et al [165], studied the effect of chloride and nitrate precursor of Ru in Ni-Ru bimetallic supported on SiO₂ (2.5%Rh-2.5%Ni/SiO₂) catalyst and observed significantly higher dispersion with nitrate precursor as compared to chloride precursor. However, the presence of Cl from the chloride also blocked the active site and result in lower activity [23, 165]. The nitrate precursor of Rh in 2.5%Rh-2.5%Ni/SiO₂ showed much lower carbon formation (5.6 wt %) than the chloride precursor (36.5 wt %) for the same catalyst composition [167]. Using a nitrate precursors enables stronger interaction and formation of Ni-
Ru or Ni-Rh bimetallic clusters which leads to enhanced activity, increased Ni dispersion which means smaller Ni particles which increases resistance to carbon formation [187]. The effect of dispersion on carbon formation for a Pt/Al₂O₃ reforming catalyst was reported by Barbier, et al [183, 188]. Figure 2.15 shows the relationship between carbon deposited per surface Pt atom and the Pt dispersion for Pt/Al₂O₃ catalyst. This shows that with increase in dispersion there is a significant drop in the carbon atoms per Pt atom. Thus one of the most advantageous ways to limit carbon formation during reforming reactions is to increase the dispersion of the active metal on the support.

![Figure 2.15](image.png)

Figure 2.15. Plot of number of carbon atoms deposited per surface Pt atom v/s the percent dispersion of the Pt metal on the reforming Pt/Al₂O₃ catalyst. (Reprinted with permission from [183, 188]. Copyright 1986 Elsevier.)

It is advantageous to use supports with high surface areas (160-300 m² g⁻¹cat), since they allow improved dispersion of active metals through their pore structures and provide larger active surface area per unit weight of the active metal [128, 189]. However, high surface area
supports have small pores which can inhibit the diffusion of reactants. Thus using supports with bimodal pores; micropores and macropores, would be expected to produce a stable and active catalyst for DRM [189]. Using bimodal pore supports like ZrO$_2$ nanoparticles on SiO$_2$ provide not only multi-porous supports but also has a promotional effect with the basic nature of ZrO$_2$ in resisting carbon formation during DRM [189]. Structured materials like ceramic or metal foams have several other engineering advantages over other conventional supports; (a) they result in lower pressure drop, (b) improved heat transfer within the foam to all metallic sites, (c) minimum diffusion resistance and hence high effectiveness factor. These properties of catalyst foams can increase the activity and long term stability of the catalyst [40].

Increasing the basicity of the catalysts increases the rate of activation of mildly acidic CO$_2$, which assists in oxidation of surface carbon and increases the catalyst resistance to deactivation [20, 52, 156]. The presence of activated CO$_2$ on the catalyst surface inhibits carbon that is formed from CH$_4$ dehydrogenation [31]. Increased CO formation was observed over Rh/La$_2$O$_3$ compared to Rh/SiO$_2$, suggesting increased carbon oxidation in the presence of basic La$_2$O$_3$ support [14, 86]. Addition of basic promoters like CeO$_2$, La$_2$O$_3$, Nd$_2$O$_3$ and alkaline earth metal oxide like MgO, CaO, SrO, BaO, K help in the activation of CO$_2$ to form reactive carbonates [190, 191]. This increases the oxygen availability for carbon oxidation and resists deactivation due to carbon formation [67, 192]. The mechanism by which the promoters limit deactivation on Ni catalysts is that the Ni forms a closely bonded structure or alloy with the promoting metal, which preferentially forms C-O bonds instead of C-C bonds, which helps in oxidation of surface carbon [193]. The proportion of the basic promoter is also important in optimizing the activity of the catalyst as shown by Ballarini, et al [50]. They observed that Pt/0.3%Na-Al$_2$O$_3$ and Pt/0.3%K-Al$_2$O$_3$ showed higher resistance to carbon formation and higher
activity than Pt/1%Na-Al₂O₃ and Pt/0.5%K-Al₂O₃ respectively. There has to be an optimum concentration of basic promoters on the surface; since excess could possibly mask the active metal, thus lowering the activity and too less of an amount would not show any acceptable or significant promotion effect in resisting carbon formation.

The addition of CeO₂ creates a metal-ceria interaction and helps to create an oxygen reservoir through the redox behavior Ce⁴⁺/Ce³⁺ under reducing conditions [85]. This oxygen storage capacity and ability to undergo cycles of oxidation-reduction by CeO₂ provides the metal with oxygen during DRM reaction to suppress carbon deposition [194]. Thus CeO₂ can be used as a promoter or as a support itself. The oxygen conductivity of ceria can be increased by doping it with other rare earth metals like La, Gd, and Pr [195]. Since carbon formation is the major problems associated with DRM; increasing the oxygen conductivity of the catalyst helps in oxidation of the carbon which results in higher reactant conversion. Sadykov, et al [195], observed that Pr doped 1.4%Pt/Pr₀.₃-Ce-Zr-O catalyst improved the oxygen conductivity of Ce support and thus showed higher CH₄ conversion as compared to Gd and La doped supports above 700°C [Figure 2.16]. Similarly, an example is reported by Sazonova, et al [196], who studied Pt promoted fluorite-like oxides (PrCeZrO, GdCeZrO, and LaCeZrO), and observed that the Pr-promoted catalyst had the highest activity above 700°C followed by Gd and La-promoted catalyst. The enhanced activity of the Pr-catalyst was attributed to the improved oxygen conductivity above 700°C [196].

A combination of CeO₂ and ZrO₂ also performs similar function of enhancing CO₂ activation and improving resistance of the catalyst towards carbon formation [178]. Although it is widely reported in the literature that addition of CeO₂ also increases the activity of the catalyst, this is not a completely general conclusion. For example, Damyonova, et al [197], observed that
increasing the CeO₂ content of the Pt/ZrO₂ catalyst, actually decreased the conversion. This contradiction to the generally accepted effect of ceria promotion could be attributed to the different precursor (diammonium hexanitrato cerate) used by Damyonova, et al. unlike cerium nitrate used by other researchers which could have affected the O exchange ability of Ce, thereby affecting its activity.

A very effective way of resisting carbon formation is incorporation of the active metal in the support structure with high oxygen mobility [185]. This concept has been reported by Pakhare, et al [113, 114], and Haynes, et al [107-109] where they reported Ru and Pt substituted pyrochlores, which have reactive lattice oxygen that can gasify surface carbon, limiting
deactivation due to carbon formation. Stagg, et al [65], performed O₂ TPD for LaCoO₃ perovskites and observed significant amount of O₂ desorbed at 700°C and proposed that this reactive O₂ helps in oxidation of the surface carbon during reforming reaction on Pt/LaCoO₃. Using oxygen-conducting membrane catalysts like La₂NiO₄ doped with Pt also increases the gasification of the surface carbon formed during DRM. The surface Pt helps to maintain the DRM activity [198].

Although some supports are catalytically inert, they may still promote the activity of the catalyst by improving the dispersion of the metal. This phenomenon was observed by Pedrero, et al [199], who studied Rh supported on TiO₂-anatase (TiO₂-A) and TiO₂-rutile (TiO₂-R). The activity of Rh/TiO₂-A was much higher and more stable than that of Rh/TiO₂-R. They attributed this to the promotional effect of the anatase phase on dispersion of Rh compared to rutile. Also the increased reducibility of Rh in Rh/TiO₂-A inhibits the oxidation of these Rh atoms during reaction and keeps the Rh in a metallic state, which is the active site for CH₄ activation [199].

Another example of the effect of the support on carbon formation is a study comparing Rh-Ni/BN and Rh-Ni/γ-Al₂O₃. In this study, Rh-Ni/BN showed less carbon formation than Rh-Ni/γ-Al₂O₃, suggesting that the support has an important role to play in the oxidation of the carbon formed. Similar to Rh; using other noble metals like Pt [48] and Au [178] can also be used to promote Ni catalysts to increase the stability and improve Ni dispersion and thus its DRM activity. However, simply promoting the Ni catalyst with noble metals does not increase the activity unless the appropriate synthesis method is adopted. Arbag, et al [119], synthesized Ni-substituted silicate mesoporous MCM-41 catalysts and promoted it with Rh by using impregnation and hydrothermal synthesis. They observed that although the same amount of Rh was used to promote the catalyst, the catalyst which had impregnated Rh showed deactivation
after 11 h of DRM at 600°C. However, the hydrothermally synthesized Rh promoted catalyst had enhanced activity and time-on-stream stability. Also the hydrothermally synthesized Rh bimetallic catalysts showed lower selectivity for RWGS as compared to impregnated bimetallic catalysts. Thus it is not only the promotion of the noble metal but also the synthesis method that affects the stability of the catalyst.

The calcination step is also important. Keeping the synthesis procedure consistent but changing the gas used to calcine the catalyst and the calcination temperature also has a significant effect on the final catalyst performance [175]. Steinhauer, et al [60], studied bimetallic 4%Ni-1%Pd supported on 93%ZrO2-7%La2O3 calcined at 200, 400, 600 and 800°C and observed that the catalyst calcined at 600°C showed the highest activity [Figure 2.17]. The catalyst calcined at lower temperature resulted in insufficient interaction between Ni and Pd, while, high temperature calcination resulted in sintering of metal particles. This is attributed to the influence of the calcination process on increasing the Ni-Pd interaction-the closer/stronger the interaction, the higher the activity of the catalyst.

Figure 2.17. Comparison of the reactant conversion and syngas yield at 500, 600, 700°C for 7.5%(Ni0.8Pd0.2) supported on [93%ZrO2:7%La2O3] as a function of calcination temperatures of 200, 400, 600, and 800°C. (Reprinted with permission from [60]. Copyright 2009 Elsevier.)
Apart from changing the catalyst to control deactivation, incorporation of additional oxidants like H$_2$O or O$_2$ in the reactant stream can improve the resistance of the catalyst to deactivation [58, 175, 200]. A thermodynamic calculation performed with O$_2$ in the DRM feed shows a significant reduction in carbon formation with an increase in O$_2$/CH$_4$ ratio [45]. Garcia, et al [58], reported that over Rh-Ni/Al$_2$O$_3$ bimetallic catalysts addition of small amounts of H$_2$O (steam) along with CH$_4$ and CO$_2$ improves the gasification of the carbon formed during DRM as compared to the gasification carried out by only CO$_2$. A similar concept using multiple oxidants was reported by Nematollahi, et al [201], and Soria, et al [200], where they observed that increasing the concentration of steam as a co-feed inhibits the RWGS and increases H$_2$ selectivity while decreasing the CO$_2$ conversion. They studied combination of DRM and partial oxidation of CH$_4$ (POM) and observed several advantages of this process; namely, coupling of exothermic (POM) and endothermic (DRM) reaction minimizes heat transfer requirements. By altering the feed composition of O$_2$ and CO$_2$, the final desired H$_2$/CO ratio between 0.5-2 can be obtained [201]. A similar process was reported by McGuire, et al [202], who showed that addition of low levels of O$_2$ in the feed significantly increases CH$_4$ conversion and decreases carbon formation. The effect of the addition of O$_2$ and H$_2$O is reversible, i.e., the H$_2$/CO product ratio change when the additional co-reactants are added but the normal DRM yields are restored when H$_2$O and O$_2$ are removed from the feed [41, 176]. This could be perhaps because the addition of H$_2$O or O$_2$ brings about a change in the oxidation state of the metal or changes the kinetics of the intermediate reaction steps which results in the apparent change in the DRM yields, but when flow of H$_2$O and O$_2$ are stopped the oxidation state of the metal reach the metallic state which restores the DRM activity of the catalyst [139].
2.7. Kinetics and Mechanism of DRM

2.7.1. Activation Energies of CH$_4$ and CO$_2$

A wide spectrum of catalysts have been studied for DRM, thus a wide range of mechanistic steps have been reported in the literature, depending upon the temperature and partial pressure range used. The sites for activation of CH$_4$ and CO$_2$ depend strongly on the type of the catalyst used. In case of Pt/SiO$_2$, CH$_4$ and CO$_2$ both are activated on Pt metal, however, when Pt is dispersed on ZrO$_2$, CO$_2$ is activated on ZrO$_2$ support due to involvement of the oxygen vacancies and not on Pt [125]. In-situ XANES study of Pt/ZrO$_2$ under flowing CO$_2$ has shown that during CO$_2$ dissociation to CO and O; there was no change in the Pt spectra suggesting that the dissociated O is a part of ZrO$_2$ and not Pt [16]. An opposite mechanism was observed for Rh/SiO$_2$ where the dissociation of CO$_2$ occurred at Rh site and the metallic Rh was oxidized to Rh$^{+3}$ as seen in XANES [146]. Similar dissociative adsorption of CO$_2$ was proposed by the results obtained from SSITKA study over Ru/SiO$_2$ [138]. In the presence of La$_2$O$_3$, CO$_2$ is activated on La$_2$O$_3$ forming La-oxycarbonates which then react with the carbon formed from CH$_4$ activation at the metal-La interface [203].

Studying the mechanism of DRM and determining the kinetic parameters is important for developing an effective catalyst and for commercializing methane reforming technology. The mechanism and the kinetics of DRM depend on the type of the catalyst used as well as the reactants involved. A few activation energies based on the consumption of CH$_4$ (Ea) and CO$_2$ (Ea) have been reported and selected results are summarized in Table 2.2.
In all cases, the activation energy for CH₄ is greater than that based on CO₂. This is consistent with other reactions involving CH₄ and is due to the energy required to activate the relatively stable CH₄ molecule [127]. For Pt catalysts, the activation energy for the rate of CH₄ and CO₂ disappearance vary for different supports. The difference in the activation barrier can be attributed to the difference in the basicity of the support.

Table 2.2. Activation energies for DRM over different catalysts.

<table>
<thead>
<tr>
<th>Catalyst used</th>
<th>Temperature range (K)</th>
<th>Activation Energy $E_a$ (kcal/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CH₄</td>
<td>CO₂</td>
</tr>
<tr>
<td>1% Pt/Al₂O₃</td>
<td>733-823</td>
<td>21.8</td>
<td>20.2</td>
</tr>
<tr>
<td>1% Pt/ZrO₂</td>
<td>733-823</td>
<td>18.4</td>
<td>15</td>
</tr>
<tr>
<td>1% Rh/MgO</td>
<td>773</td>
<td>23.2</td>
<td>20.3</td>
</tr>
<tr>
<td>1% Rh/Al₂O₃</td>
<td>773</td>
<td>18.2</td>
<td>16.2</td>
</tr>
<tr>
<td>0.5% Rh/Al₂O₃</td>
<td>600-1100</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>0.5% Rh/SiO₂</td>
<td></td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>0.5% Rh/TiO₂</td>
<td></td>
<td>21</td>
<td>-</td>
</tr>
<tr>
<td>0.5%Pt/SrTiO₃</td>
<td>813-893</td>
<td>29.3</td>
<td>-</td>
</tr>
<tr>
<td>0.3%Pt-10%Ni/Al₂O₃</td>
<td>853-893</td>
<td>26.9</td>
<td>23.6</td>
</tr>
<tr>
<td>0.2%Pt-15%Ni/Al₂O₃</td>
<td>853-893</td>
<td>26.6</td>
<td>23.6</td>
</tr>
</tbody>
</table>

2.7.2. Intermediate Mechanistic Steps of DRM

Dissociation of CH₄ is typically the most kinetically significant step in DRM [72, 132, 133, 206]. However, Efstathiou, et al [207], conducted SSITKA and observed that the converse is true for some of the supports. For example, they observed that for Rh supported on yttria stabilized zirconia, the activation of CH₄ was a fast step whereas the activation of CO₂ was the slow step. A similar conclusion was reached by Nakamura, et al [92], who determined DRM was -0.6 order in CH₄ and first order in CO₂. However, they did not mention the relation between the negative kinetic order in CH₄ and the possibility of a decrease in rate due to carbon deposition from the excess of CH₄ in the feed. They also showed that the dissociation probability of CH₄ and CO₂ over Rh/SiO₂ is $1 \times 10^{-4}$ and $2 \times 10^{-5}$, respectively, thus suggesting that dissociation of
CO\(_2\) is the slow step compared to dissociation of CH\(_4\) [92]. This claim could however be true for inert supports like SiO\(_2\) but not when the support is electrophilic or nucleophilic. Pant, et al [177], reported mechanistic steps for DRM on Pt/LaCoO\(_3\) catalysts and proposed that CH\(_4\) activated on Pt forming C(s) and H\(_2\). This C(s) is oxidized by the lattice O of the LaCoO\(_3\) perovskite phase creating O vacancy. This vacant site activates and dissociates CO\(_2\) to form CO and replenish the lattice O. A balance between the loss and replenishment of the lattice O determines the activity and stability of the catalyst. The stability is enhanced when O\(_2\) is present in the DRM feed [177]. This same mechanism of CH\(_4\) dissociation on Pt and dissociation of CO\(_2\) on ZrO\(_2\) was reported by Stagg, et al [184] for 1.5%Pt/ZrO\(_2\) catalysts. They found that the presence of promoters like La and Ce does not change the mechanism but accelerates the rate of intermediate steps like rate of carbon oxidation [184]. Bradford, et al [208] and O’Connor, et al [72] proposed the exact same mechanism for Pt/ZrO\(_2\) catalyst, however, they reported the presence of hydroxyls on catalyst surface unlike that reported by Stagg, et al [184]. This could be because Stagg studied the mechanism at 800°C, while Bradford and O’Connor studied it at ~600°C, so that the hydroxyls were absent in the Stagg study. This suggests that the temperature of reaction alters the intermediate steps in the mechanism of DRM over catalysts. These different conclusions regarding the kinetics of DRM are at least in part due to different temperature and partial pressure ranges used to study the kinetics and mechanism of DRM. This makes truly direct comparison among these studies difficult and often inconclusive [75].

To examine this more closely, Cui et al [75], performed kinetic analysis at consistent partial pressure in the temperature range 823-1023K and observed that the rate-determining step (rds) changed with temperature. They reported that CH\(_4\) dissociation was the rds for 823-848K range, whereas the reaction between CH\(_x\) and CO\(_2\) was the rds in 923-1023K range. Bradford, et
al [68, 143, 148], have shown in their detailed study on mechanism of DRM over Pt, Ni and Ru catalysts that CH$_4$ dissociates reversibly to form CH$_x$ species. The dissociative adsorption of CO$_2$ forms CO and O on the surface, this O reacts with CH$_x$ and leads to formation of CH$_3$O. This CH$_3$O then dissociates to form CO and H$_2$. Spectroscopic methods have also been used to follow the reaction mechanism. A detailed FTIR study of the mechanism CH$_x$ reaction with CO$_2$ was reported by Rasko, et al [209]. In that study they selectively adsorbed CH$_3$ by dissociation of azomethane species on Rh/SiO$_2$ surface, then studied the changes in the IR spectra of C-H stretching as a result of (a) evacuation, (b) 1Torr flow of CO$_2$. The IR spectra of adsorbed CH$_3$ species is shown in Figure 2.18 (A). The band at 2922 cm$^{-1}$ is attributed to the C-H stretching frequencies of the adsorbed CH$_3$ species and 2960, 2854 cm$^{-1}$ are attributed to the C-H stretching of the CH$_3$O species. When the adsorbed CH$_3$ species on Rh/SiO$_2$ were heated in vacuum, there was a drop in the intensity of the absorbance as shown in Figure 2.18 (B), suggesting a drop in surface population of CH$_3$ species. When the adsorbed CH$_3$ was heated in flowing CO$_2$, the drop in the absorbance (2922 cm$^{-1}$) was more rapid than in vacuum and CO was formed, as judged by the appearance of band at 2024 cm$^{-1}$. Formation of CO was observed only for Rh/SiO$_2$ and not for SiO$_2$, suggesting that the reaction of adsorbed CH$_3$ and CO$_2$ takes place at the periphery of Rh particles.

A similar stepwise mechanism proposed by Topalidis, et al [205], over 0.5% Pt/SrTiO$_3$ suggests that the activation of CH$_4$ occurs at the metallic Pt site whereas the CO$_2$ is activated at the basic metal oxide support. They report dissociative adsorption of CH$_4$ to form C(s) and H$_2$. This H$_2$ may either desorb or react with the adsorbed CO$_2$ to form CO and H$_2$O by RWGS. Whether H$_2$ desorbs or reacts by RWGS, depends on the catalyst type, temperature, and partial pressure (surface concentration) of CO$_2$. The adsorbed CO$_2$ must dissociate to form CO and O,
this O later reacts with the C(s) to form another CO. The reaction between O and C(s) occurs at the interface of Pt and the support [205]. However, they did not discuss the reduction process of CO$_2$ to CO in detail. The cleavage of the C-O bond in CO$_2$ could be occurring either by the activation by basic SrO or by the O deficiencies in TiO$_2$ from the SrTiO$_3$ oxide support. Both could be significant; SrO adsorbs CO$_2$ and TiO$_2$ dissociates it to CO and O.

Figure 2.18. (A) FTIR spectra for C-H stretching of adsorbed CH$_3$/CH$_3$O species on Rh/SiO$_2$, (B) Changes in the ratio of integrated absorbance of CH$_3$ adsorbed species at 2922 cm$^{-1}$ due to evacuation and presence of 1 Torr of CO$_2$ at 423 K. (Reprinted with permission from [209]. Copyright 1997 Springer.)
Other studies on Pt and Ru catalysts have shown that CH₄ adsorbs dissociatively to form C(s) and H₂, with no evidence of CH₃ species on the catalyst surface [132, 133]. The sequence and reversibility of the kinetically significant steps in the DRM mechanism are subject to even slight changes in the catalyst metal, support, temperature, and space velocity. Bradford, et al [96], used a novel approach to study the active sites of DRM for Pt/TiO₂ catalysts. They conducted DRM tests on Pt powder, TiO₂ powder and Pt/TiOₓ catalyst. They observed that there was no activity for pure Pt or TiO₂ powder, but Pt/TiOₓ was quite active. They attributed this to the creation of a new type of metal-support interfacial region which catalyzes the dissociation and reaction of intermediates formed from CH₄ and CO₂ activation [96].

Most catalysts studied for DRM, except for the ones with inert supports, follow bi-functional pathway for DRM. In this pathway, the activation of CH₄ and CO₂ occur at two different sites and the reaction between the intermediates takes place at the metal–support interface. This bi-functional pathway has general support in the literature, with the reaction taking place on catalysts with active metal, and support having either electrophilic or nucleophilic character. For active metals on inert supports, the metal catalyzes all the surface reactions and is more prone to deactivation due to carbon deposition or sintering.

2.7.3. Kinetic Rate Modeling

Many researchers have used simple power law models to study the reaction mechanism for DRM [9, 210, 211]. These models can be used to explain how presence of Pt helps in reducing carbon formation on the Ni/Al₂O₃ catalyst. When the Ni/Pt ratio was 75/1, the order in CO₂ was 1.4 and when it was 33/1, the order was 0.87. This suggests that the presence of Pt enhances the reactivity of the oxygen from CO₂ and aids in the reaction of this oxygen with the
deposited carbon [129, 130]. This explains why promotion with Pt increases the stability of Ni catalysts. The presence of Pt also decreases the inhibition effect of CO on the rate of DRM [129, 130]. However, a power law model is generally valid for only a narrow range of partial pressures. In order to attain a rate model that is valid over a wider range of conditions, a model based on a fundamentally sound mechanism is needed. Quiroga, et al [212] performed kinetic rate modeling on Ni-Rh/Al₂O₃ catalyst and present a series of mechanistic steps involved in DRM [Figure 2.19]. They then assumed different surface reactions as the rate limiting steps. Using Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism, they derived a set of 27 rate expressions and fit the obtained kinetic data to the rate expressions. They performed the parameter estimation by minimizing the objective function;

$$\Phi = \sum_{i=1}^{n} (x_{CH_4, exp} - x_{CH_4, calc})^2$$

where, n is the number of conditions the experiments are carried out, $x_{CH_4, exp}$ is the experimental conversion of CH₄ and $x_{CH_4, calc}$ is the conversion of CH₄ calculated by the kinetic rate expression. Minimizing this parameter ($\Phi$) by using the Marquardt’s algorithm gives the best fit values for the adsorption and rate constants that are used in the rate expressions. This methodology of deriving a mathematical model and fitting it with a kinetically relevant dataset makes the model quantitative and predictive which helps in understanding the DRM mechanism.

Other detailed mechanisms and models have also been proposed in the literature and statistically compared to experimental results [9, 49, 53, 70, 134, 143, 207, 210, 213, 214]. For example, Richardson, et al [210], derived a rate expression based on the LHHW mechanism
where CH₄ and CO₂ are both adsorbed and these adsorbed CH₄ and CO₂ take part in the rate determining step. They observed that the kinetic experimental data obtained over Rh/Al₂O₃ was in agreement with the derived rate model [Eqn 11]. However, they did not show the forms of adsorption or the sequence of reaction steps that led to this model equation.

Figure 2.19. Kinetic scheme of the DRM mechanism. (Reprinted with permission from [212]. Copyright 2007 American Chemical Society.)

Luo, et al [49], assumed that the dissociation of CH₃O species to CO and xH as the rate determining step but did not present the derived rate model for the same. Mark, et al [70, 215], argued that the conventional Langmuir-Hinshelwood (LH) or Eley-Rideal models are not suitable for representing the kinetics of the reaction over Ir/Al₂O₃. Based on their experiments they proposed a model [Table 2.3, Eqn 12] with CH₄ dissociation to surface carbon and H as the rate determining step while the oxidation of CH₃ to CO, and dissociation of CO₂ to CO as fast step.
Table 2.3. Representative rate models for DRM over various catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Assumption</th>
<th>Rate Model</th>
<th>Eqn</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh/Al₂O₃</td>
<td>LH mechanism</td>
<td>[ r_{CH_4} = \frac{k_R K_{CO_2} K_{CH_4} P_{CO_2} P_{CH_4}}{(1 + K_{CO_2} P_{CO_2} + K_{CH_4} P_{CH_4})^2} ]</td>
<td>11</td>
<td>[210]</td>
</tr>
<tr>
<td>Ir/Al₂O₃</td>
<td>CH₄ dissociation as rds</td>
<td>[ r_{CH_4} = \frac{k_R (P_{CH_4} - \frac{P_{H_2} P_{CO_2}^2}{K P_{CO_2}})}{(1 + \frac{P_{CO_2}^2}{K_{C-S} P_{CO_2}})} ]</td>
<td>12</td>
<td>[215]</td>
</tr>
<tr>
<td>Rh-Ni/La₂O₃</td>
<td>CH₄ dissociation and C(s) oxidation as rds</td>
<td>[ r_{CH_4} = \frac{k_k k_c K_{CO_2} K_{CH_4} P_{CO_2} P_{CH_4}}{(k_k K_{CO_2} P_{CO_2} + k_c K_{CO_2} K_{CH_4} P_{CO_2} + k_k K_{CH_4} P_{CH_4} + k_c K_{CO_2} K_{CH_4} P_{CO_2})} ]</td>
<td>13</td>
<td>[206]</td>
</tr>
<tr>
<td>Pt/ZrO₂</td>
<td>Oxidation of CH₄ by CO₂ as rds</td>
<td>[ r_{CH_4} = \frac{k_k k_c K_{CO_2} K_{CH_4} P_{CO_2} P_{CH_4}}{(k_k K_{CO_2} P_{CO_2} + (1 + K_{CO_2} P_{CO_2})(k_k P_{CH_4} P_{CH_4} + k_k P_{CO_2} P_{CO_2} P_{CH_4}^2)} ]</td>
<td>14</td>
<td>[204]</td>
</tr>
<tr>
<td>Ni-Rh/Al₂O₃</td>
<td>Oxidation of C(s) is the rds</td>
<td>[ r_{ref} = \frac{k_k K_{CO_2} K_{CH_4} (P_{CO_2} P_{CH_4} / P_{H_2}^{0.5} - P_{H_2}^{1.5} P_{CO_2}^2 / K_{ref} (1 + K_{CO_2} P_{CO_2} + P_{CH_4} / P_{H_2}^{0.5} K_{CH_4}^2) ]</td>
<td>15</td>
<td>[212]</td>
</tr>
</tbody>
</table>

Many investigators assume that the activation of CO₂ and CH₄ takes place on different sites [16, 18, 216]. For instance, Gallego, et al [206], observed S1 and S2 as sites for activation of CH₄ and CO₂, respectively. They derived a rate model where CH₄ dissociates on S1 to form adsorbed carbon C-S1, and CO₂ adsorbs on S2 to form CO₂-S2. They reported two rate determining steps, (i) dissociation of CH₄, and (ii) oxidation of C-S1 by CO₂-S2, which results in the rate model given by eqn 13. Souza, et al [204], observed similar bi-functional mechanism with dissociation of CH₄ and reaction between adsorbed CHₓ and non-dissociated adsorbed CO₂ as the rds for their rate model [Eqn 14] over Pt/ZrO₂. Quiroga, et al [212], proposed twenty-seven different models varying in sequence of reaction steps like dissociative and associative adsorption of CH₄ and CO₂. They observed that the model that was the best fit to the kinetic data was denoted by eqn 15 [Table 2.3] for Ni-Rh/Al₂O₃ catalyst. The model considers dissociative
adsorption of CH\(_4\) and molecular adsorption of CO\(_2\). The rate determining step is the reaction between surface carbon and adsorbed CO\(_2\). Although the types of catalyst used (noble or non-noble metal like eqn 13), temperature and partial pressure range used to study the mechanism vary [Table 2.3], the predicted rate determining step remains the same, viz dissociation of CH\(_4\) or oxidation of C(s) unless the catalyst support is inert. A summary of some of the above mentioned rate expressions are shown in Table 2.3.

2.8. Conclusion

The highly endothermic nature of DRM could be a problem due to high energy requirement but can be handled by utilizing it with exothermic partial oxidation or combustion which can make the process thermo-neutral. Another major issue with this reaction is inevitable deposition of surface carbon and the nature and morphology of this surface carbon is a function of the metal used, dispersion of the metal, duration of reaction, temperature of reaction, and activation rate of CO\(_2\). Depending on the morphology of the carbon, the catalyst may or may not show deactivation effect. This carbon formation can be inhibited by choosing appropriate basic support or promoters and using noble metals which resist carbon deposition and show high activity. However, noble metals are expensive and so to make the process economical, noble metals can be used to decorate the cheaper Ni catalyst which helps in increasing the dispersion of Ni, thus increasing the activity of the catalyst. Using noble metals and basic promoters help in maintaining a balance between formation and oxidation of carbon which results in prolonged uninterrupted performance of the catalyst. Using appropriate catalyst activation/calcination procedure, promoter to metal ratio, metal precursor can lead to synthesis of a catalyst with enhanced resistance to deactivation due to carbon formation by decreasing the formation of carbon or by increasing the reactivity of the formed carbon towards oxidation.
Mechanistically the most important and the slowest step in DRM is the activation of CH$_4$ which occurs primarily on the metallic site and thus having high dispersion of the metal is important. Activation of CO$_2$ is relatively a faster process and occurs mainly on the support or the metal-support interface in case of acidic and basic supports. Thus most catalysts with acidic or basic supports follow a bi-functional pathway where CH$_4$ and CO$_2$ activate on different sites and the reaction intermediates react at the metal-support interfacial sites. In case of inert supports, activation of CH$_4$ and CO$_2$ occurs on the metal alone (uni-functional pathway) and thus the inert support catalysts are more prone to deactivation due to carbon deposition than acidic or basic supports. Thus selecting an appropriate catalyst, temperature and partial pressure range is very vital in avoiding deactivation and stable performance of the catalyst for DRM.

2.9. References


3.1. Introduction

Dry reforming of methane ( DRM) produces commercially important syngas that can be used for chemical processes like Fischer-Tropsch or synthesis of various chemicals [1,2]. One of the problems associated with DRM is catalyst deactivation due to carbon deposition [1,3,4]. In addition to carbon deposition, DRM is highly endothermic reaction ($\Delta H_{298K} = 59.1$ kcal mol$^{-1}$) and requires temperatures approaching 900-1000°C to reach high equilibrium syngas yields. These temperatures lead to sintering of conventional supported metal catalysts. Thus there is a need to develop catalyst that will resist deactivation due to sintering and carbon deposition [5-8]. Pyrochlores are ternary metal oxides based on the fluorite structure with general formula of $A_2B_2O_7$ [9]. Large cations like rare earth elements usually occupies the A-site whereas the B-site is occupied by a transition metal with a smaller atomic radius [10]. The pyrochlore structure allows limited isomorphic substitution of catalytically active metals like Ru, Rh, and Pt at the B-site.

The most preferred metal for the DRM reaction is Ni due to its low cost and availability [4,11-14], however, this metal undergoes severe deactivation due to carbon deposition. Noble metals like Ru, Rh, and Pt have greater resistance to carbon deposition but are not economical [15-19]. In our previous work we have studied Ru (on B-site) and Sr (on A-site) substituted pyrochlores for DRM [20]. In the present work, we report a study of Ru and Pt substituted (at the B-site) lanthanum zirconate pyrochlores. Despite their well-known thermal stability and reports

of their use for other purposes such as thermal barrier coatings, we are aware of only one study of these materials for DRM i.e., by Ashcroft, et.al [21]. In that paper, Ashcroft et al. studied Eu₂Ir₂O₇ pyrochlores and observed that above 342°C under DRM conditions, these materials completely decompose to Eu₂O₃ and Ir metal. However, in one of our previous works we have used Ru and Sr substituted pyrochlores which have proven to be extremely thermally stable at 850°C [20]. Here, we perform ICP-OES, XRD, and TPR using H₂ and CH₄ as reducing gases and study the effect of substitution of Ru and Pt (separately) at the B-site of the pyrochlore structure. Temperature programmed surface reaction (TPSR) was conducted to study the changes in the catalyst light-off temperatures as a result of change in the active metal substituted on the B-site.

3.2. Experimental Section

3.2.1. Catalyst Synthesis

The LZ, LRuZ, and LPtZ pyrochlores were synthesized by modified Pechini method using salts of lanthanum nitrate hexahydrate (La(NO₃)₃.6H₂O), zirconium oxynitrate (ZrO(NO₃)₂.xH₂O), and either ruthenium chloride (RuCl₃) or hydro-chloroplatinic acid (H₂PtCl₆·(H₂O)₆) salts as precursors, and anhydrous citric acid (C₆H₈O₇), ethylene glycol (C₂H₆O₂) as complexing and polymerizing agents respectively. Stoichiometric amounts of metallic precursors were separately dissolved in 50 ml of deionized water, and then combined into a larger beaker with continuous stirring. An aqueous citric acid (CA) solution was then added to the stirring solution in the beaker. The molar ratio between CA and total metal ions was kept at 1:2. The solution was heated to 70 °C and while stirring on a hot plate before ethylene glycol (EG) was added. The molar ratio of EG to CA was 1:1. The solution was stirred under
isothermal conditions for several hours until a clear viscous gel was obtained. To promote polyesterification reaction between CA and EG, the gel was further heated in a heating mantle at 130°C. This resulted in an amorphous polyester-type resin. The solid material was then collected and calcined at 1000 °C for 8 hours to form the mixed metal oxide material.

3.2.2. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

The samples were quantitatively weighed to the nearest 0.00001g and then transferred to a Teflon digestion sample holder. Four mL of concentrated trace metal grade hydrochloric acid was added to the sample and was loosely covered for 16 hrs. The sample was then heated in a sand bath for 1 h at 95°C. After cooling, the samples were sealed and digested in a CEM Mars 5 microwave. After digestion, the Teflon sample holders were heated on a sand bath at ~95°C until acid was nearly evaporated. Then 5 mL of freshly prepared aqua regia was added to each sample and loosely covered overnight. The microwave digestion was repeated with holding at 200°C for 20 min. The samples were then cooled and sat overnight. The so prepared samples were then analyzed on a Perkin Elmer 2000 DV Inductively coupled plasma optical emission spectrometer at wavelengths of 240.272 nm for Ru, 333.749 nm for La, 257.139 nm for Zr, and 214.423 nm for Pt.

3.2.3. X-Ray Diffraction (XRD)

Crystalline nature of the freshly calcined pyrochlores was studied using X-Ray Diffraction spectra obtained from a Bruker/Siemens D5000 system. The system was composed of a ceramic X-ray tube with Cu Kα radiation operating at a wave length of 1.54184 Å. X-Ray tube operated at a voltage of 40 kV and current of 30 mA. Angle of divergence slit was 1° and antiscatter slit was 0.5°. For analysis 2Θ was varied from 10° to 80° at a sweep rate of 0.02°/min.
3.2.4. Temperature Programmed Reduction (TPR)

3.2.4.1. Temperature Programmed Reduction by H$_2$

Temperature programmed reduction (TPR) of the catalysts was conducted in an AMI 200 (Altamira instruments, Pittsburgh, PA) fixed bed reactor. For each run, 50 mg of catalyst was loaded into the 6.5 inch (length) by 6 mm (outer diameter) by 4 mm (inner diameter) quartz tube. The catalyst was packed in place by using quartz wool plugs. Thermocouple that ran axially through the tube touching the quartz wool was used to monitor the bed temperature continuously. TPR was performed on LZ, LPtZ and LRuZ pyrochlores. Before starting TPR, samples were oxidized in flowing O$_2$/He at 30 mL/min from ambient (ca. 35º C) to 950ºC at a rate of 5ºC/min. This was done to oxidize the metals on the surface and in the bulk which could then consume H$_2$ during the TPR. The sample was then cooled to room temperature in flowing He at 30 mL/min. This also ensured oxidation and desorption of any adsorbed species on the catalyst surface. Next, the sample was exposed to mixture of 10% H$_2$/Ar flowing at 30 mL/min with the temperature ramped from 40ºC to 950ºC at 5ºC/min. The temperature was held at 950ºC for 30 minutes and then cooled to room temperature.

The amount of metal reduced in pyrochlores was quantified. This estimation of the extent of metal reduction in the catalyst was done using silver oxide (Ag$_2$O) standards. Known quantity of Ag$_2$O was reduced under similar conditions as the catalysts. From stoichiometric calculations, the amount of hydrogen required for reduction of the given amount of Ag$_2$O was determined. Repeating TPR of the Ag$_2$O standard gave a calibration curve relating the area under the TPR profile of the catalyst to the hydrogen consumption of that catalyst during the reduction reaction. The area under the TPR peak of the catalyst was related to the H$_2$ uptake by that catalyst during TPR.
3.2.4.2. Temperature Programmed Reduction by CH₄

This characterization method was used to study the oxygen conductivity of the pyrochlore structure. For this about 50 mg of catalyst was dried at 500°C in flowing He at 30 mL/min and cooled to room temperature in flowing He. The catalyst bed was then subjected to reduction by 10% CH₄/He flowing at 30 mL/min and the temperature was ramped from 40°C to 950°C at the ramp rate of 5°C/min. The conditions were maintained isothermal at 950°C for 30 min. The product stream during the CH₄ TPR was analyzed using the mass spectrometer (MS) that was hooked up with the reactor outlet. The MS was calibrated for known concentration of CO and CO₂ and the concentration of CO and CO₂ in the product line was determined.

3.2.5. Temperature Programmed Oxidation (TPO)

After subjecting the catalysts to TPR by CH₄, a TPO was conducted for studying quantitatively and qualitatively the oxygen conductivity of the pyrochlores. For conducting the TPO, the catalyst was cooled to room temperature (ca. 35°C) in flowing He at 20 mL/min. Then it was oxidized in flowing 5% O₂/He at 30 mL/min from room temperature to 950°C and the ramp rate was 5°C/min. The conditions were maintained isothermal at 950°C for 30 minutes. The CO and CO₂ emitted during the TPO were tracked using the mass spectrometer (MS) hooked up to the reactor outlet. The amount of CO and CO₂ formed during TPR by CH₄ and TPO was calculated using the calibration gases of 5% CO/He and 10% CO₂/He.

3.2.6. Temperature Programmed Surface Reaction (TPSR)

For carrying out TPSR experiment, 50 mg of catalyst was loaded into the U-tube quartz reactor and was dried at 300°C in flowing He. After treatment with He it was cooled to room temperature (ca. 25°C) and the reactant gases were allowed to flow over the catalysts. The
temperature was then programmed to rise from 25°C to 900°C with the ramp rate of 5°C/min and the gas hourly space velocity (GHSV) was maintained at 48,000 mL gcat⁻¹ h⁻¹. The MS signal for the products from the reactor was recorded.

3.3. Results and Discussion

3.3.1. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

Table 3.1 shows the bulk concentration of the metals in the pyrochlores determined using ICP-OES. These results show similar atomic level substitution for Ru and Pt at the B-site.

<table>
<thead>
<tr>
<th>Catalyst\Metal</th>
<th>La</th>
<th>Zr</th>
<th>Pt or Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atom %</td>
<td>ICP (wt %)</td>
<td>Atom %</td>
</tr>
<tr>
<td>LZ</td>
<td>32.8</td>
<td>45.6</td>
<td>47.5</td>
</tr>
<tr>
<td>LPtZ</td>
<td>33.1</td>
<td>45.8</td>
<td>34.4</td>
</tr>
<tr>
<td>LRuZ</td>
<td>33.9</td>
<td>47.2</td>
<td>34.7</td>
</tr>
</tbody>
</table>

3.3.2. X-Ray diffraction (XRD) Study of Fresh Catalyst

XRD pattern of the freshly calcined catalysts [see Figure 3.1] showed the formation of the cubic unit cell crystalline La₂Zr₂O₇ phase. The triangle marked peaks denote the angle of diffraction of the X-rays from the La₂Zr₂O₇ phase of the catalyst. The diffraction angles attributed to the La₂Zr₂O₇ phase observed in this work are in accordance with the ones observed in the literature [22, 23]. As expected, the substitution of Pt and Ru on the B-site did not affect the pyrochlore crystalline structure.

Haynes, et al [10, 23, 24], have studied pyrochlores with Sr and Ru substitution on A and B site respectively for other fuel reforming reactions. They observed that when substitution of Sr and Ru was beyond a certain limit, a SrZrO₃ perovskite phase was formed, which diffracted X-rays at the angle of about 32°. This is in agreement with the fact that there is a limit to the extent
of substitution at either the A or B sites, beyond which the excess of the substituted metal separates out as a perovskite phase [22]. There was no formation of any such perovskite phase observed in Figure 3.1, suggesting that the extent of substitution of Pt and Ru are low enough to avoid the formation of any separate perovskite phase. Comparing the diffraction pattern for LZ with LPtZ and LRuZ shows that there was no shift in the diffraction angle as a result of Pt (3.3 wt%) or Ru (2 wt%) substitution on the Zr$^{4+}$ site. The substitution of Pt and Ru atoms on the B-site caused no apparent change in the lattice constant of the lanthanum zirconate.

![Figure 3.1. XRD pattern of the freshly calcined LZ, LPtZ, and LRuZ pyrochlores.](image)

3.3.3. Temperature Programmed Reduction (TPR)

3.3.3.1. Temperature Programmed Reduction (TPR) by H$_2$

The H$_2$ TPR profile for LZ, LPtZ, and LRuZ is shown in Figure 3.2. LZ pyrochlore shows reduction at 490°C and 580°C, and the total consumption of H$_2$ during reduction amounts to 0.155 mg H$_2$/gcat. This suggests that only 0.6% of the total lanthanum zirconate is reduced
during TPR. Reduction of LPtZ shows a small peak at 343°C and two peaks at 499°C and 558°C. The 343°C peak could be due to the reduction of either PtOₓ in the pyrochlore lattice to Pt metal or to the reduction of Zr at the Pt-Zr interface [25]. Souza et al [25] observed similar reduction peaks for Pt/ZrO₂ catalysts and attributed it to the Pt-assisted reduction of Zr, possibly by hydrogen spillover where Pt activates and homolytically dissociates H₂ which then reduces the Zr at the Pt-Zr interface. A similar phenomenon could be occurring over LPtZ. However, it is important to consider the fact that the class of catalysts used in the work by Souza and in this work is different.

Figure 3.2. Temperature Programmed Reduction of freshly calcined LZ, LPtZ, and LRuZ pyrochlores.
The reduction peaks at 499°C and 558°C for LPtZ can be attributed to the reduction of lanthanum zirconate as seen in the profile of LZ. The total hydrogen consumption by LPtZ is 0.161 mg H₂/g_{cat} which is very close to that consumed by LZ i.e., 0.155 mg H₂/g_{cat}. This indicates that the presence of Pt does not significantly increase the reducibility of the pyrochlore itself. Also, if all of Pt (assuming PtO₂ form) in the pyrochlore was reduced during TPR, then the hydrogen consumed by Pt would be 1.3 mg H₂/g_{cat} which is much greater than the total hydrogen consumption of LPtZ (0.161 mg H₂/g_{cat}). In pyrochlores, most of the metal is substituted in the bulk of the pyrochlore and is inaccessible to H₂ during TPR experiment. The extent of reduction of LPtZ during TPR is only 0.64% of the total metal content, showing that the reduction is limited to the surface atoms, as expected.

TPR of LRuZ, however, shows multiple reduction peaks at 100°C, 238°C, 450°C, and 551°C. The presence of a low temperature reduction peak at 100°C suggests that at least a small amount of Ru at the pyrochlore surface is not strongly bound to the pyrochlore structure. Though not detectable by XRD, these small clusters of Ru exhibit a reduction behavior similar to that for RuO₂/Al₂O₃ [10]. This surface Ru appears to be formed by the oxygen pretreatment (to 950°C; section 3.2.4.1), during which Ru in the pyrochlore is destabilized from the B-site and diffuses to the surface. The peak at 238°C is assigned to the reduction of Ru substituted in the pyrochlore structure. In one of our earlier work with Ru (at B-site) and Sr (at A-site) substituted pyrochlores, we observe reduction of Ru at 280°C [20]. The reduction of Ru in the LRuZ here is about 40°C lower than that reported in the earlier study, possibly due to a slightly weaker interaction of Ru in the pyrochlore structure. The similarity of the reduction peaks at 450°C and 551°C for LRuZ and those at 490°C and 580°C for LZ in Figure 3.2 suggest that both are attributed to reduction of the lanthanum zirconate pyrochlore. Presumably, the slightly lower peaks for LRuZ suggest that the
reduction of LZ is enhanced somewhat by Ru via hydrogen spillover. The amount of hydrogen consumed by LRuZ is 0.534 mg H\textsubscript{2}/g\textsubscript{cat} which is much greater than that by LPtZ or LZ, largely due to reducibility of the Ru that appears to be on the pyrochlore surface rather than in the structure. If all the Ru in LRuZ reduces, then the hydrogen consumption by Ru (assuming RuO\textsubscript{2} form) alone would be 1.4 mg H\textsubscript{2}/g\textsubscript{cat} which is far greater than the total hydrogen consumption of LRuZ of 0.534 mg H\textsubscript{2}/g\textsubscript{cat}. This suggests that most of the Ru is still substituted in the pyrochlore structure which is inaccessible during TPR. The total metal (La, Zr, and Ru together) reduced during LRUZ TPR is 2.12\% of the total metal content, again consistent with the premise that the reduction is limited to the surface of the pyrochlore.

3.3.3.2. Temperature Programmed Reduction (TPR) by CH\textsubscript{4}

Lanthanum zirconate pyrochlores similar to those reported here have been used by Haynes, et al [10, 23, 24], for reforming of diesel-range alkanes. They observed that the lattice oxygen of these materials is reactive and helps in resisting carbon formation during reforming reactions. To study lattice oxygen conductivity of the pyrochlores, TPR of these materials using CH\textsubscript{4} as a reducing agent was carried out. CH\textsubscript{4} is believed to activate on the catalyst to form surface carbon and hydrogen. This surface carbon then must be oxidized in order to limit accumulation of carbon deposits. During DRM, CO\textsubscript{2} acts as an oxidizing agent and helps in limiting carbon formation over the catalyst. However, during CH\textsubscript{4} TPR, there is no CO\textsubscript{2} or O\textsubscript{2} in the feed or in the pre-treatment of the catalyst. Thus the only oxygen available for oxidation of surface carbon is the lattice oxygen. Figure 3.3 (a) shows the CO and CO\textsubscript{2} formation during the CH\textsubscript{4} TPR of LZ pyrochlore. The signal for CO\textsubscript{2} was very weak and no distinct peak could be identified. CO formation begins at about 560 °C and reaches a first peak at 605 °C. Other peaks at 720 °C and 920 °C were also observed for CO formation.
Figure 3.3. TPR by CH$_4$ of freshly calcined (a) LZ, (b) LPtZ, and (c) LRuZ from 50 ºC - 950 ºC at the ramp rate of 5 ºC/min. [ISO represents that the conditions were isothermal at 950 ºC for 30 min for LZ and 60 min for LPtZ and LRuZ]. The plots (a), (b), and (c) differ in Y-axis scale.
Substitution of Pt and Ru on the B-site decreases the temperature at which the lattice oxygen in the pyrochlore begins to react with methane [see Figure 3.3 (b) and (c)]. For LPtZ, \( \text{CH}_4 \) TPR resulted in CO formation at 397°C, 650°C and 950°C. Substantial amounts of \( \text{CO}_2 \) were also formed during \( \text{CH}_4 \) TPR of LPtZ, unlike LZ. For LRuZ [Figure 3.3 (c)], the reduction temperatures were much lower compared to LPtZ and LZ. The first peak for CO formation was observed at 283°C followed by a large peak at 449°C and small peaks at 582°C and 814°C.

High temperature reduction peaks (720°C and 920°C) were observed for LZ and one similar reduction peak (950°C) was also observed for LPtZ. This suggests that these high temperature peaks in LPtZ profile is due to the reaction of oxygen associated with the lanthanum zirconate part of LPtZ pyrochlore. The low temperature peaks (397°C and 650°C) are due to the reaction of oxygen associated with Pt in the pyrochlore structure. For LRuZ, the reduction peaks
were at very low temperatures (283°C and 449°C) compared to LZ (605°C and 720°C) and LPtZ (397°C and 650°C). This is consistent with the H$_2$ TPR results, which suggested that Ru is not stable within the pyrochlore structure, and migrates from the B-site to the surface. The low temperature reduction peaks for LRUZ [Figure 3.2] could be due to reaction of oxygen associated with Ru. H$_2$-TPR of LRUZ showed that Ru substitution increases the reducibility of lanthanum zirconate, causing it to reduce at temperatures (450°C and 551°C) lower than LZ (490°C and 580°C) [Figure 3.2]. A similar phenomenon was observed in CH$_4$-TPR of LRUZ where the reaction of oxygen associated with lanthanum zirconate was observed at 814°C compared to 920°C for LZ and 950°C for LPtZ. Because H$_2$ is a stronger reducing agent than CH$_4$, it reduces the catalyst at much lower temperatures than CH$_4$. A comparison of Figure 3.2 (H$_2$ TPR) and Figure 3.3 (CH$_4$ TPR) shows this to be true for all the catalysts. We are not aware of any reports in which CH$_4$-TPR has been used to study the lattice oxygen reactivity of Ru and Pt pyrochlores and in which CH$_4$-TPR and H$_2$-TPR are directly compared.

3.3.4. Temperature Programmed Oxidation (TPO)

The surface carbon formed during CH$_4$ TPR was oxidized and the resultant CO/CO$_2$ profiles (TPO) plots for LZ, LPtZ, and LRUZ are shown in Figure 3.4 (a), (b), and (c) respectively. The major product during TPO was CO$_2$ and very small amounts of CO were formed at the same temperatures as CO$_2$. The oxidizable carbon formed on the surface were then quantified and normalized with respect to the weight of the catalyst.

TPO of the LZ pyrochlore shows a low temperature CO$_2$ peak at 340°C and CO peak at 335°C [see Figure 3.4 (a)]. Zhang, et. al [26]. in their work on Rh/Al$_2$O$_3$ catalysts observed surface carbon which oxidized at 330°C and called it ($\delta$) phase of carbon. The peak at 340°C could be due to the oxidation of this C$_{(\delta)}$ phase. Dehydrogenated carbon often oxidizes at higher
temperatures compared to the partially hydrogenated surface carbon [27]. A similar dehydrogenated form of carbon could be responsible for the 600°C TPO peak. The total amount of carbon formed over LZ during CH$_4$ TPR which was later oxidized to CO and CO$_2$ is 0.261 g$_C$/g$_{cat}$. The carbon formed over the LPtZ was qualitatively found to be more reactive, and presumably more hydrogenated, than the carbon formed on LZ pyrochlores. The low temperature peak was found to be at 260°C [Figure 3.4 (b)]. This carbon could be polymeric in nature deposited near the metal (Pt) site in the pyrochlore structure[27]. The high temperature peaks at 503°C and 569°C could be due to the oxidation of more dehydrogenated type of carbon deposited away from the Pt site [10, 27]. The total amount of carbon formed over LPtZ is about 1.67 g$_C$/g$_{cat}$, which is much greater than that compared to LZ. This suggests that Pt is the active site for activation of CH$_4$ during DRM.

Figure 3.4. Temperature Programmed Oxidation of the catalysts spent for CH$_4$ TPR (a) LZ, (b) LPtZ, and (c) LRuZ. Oxidized from 50°C – 950°C at the ramp rate of 5°C/min. The plot of each catalyst differs in Y-axis scale.
(Figure 3.4 continued)
The TPO of the LRUZ pyrochlores after CH4 TPR suggest that the carbon formed was qualitatively different from that observed over LZ and LPtZ pyrochlores. The peak at 516°C could be due to the oxidation of the same dehydrogenated polymeric carbon found on the LPtZ deposited away from the active metal [10, 27]. A high temperature peak was observed at 776°C, which was not observed over LZ or LPtZ. This carbon could be graphitic in nature and is extremely stable, requiring a high temperature for oxidation. In one of our earlier studies with Ru and Sr substituted pyrochlores, we observed similar graphitic carbon oxidizing at 790°C [20]. This carbon could be considered to be progressively formed during CH4 TPR, first starting with hydrogenated polymeric carbon that is further dehydrogenated with increasing temperature.

Table 3.2 shows the total amount of carbon formed over the three catalysts. Carbon on LRUZ is 1.17 gC/gcat, somewhat less than for LPtZ (1.67 gC/gcat).

Table 3.2. Summary of carbon formed; as computed from the TPO of the catalysts spent during TPR by CH4.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Total amount of carbon formed during TPR by CH4 (gC/gcat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LZ</td>
<td>0.261</td>
</tr>
<tr>
<td>LPtZ</td>
<td>1.67</td>
</tr>
<tr>
<td>LRUZ</td>
<td>1.17</td>
</tr>
</tbody>
</table>

Recall from the CH4 TPR spectra in Figure 3.3 (b) and (c) that LRUZ has more reactive lattice oxygen than LPtZ. This is likely the reason for smaller amount of carbon formation over LRUZ. A significant difference is observed in the reactivity of carbon formed over LRUZ and LPtZ. The reason could be due to the difference in the activation mechanism of CH4. Activation of CH4 occurs by either formate formation or by direct decomposition to form C(s) and H2(g) over the catalyst [28]. As the carbon formed over LPtZ is observed to be more reactive than that over LRUZ; Pt could be activating CH4 via formate formation.
Direct decomposition would result in a dehydrogenated form of carbon which could become more graphitic and less reactive, resulting in a higher TPO peak. Thus the TPO results suggest that Ru could be activating CH$_4$ via direct decomposition.

3.3.5. Temperature Programmed Surface Reaction (TPSR)

TPSR of LZ, LPtZ and LRuZ is shown in Figure 3.5 (a), (b), and (c) respectively. This experiment was performed to determine the catalyst light-off temperature and to study the effect of metal substitution on the B-site of the pyrochlore. TPSR plot shows that LZ does not convert CH$_4$ or CO$_2$ to any significant extent at any temperature. The initial drop in CO$_2$ signal is due to experimental error as it is observed over all catalysts. Lack of any activity on LZ could be attributed to the absence of any active metal in the pyrochlore structure that is needed to activate CH$_4$.

![TPSR plots for (a)LZ, (b)LPtZ, and (c) LRuZ from 40 °C to 900°C at pressure of 1 atm and gas hourly space velocity of 48,000 mL h$^{-1}$ g$_{cat}^{-1}$](image)

Figure 3.5. TPSR plots for (a)LZ, (b)LPtZ, and (c) LRuZ from 40 °C to 900°C at pressure of 1 atm and gas hourly space velocity of 48,000 mL h$^{-1}$ g$_{cat}^{-1}$. 
(Figure 3.5 continued)
It appears that LPtZ [see Figure 3.5 (b)] activates in two stages. It starts to form CO and H₂ at about 460°C but the rate of product formation increases more rapidly after 615°C. These catalysts were not reduced during pre-treatment before TPSR. During TPSR, CH₄ appears to start in-situ reduction of Pt, creating more active sites for DRM with time [21]. Once formed, H₂ and CO continue to reduce Pt to a greater extent resulting in faster creation of active sites, and increasing reaction rate with temperature. This suggests that metallic Pt in the pyrochlore is the active site for DRM.

Figure 3.5 (c) shows that LRuZ has a single light-off temperature of 415°C which is about 45°C lower than for LPtZ. As a result of simultaneous occurrence of RWGS small amount of water was also formed over both the catalysts. The temperature for water formation corresponds to the light-off temperature of each catalyst. In case of LPtZ, water formation began at about 460°C but the rate increased at 615°C. However for LRuZ, water formation started at about 415°C and was almost constant up to 900°C.

3.4. Conclusion

XRD confirmed the formation of the La₂Zr₂O₇ phase in the freshly calcined pyrochlores. H₂ TPR showed that the reduction profile for LPtZ was very similar to that of LZ, suggesting that Pt is strongly bound within the pyrochlore structure. A somewhat lower reduction peak for LPtZ compared to LZ suggests that hydrogen spill-over from Pt reduces Zr ions at a lower temperature than when Pt is not present. For LRuZ, very low TPR peaks were observed suggesting that surface Ru was likely formed during a 950°C oxygen pretreatment and was reducible at temperatures expected for conventional supported Ru clusters. Ru substitution also assists in reduction of lanthanum zirconate. Quantitative and qualitative analysis of carbon formed over LRuZ and LPtZ during CH₄ TPR suggest a difference in the mechanism of CH₄
activation. Ru appears to activate CH$_4$ via direct decomposition resulting in formation of surface carbon and hydrogen. Pt seems to activate CH$_4$ via formyl or formate group formation. Thus the carbon formed over LPtZ is more hydrogenated and oxidizes at a lower temperature compared to that formed over LRuZ.

TPSR experiments suggest that the light-off temperature of LRuZ is about 45 °C lower compared to LPtZ. Greater surface coverage of Ru metal due to migration of Ru to surface as a result of unstable substitution on the B-site could be the reason for lower light-off temperature of LRuZ compared to LPtZ.

3.5. References


Chapter 4 : Effect of Reaction Temperature on Activity of Pt and Ru Substituted Lanthanum Zirconate Pyrochlores (La$_2$Zr$_2$O$_7$) for Dry (CO$_2$) Reforming of Methane (DRM) *

4.1. Introduction

Dry reforming of methane (DRM) produces synthesis gas with H$_2$/CO ratio of ~ 1 [1], which can be used for processes like Fischer-Tropsch or synthesis of various chemicals [2-6]. Both CH$_4$ and CO$_2$ are potentially valuable feedstock for synthesizing commercially important higher-value products [7]. However, one of the major problems associated with DRM is catalyst deactivation due to carbon deposition [2, 4, 8]. In addition to carbon deposition, DRM is highly endothermic reaction and requires temperatures above 800°C to achieve high equilibrium syngas yields. These temperatures lead to deactivation due to sintering of conventional supported metal catalysts [9-12].

Pyrochlores are thermally stable ternary metal oxides with general formula of A$_2$B$_2$O$_7$ [13, 14]. Large cations like rare earth elements usually occupy the A-site and transition metals occupy the B-site [15]. Isomorphic substitution of catalytically active metals like Ru or Pt in the B site produces thermally stable and active catalysts that are resistant to carbon formation due to increased oxygen conductivity within the lattice [15]. Perhaps the most widely studied catalysts for the DRM reaction are based on Ni due to its low cost and availability; however, many Ni-based catalysts undergo severe deactivation due to carbon deposition [8, 16-19]. Metals like Pt, Ru can be used to inhibit carbon formation [7].

Despite the well-known thermal stability of pyrochlores [13, 15], we are aware of only one study of these materials for DRM other than our group, i.e., by Ashcroft, et al [20]. In that paper, Ashcroft, et al [20], studied Eu$_2$Ir$_2$O$_7$ pyrochlores with Eu occupying the A-site and the catalytically active metal Ir occupying the B-site. Above 342°C, these materials completely decomposed to Eu$_2$O$_3$ and Ir metal. Here, we report the DRM reaction over two substituted pyrochlores in which Ru or Pt is substituted at the B site at equal atomic levels. These materials have been characterized and reported in our earlier work [21]. Here, we determine the activation energies for the reaction rates based on both CH$_4$ and CO$_2$ over these materials. The DRM reaction was carried out at 525°C, 575°C, and 625°C for 600 min and the conversion of CH$_4$, CO$_2$ and formation of H$_2$ and CO was monitored as a function of time. The reaction was followed by temperature programmed oxidation to characterize the carbon formed over the catalyst.

4.2. Experimental Section

4.2.1. Catalyst Synthesis

The Ru and Pt substituted pyrochlores were synthesized by modified Pechini method and the obtained metallic composition of these materials determined by ICP-OES has been reported in our earlier work [21].

4.2.2. Activation Energy (Arrhenius plot)

Activation energies were determined in an AMI-200 lab-scale fixed bed reactor using 10 mol% CO$_2$/He and 10mol% CH$_4$/He. The catalysts were diluted with α-alumina with mass ratio catalyst: alumina=1:11 to a total mass of 120 mg. The temperature range was selected to limit the reactant conversion below 15%, minimizing the temperature and concentration gradients across
the catalyst bed. The reaction time was 60 min at steady state at each temperature. The activation barrier energies were calculated based on the rates of CH$_4$ and CO$_2$ determined by monitoring the rate of consumption at temperatures low enough to avoid both transport and equilibrium limitations. Due to higher activity of LRuZ compared to LPtZ, the temperature range chosen for LRuZ (510°C - 530°C) was lower than that for LPtZ (660°C – 680°C).

4.2.3. Activity Study

We studied the activity of the catalysts for DRM at different temperatures 525°C, 575°C, and 625°C. A blank run with only the α-alumina was carried out to determine the extent of reaction without any catalysts. The mass spectrometer (MS) connected to the reactor gave the mole fractions of the reactants in the blank condition. The reaction gases of 10 mol% CO$_2$/He and 10 mol% CH$_4$/He were used for calibration of CO$_2$ and CH$_4$, 5 mol% CO/He and 10 mol% H$_2$/He were used to calibrate the mass spectrometer for CO and H$_2$ respectively. DRM was performed with an equimolar reactant feed of 20 mL/min of each of the reactant gases to give a total gas space velocity of 48,000 mL/gcat/h. For each run, 50 mg of the catalyst (without alumina) was loaded in the U-tube reactor. Before each reaction run, the catalyst was purged with He flowing at 20 mL/min and heated to the reaction temperature removing any surface species and moisture. No reduction of the catalyst was performed before DRM. The reactants CO$_2$ and CH$_4$ were introduced after this into the reactor at desired flow rates once the specified bed temperature was reached. The mole fractions of the reactants and products were measured by the Ametek quadrapole mass spectrometer.

4.2.4. Temperature Programmed Oxidation (TPO)

Immediately after each steady state DRM run, a TPO was conducted to characterize the carbon formation as a function of run temperature. The catalyst was cooled to room temperature
(ca. 35°C) in flowing He at 20 mL/min. The TPO was carried out by flowing 5 mol% O₂/He at 30 mL/min from room temperature to 950°C at a ramp rate of 5°C/min. The conditions were maintained isothermal at 950°C for 30 minutes. The CO and CO₂ formed during the TPO were tracked using the mass spectrometer (MS) connected to the reactor outlet. The concentration of CO and CO₂ formed during TPO was calculated using the calibration gases of 5 mol% CO/He and 10 mol% CO₂/He.

4.3. Results and Discussion

4.3.1. DRM Reaction Study

4.3.1.1. Thermodynamic Equilibrium

The thermodynamic equilibrium composition of all compounds as a function of temperature at 1 atm is shown in Figure 4.1. These molar compositions are calculated using Gibbs free energy minimization simulations using HSC Chemistry 7.1.

![Thermodynamic equilibrium composition for 1 kmol of CH₄ and CO₂ each at 1 atm as calculated by HSC Chemistry 7.1.](image)
These simulations were performed by assuming an initial equimolar mixture of \( \text{CH}_4(g) \) and \( \text{CO}_2(g) \), with \( \text{H}_2(g) \), \( \text{CO}(g) \), \( \text{H}_2\text{O}(g) \), \( \text{C}_s \) allowed as products of the equilibrium mixture. This accounts for the simultaneous occurrence of RWGS and methane decomposition along with DRM. The equilibrium compositions and \( \text{H}_2/\text{CO} \) ratios at different temperatures are shown in Figure 4.1.

### 4.3.1.2. Activation Energy (Arrhenius Plot)

The experimental apparent activation energies based on \( \text{CH}_4 \) and \( \text{CO}_2 \) disappearance are shown in Table 4.1. The apparent activation energies obtained over LPtZ and LRuZ are significantly different from those reported in the literature for Pt/Al\(_2\)O\(_3\) [22] and Ru/Al\(_2\)O\(_3\) [7], indicating that the mechanisms of the DRM reaction over the LPtZ and LRuZ are different than over conventional supported metals, as expected because Pt and Ru are bound within the pyrochlore structure rather than supported on an oxide.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( E_{\text{app}}(\text{CH}_4) ) (kcal/mol)</th>
<th>( E_{\text{app}}(\text{CO}_2) ) (kcal/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPtZ</td>
<td>36.5 ± 0.4</td>
<td>27.9 ± 0.2</td>
<td>This work</td>
</tr>
<tr>
<td>LRuZ</td>
<td>14.5 ± 0.7</td>
<td>11.5 ± 0.8</td>
<td>This work</td>
</tr>
<tr>
<td>Pt/Al(_2)O(_3)</td>
<td>22.5</td>
<td>20.2</td>
<td>[22]</td>
</tr>
<tr>
<td>Ru/Al(_2)O(_3)</td>
<td>26</td>
<td>18</td>
<td>[7]</td>
</tr>
</tbody>
</table>

The Arrhenius plots for LPtZ and LRuZ are shown in Figure 4.2 (a) and (b) respectively. The activation energy based on the consumption of \( \text{CH}_4 \) is greater than that based on \( \text{CO}_2 \) for both LPtZ and LRuZ. This agrees with the kinetic and mechanistic studies reported in the literature on Pt- and Ru-supported catalysts including Pt/Al\(_2\)O\(_3\) [22] and Ru/Al\(_2\)O\(_3\) [7], suggesting that activation of \( \text{CH}_4 \) is the rate limiting step during DRM [12, 23, 24].
Figure 4.2. Arrhenius plot for consumption of CH₄ and CO₂ for (a) LPtZ, and (b) LRuZ over temperature ranges 660-680°C and 510-530°C respectively.
The activation energy for both CH_4 and CO_2 reaction is significantly lower for LRUZ than LPtZ, meaning that there is a difference in the transition state and thus mechanism over the two catalysts. Lower activation barriers over LRUZ could also be due surface enrichment of LRUZ with Ru as observed in H_2 TPR reported in our previous work [21]. It was observed in that study from hydrogen temperature programmed reduction (H_2-TPR) for LPtZ that Pt was primarily substituted in the pyrochlore structure, whereas a relatively low-temperature H_2-TPR peak for LRUZ suggests some degree of surface enrichment of Ru in the LRUZ. However, the higher H_2-TPR peak for Ru in LRUZ indicates that this surface Ru is much more closely associated with the pyrochlore than supported Ru.

Several activation mechanisms such as direct decomposition of CH_4, activation via formates, and carbonate formation have been reported in the literature over Ru and Pt catalysts [25, 26]. The present results do not allow us to distinguish among these mechanisms, but there is clearly a fundamentally different mechanism for DRM over these two pyrochlores.

4.3.1.3. Effect of Reaction Temperature on Activity

CH_4 Conversion: The effect of reaction temperature and time on stream on the conversion of CH_4 over LPtZ and LRUZ is shown in Figure 4.3 (a) and (b) respectively. The CH_4 conversion for LZ pyrochlores was found to be less than 1% at all temperatures and is not reported in the plots. This is expected since there is no catalytically active B-site metal on LZ. The values on the right hand y-axis show the thermodynamic equilibrium CH_4 conversion at the respective temperatures as calculated from Figure 4.1.
Figure 4.3. Effect of temperature on CH$_4$ conversion for (a) LPtZ, and (b) LRuZ catalysts at 525°C, 575°C, and 625°C at 1 atm and GHSV=48,000 mL g$_{\text{cat}}^{-1}$ h$^{-1}$. The values on the right hand y-axis show the thermodynamic equilibrium values at that particular temperature as obtained from Figure 4.1.
The CH₄ conversion for both LPtZ and LRuZ is lower than the equilibrium CH₄ conversion at all times during the 600 min of time on stream. CH₄ conversion increases with time for both catalysts. Because these catalysts were not reduced as a part of the pre-treatment, it is likely that the increase in CH₄ conversion with time is a result of in-situ reduction, first by CH₄ and then by CO and H₂ at later times on stream. This increase in CH₄ conversion with time on stream is more pronounced on LPtZ than LRuZ. Our earlier temperature programmed surface reaction (TPSR) results on this same LPtZ [21] showed the formation of more active sites for DRM at temperatures in this range, and the results here [Figure 4.3 (a)], showing continuous increase is CH₄ conversion with time, are consistent with these previous results. Figure 4.3 also shows that LRuZ is far more active than LPtZ at each temperature studied.

H₂-TPR reported in our previous work showed higher amounts of reducible Ru on the LRuZ surface compared to that of Pt on LPtZ [21]. Higher CH₄ conversion over LRuZ compared to LPtZ could be attributed to surface enrichment of LRuZ with Ru. Because activation of CH₄ is generally believed to be the rate determining step [4, 9, 27-30], increased active metal concentration on surface would increase the observed rate of CH₄ disappearance.

CO₂ Conversion: Conversion of CO₂ as a function of time at three temperatures for LPtZ and LRuZ is shown in Figure 4.4 (a) and (b) respectively. Conversion of CO₂ was insignificant for LZ at all temperatures and thus is not plotted here.

Experimental CO₂ conversion for LPtZ at 525°C and 575°C is below the calculated thermodynamic equilibrium conversion. However, the experimental conversion at 625°C is slightly greater than the equilibrium values.
Figure 4.4. Effect of temperature on CO$_2$ conversion for (a) LPtZ, and (b) LRuZ catalysts at 525°C, 575°C, and 625°C at 1 atm and GHSV=48,000 mL g$_{\text{cat}}^{-1}$ h$^{-1}$. The values on the right hand y-axis show the thermodynamic equilibrium values at that particular temperature as obtained from Figure 4.1.
For LRUZ, the CO$_2$ conversion is consistently greater than the equilibrium values at all temperatures. The equilibrium values are computed with C(s) as a part of the final product. Formation of this solid phase carbon is thermodynamically more favored compared to conversion of CO$_2$ at these temperatures. However, the kinetics for carbon formation are slower than that for conversion of CO$_2$ (as will also be seen later from the H$_2$/CO ratio plots), which results in greater than equilibrium CO$_2$ conversion during this experiment. A comparison of the measured CO$_2$ conversion with the equilibrium conversion calculated without allowing solid carbon shows that the measured CO$_2$ conversions are less than the equilibrium conversion predicted without solid carbon in the simulation.

Surface basicity of the catalyst helps in the activation of mildly acidic CO$_2$ [12]. Verykios et al. studied the kinetics of DRM over catalysts supported on La$_2$O$_3$ and found that CO$_2$ is activated by La$_2$O$_3$ and forms lanthanum oxycarbonate (La$_2$O$_2$CO$_3$) which then reacts with activated CH$_4$ to form CO. Thus it is the basic nature of the La$_2$O$_3$ support that helps in the reduction of CO$_2$ to CO. It can be postulated in our case that the La-O phase of the lanthanum zirconate could be activating CO$_2$ to form oxycarbonates which are then reduced to CO by activated surface CH$_x$ species.

H$_2$/CO ratio: The change in the H$_2$/CO ratio with temperature and time on stream for LPtZ and LRUZ is shown in Figure 4.5 (a) and (b) respectively. The H$_2$/CO ratio for LZ was found to be consistently lower than 0.1 at all temperatures. The H$_2$/CO ratio of the product gas over LPtZ and LRUZ was found to be significantly lower than the calculated equilibrium values at all temperatures. Recall that these thermodynamic values include C(s) as one of the products [Figure 4.1], and that C(s) formation is thermodynamically favored at these temperatures.
Figure 4.5. Effect of temperature \( \text{H}_2/\text{CO} \) ratio for (a) LPtZ, and (b) LRuZ catalysts at 525°C, 575°C, and 625°C at 1 atm and GHSV=48,000 mL g\(_{\text{cat}}\) h\(^{-1}\). The values on the right hand y-axis show the thermodynamic equilibrium values at that particular temperature as obtained from Figure 4.1.
C(s) formation would decrease the equilibrium levels of CO compared to the equilibrium levels that would be calculated without allowing C(s). This would then increase the equilibrium H₂/CO ratios. However, the results here can be explained by relatively slow rates of C(s) formation and also that the CH₄ activation is limited at these temperatures, resulting in lower H₂ production and thus a lower H₂/CO ratio. The reverse water gas shift (RWGS) also consumes H₂ and produces CO, greatly reducing the H₂/CO ratio. The net effect is a lower H₂/CO ratio than equilibrium.

The H₂/CO ratio for LPtZ is found to be significantly lower than LRuZ for all temperatures. This could be due to lower CH₄ conversion observed over LPtZ which would limit the formation of H₂ and decrease the H₂/CO ratio. The H₂/CO ratio is also a measure of simultaneous occurrence of RWGS. Thus it can be postulated that RWGS occurs to a greater extent over LPtZ as compared to LRuZ at these reaction temperatures.

4.3.2. Characterization of the Spent Catalyst

4.3.2.1. Temperature Programmed Oxidation (TPO)

After 600 min on stream, the carbon formed over the catalyst was characterized by TPO. The results after reaction at 525°C, 575°C, and 625°C are shown in Figure 4.6 (a), (b), and (c).

Catalyst spent at 525°C: The TPO profile for LPtZ and LRuZ after reaction at 525°C is shown in Figure 4.6 (a). There is negligible carbon formation over spent LPtZ, which was a relatively inactive catalyst at this temperature as measured by CH₄ conversion [Figure 4.3 (a)]. Over LRuZ, about 0.12 g_c/g_cat was formed during DRM at 525°C for 10 h. There appears to be only one form of carbon formed over LRuZ, with a TPO peak at ~ 625°C. This could be some form of dehydrogenated carbon deposited on the catalyst [15]. There is a small shoulder at about 550°C corresponding to a more hydrogenated and reactive carbon.
Figure 4.6. TPO profile of carbon formed over LRuZ and LPtZ at (a) 525°C, (b) 575°C, and (c) 625°C during the 10 h DRM reaction. These plots differ in the y-scale axis.
Catalyst spent at 575°C: Figure 4.6 (b) shows the TPO profile of LPtZ and LRuZ spent at 575°C for 10 h under DRM. As at 525°C, no significant oxidizable carbon was observed for LPtZ because the CH₄ conversion was low. Qualitatively, the reactivity and therefore the chemical nature of the carbon formed over LRuZ is essentially the same as that formed at 525°C. The TPO peak for LRuZ spent at 575°C is oxidized at a slightly higher temperature of 640°C. However, less carbon is formed at 575°C (0.086 gₐ/gₖ at 575°C compared to 0.12 gₐ/gₖ at 525°C), consistent with the equilibrium calculation [Figure 4.1]. This amount of carbon formation at 575°C is far less than that formed at comparable conditions over other conventional supported catalysts [8].

Catalyst spent at 625°C: As with the catalysts tested at 525°C and 575°C, the LPtZ showed no detectable carbon. The amount of carbon formed over LRuZ at 625°C was 0.05 gₐ/gₖ [see Figure 4.6 (c)]. The TPO peak, and thus the reactivity of this carbon, was different than that
observed over LRuZ spent at 525°C and 575°C. This carbon was less reactive, with a single TPO peak at 770°C, suggesting highly dehydrogenated and more graphitic form of carbon formed away from the metallic site [31, 32].

4.4. Conclusion

The mechanism of the DRM reaction over LPtZ differs from that over LRuZ as shown by the difference in the activation energies, with LRuZ having a far lower activation energy than LPtZ. Because activation of the first C-H bond in methane is likely the rate determining step, this shows that LRuZ activates this bond more rapidly than LPtZ. In addition to any inherent differences in the activation of methane on these two active metal sites, this also appears to be associated with the greater surface concentration of Ru compared to Pt, as observed from the H₂-TPR results in our previous work on these same catalysts [21]. This may also be due to the fact that Pt is less active when it is bound within the pyrochlore structure than when it is present as a metallic cluster on a conventional support. TPO results on the spent catalysts show that the amount of carbon formed decreased with increasing reaction temperature, consistent with equilibrium calculations. Increasing reaction temperature decreases the amount of carbon formed but increases the stability of the surface carbon as measured by TPO.

4.5. References


Chapter 5: Characterization and Activity Study of the Rh-substituted Pyrochlores for CO\textsubscript{2} (Dry) Reforming of CH\textsubscript{4}\textsuperscript{*}

5.1. Introduction

Pyrochlores are a class of ternary metal oxides based on the fluorite structure with a cubic unit cell with a general formula of A\textsubscript{2}B\textsubscript{2}O\textsubscript{7}. An important property of these materials is that catalytically active noble metals can be substituted isomorphically on the B-site to form a crystalline catalyst. These materials consist of vacancies at the A and O sites, which facilitates oxygen ion migration within the structure \[1\]. The A-site is usually a large cation (typically rare earth elements) and the B-site cation has a smaller radius (usually transition metal) \[2\]. For the pyrochlore structure to be stable it is necessary that the ionic radius ratio of A and B site cations be between 1.46 and 1.78 \[1\]. The ratio of the ionic radii for La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} is 1.61 \[3\]. If the ratio of the ionic radii is greater than 1.78, a perovskite phase can be formed. Below a ratio of 1.46 a fluorite structure is formed \[4\]. Catalytically active metals like Ru, Rh, Pt can be substituted into the B-site of the pyrochlore structure because they meet this ionic radius constraint and have the required oxidation state \[5\]. The resulting materials possess the thermal stability inherent in the pyrochlore structure, which also constrains the active metal within the pyrochlore structure even at high temperatures. Steam reforming, autothermal reforming, and partial oxidation of methane are used to reform methane to synthesis gas \[5-7\]. CO\textsubscript{2} reforming of CH\textsubscript{4} is a highly endothermic reaction and has been widely studied on a number of catalysts \[8-11\].

For fuel reforming, one study shows that the activity decreases in the order Ru, Rh > Ir > Ni, Pt, Pd > Co > Fe, Cu [12], with noble metals also showing higher activity and greater resistance to deactivation by carbon deposition [13]. Carbide catalysts have also been used for studying this reaction [7, 14]. Economic evaluations have suggested a cost advantage for DRM as a route to the production of synthesis gas [15]. There are two major problems associated with dry reforming, (a) deactivation due to carbon formation on the catalyst, and (b) thermal degradation of the catalyst and/or support at the high temperatures required for this reaction, typically above 700°C.

Studies using non-noble metals like Fe, Ni, have consistently shown rapid deactivation by carbon deposition [16-18], although this can be minimized in some cases by maintaining high metal dispersion [17]. Because temperatures well above 700°C are required to reach high syngas yields, traditional supported metals are not stable, suggesting the need to develop an inherently stable material that is catalytically active. Resistance to carbon formation is also related to the oxygen conductivity of substituted pyrochlores [19]. Oxygen mobility within the pyrochlore structure is a strong function of the La content in the structure. It is shown by Diaz-Guillen, et.al [20], that the activation energy for oxygen ion conductivity decreases from 1.13 eV for Gd$_2$Zr$_2$O$_7$ to 0.81 eV for GdLaZr$_2$O$_7$ with an increase in the La substitution in the pyrochlore structure. Although pyrochlores have the thermal stability and potential for active metals to be substituted into the structure, we are aware of only one report of DRM on any pyrochlore. Ashcroft et al [21], studied pyrochlores based on Eu, Ru, Ir, Gd, but found that they decomposed into the various oxides at DRM conditions. The present study focuses on the characterization and activity of Rh-substituted pyrochlores, which have been studied for reactions such as fuel reforming [19, 22]. Specifically, lanthanum zirconates (LZ) into which 2wt% and 5wt% Rh have been
substituted at the B-site of the pyrochlore structure, are characterized by ICP, XRD, XPS, TPO and H₂-TPR. La₂Zr₂O₇ pyrochlores with Rh substitution on the Zr site (known as the B-site, based on the general formula for pyrochlores as A₂B₂O₇) were tested for their activity at 550°C, 575°C and 600°C to study the kinetics of the reaction. Post-run temperature programmed oxidation (TPO) is used to determine the coke formation.

5.2. Experimental Section

5.2.1. Catalyst Synthesis

The LZ, L₂RhZ and L₅RhZ pyrochlores were synthesized by modified Pechini method [19]. The synthesis, ICP, and TPSR procedure has been reported earlier [5, 19].

5.2.2. Catalyst Characterization

The equipment and experimental procedure details for X-ray diffraction (XRD), H₂ temperature programmed reduction (TPR), temperature programmed surface reaction (TPSR) are reported in our earlier work [5]. For this work XPS spectra were obtained for the C 1s, O 1s, La 3d, Zr 3d, and Rh 3d. In each case, the binding energy (BE) and the area of the corresponding peaks were measured.

5.2.3. Activity Studies

The composition of reactant gases used for the reaction over the catalyst was 10 mole% of CO₂/He and 10 mole% of CH₄/He. We studied the activity of the catalysts for DRM at different temperatures 550°C, 575°C, and 600°C. The mass spectrometer (MS) connected to the reactor gave the mole fractions of the reactants in the blank condition. DRM was performed with an equimolar reactant feed of 20 mL/min of each of the reactant gases to give a total space
velocity of 48,000 mL g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1}. For each run, 50 mg of the catalyst was loaded in the U-tube reactor. Before each reaction run, catalysts were heated to the reaction temperature in flowing He; no reduction was conducted before subjecting the catalysts to DRM. Reactants CO\textsubscript{2} and CH\textsubscript{4} were introduced after this into the reactor at desired flow rates. Mole fractions of the reactants and products from the mass spectrometer helped us to compare results with the blank conditions.

5.2.4. Temperature Programmed Oxidation (TPO)

After DRM, a TPO was conducted by cooling the catalyst to room temperature (ca. 35°C) in flowing He at 20 mL/min. Then it was oxidized in flowing 5% O\textsubscript{2}/He at 30 mL/min from room temperature to 950°C and the ramp rate was 5°C/min. The conditions were maintained isothermal at 950°C for 30 minutes. The CO (m/z = 28) and CO\textsubscript{2} (m/z = 44) emitted during the TPO were tracked using mass spectrometer hooked up to the reactor outlet.

5.3. Results and Discussion

5.3.1. X-ray Diffraction Study of Fresh Catalyst

Figure 5.1 shows the XRD patterns for freshly calcined pyrochlores. The star marked peaks represent the La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} (ICSD no: 50-0837) phase and the diffraction angle for these peaks are similar to the that observed in literature [19, 23]. Haynes et al [19], used L2RhZ pyrochlores for partial oxidation of n-tetradecane, and their XRD pattern for pyrochlores match those in Figure 5.1 for LZ and L2RhZ in this study. However, for L5RhZ there was an extra peak observed at ~32°. Gallego et al [17], and Araujo et al [9], studied perovskites for DRM and observed main diffraction peak for LaCoO\textsubscript{3} and LaRuO\textsubscript{3} respectively at ~32°.
The similar peak observed at 32° in the XRD pattern for L5RhZ pyrochlore (Figure 5.1) suggests that 5 wt% Rh substitution resulted in the formation of a separate LaRhO$_3$ phase. To study effect of Rh substitution in further detail, XRD with a slow sweep rate was conducted on the fresh catalysts. Figure 5.2 shows the XRD pattern for a slow sweep rate; it is observed that there is a small peak for LaRhO$_3$ for the L2RhZ pyrochlore but a prominent one for L5RhZ. The amount of Rh in the 5% and the 2% sample appears to be in excess of the maximum substitution limit of the pyrochlore structure, and thus resulted in formation of a separate LaRhO$_3$ perovskite phase. Isomorphic substitution of Rh on the B-site has caused a small shift in the diffraction peak to a smaller angle for L2RhZ and L5RhZ compared to LZ. Lower diffraction angle corresponds to an increase in the lattice parameter of LRhZ (2% and 5%) catalysts due to Rh substitution.

Figure 5.1. XRD pattern for freshly calcined LZ, L2RhZ, and L5RhZ pyrochlores. [★ – La$_2$Zr$_2$O$_7$, and ● – LaRhO$_3$]
Figure 5.2. Slow scan XRD pattern for freshly calcined LZ, L2RhZ, and L5RhZ pyrochlores.

5.3.2. X-ray Photoelectron Spectroscopy of the Fresh Catalysts

XPS spectra for the Rh 3d core level obtained from L2RhZ and L5RhZ pyrochlores is shown in Figure 5.3 (a) and (b), respectively. In the deconvolution process, the relative intensity and separation of the spin-orbit for Rh 3d$_{5/2}$ – 3d$_{3/2}$ doublet were fixed at ratio of 3:2 and 4.8 eV, respectively [24]. According to the literature, the BE of Rh$^0$ valence state is 307.1-307.6 eV and BE of Rh$^{3+}$ valence state is in a wide range from 308.8-311.3 eV depending on the surrounding environment [24-27]. For L2RhZ [see Figure 5.3 (a)], Rh$^{3+}$ was the only detected species as deduced from the binding energy of the Rh 3d$_{5/2}$ photoelectron peak at 308.9 eV. Compared to L2RhZ, the valence state of Rh for L5RhZ is more complicated. For L5RhZ, the Rh$^{3+}$ is the dominant valance state with peak at 309.0 eV [see Figure 5.3 (b)]; a smaller Rh 3d$_{5/2}$ peak is
observed at a lower binding energy of 308.3 eV which indicates the presence of another valence state of Rh. This peak at 308.3 eV is attributed to partially oxidized Rh$^{\delta+}$ species[26]. The relative distribution of Rh$^{3+}$ and Rh$^{\delta+}$ in L5RhZ are 82.8% and 17.2%, respectively [see Table 5.1].

![Figure 5.3. Photoelectron Rh 3d spectra for (a) L2RhZ, (b) L5RhZ pyrochlores.](image)
It should be noted that the FWHM (full width half maxima) of Rh peaks was significantly broader (2.0~2.7 in our measurement) when compared to those of Rh standard (about 0.7 for pure bulk Rh$_2$O$_3$). The broadening of Rh peaks may suggest a high dispersion of Rh in catalyst with little local aggregation [26, 28].

Table 5.1. XPS determined relative atomic ratio of surface Rh specie in 2wt% and 5wt% Rh catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rh$^{6+}$/Rh$^{total}$ (%)</th>
<th>Rh$^{3+}$/Rh$^{total}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 wt% Rh</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>5 wt% Rh</td>
<td>17.2</td>
<td>82.8</td>
</tr>
</tbody>
</table>

Quantitative analysis indicates the atomic percent of Rh on the surface of L2RhZ and L5RhZ pyrochlores is 0.78% and 3.15% respectively. This surface Rh concentration for individual pyrochlores is smaller than the theoretical levels obtained from inductively couple plasma – optical emission spectroscopy (ICP-OES) results [see Table 5.2]. Since XPS is a surface sensitive technique which only can detect elements several nm under the surface, this result suggests that the remaining Rh lies within the lattice, as expected. Both pyrochlores have surface Rh in similar oxidation states, but the absence of Rh$^{6+}$ signal for L2RhZ may be due to its lower Rh loadings, which limits the accuracy in deconvolution of the Rh peak due high signal to noise level. The ratio of surface Rh concentration (by wt) for L5RhZ and L2RhZ is about (3.15: 0.78 = 4), which is greater than their bulk ratio i.e., 4.4: 1.7 = 2.6, as observed in the ICP-OES analysis. This indicates that the surface of L5RhZ is enriched in Rh compared to the surface of L2RhZ. As XPS detects elements within a few nm depths from the surface, a higher surface concentration would mean that the surface Rh on L5RhZ is well dispersed. If there was any aggregation of Rh on the surface then the detected amount of Rh on L5RhZ surface would be less or close to that of L2RhZ. But a higher surface concentration indicates that the greater Rh
loading in L5RhZ did not cause any local surface aggregation of Rh, which generally would decrease the detected surface concentration of the metal. XPS analysis shows that for both L2RhZ and L5RhZ pyrochlores, the 3d5/2 peaks of La and Zr elements were 833.4-833.6 eV and 182.1-182.3 eV, respectively. These peaks positions indicated Zr and La in the pyrochlore structure and were in the Zr4+ (ZrO2) and La3+ (La2O3) oxidation states respectively[29, 30].

Table 5.2. Rh concentration (wt %) obtained by different methods

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Method for obtaining Rh concentration (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ICP-OES (bulk)</td>
</tr>
<tr>
<td>L2RhZ</td>
<td>1.7</td>
</tr>
<tr>
<td>L5RhZ</td>
<td>4.4</td>
</tr>
</tbody>
</table>

5.3.3. Temperature Programmed Reduction (TPR)

Figure 5.4 shows the hydrogen TPR profiles for the three catalysts. The LZ pyrochlore reduction profile shows reduction peaks at 490ºC and 580ºC, corresponding to an H2 consumption of 0.155 mg H2/gcat. This corresponds to 0.6% reduction of the lanthanum zirconate. The TPR profile of L2RhZ shows three distinct peaks at 380ºC, 455ºC, and 570ºC. All three catalysts show two peaks above 450ºC, which can be attributed to reduction of the LZ itself.

Comparison of the L2RhZ and LZ TPR results suggests that the 380ºC peak is due to reduction of Rh that is interacting strongly with the pyrochlore. The small additional peak 280ºC for L2RhZ may be due to reduction of Rh that is less strongly interacting with the pyrochlore [19]. For L5RhZ the 410ºC peak is close to that at 380ºC for the L2RhZ, and its larger area is consistent with the larger amount of reducible Rh in this catalyst. The similarity of the peak temperatures for this peak and that of the L2RhZ (410ºC versus 380ºC) indicates that the strength
of the interaction of this reducible Rh is similar on both catalysts. The L2RhZ consumed 0.508 mg H₂/g_cat, which includes H₂ consumed for reduction of the Rh species at 380°C and a small portion of lanthanum zirconate at 455°C and 570°C. The H₂ consumption for L5RhZ is 1.57 mg H₂/g_cat. It is difficult to quantify exactly the percentage of reduction of Rh in the pyrochlore structure due to overlapping reduction peaks of Rh and lanthanum zirconates. However, the H₂ consumption by L2RhZ and L5RhZ is smaller than their respective theoretical consumption assuming complete Rh reduction (and no reduction of the pyrochlore) i.e., 0.66 mg H₂/g_cat for L2RhZ and 1.7 mg H₂/g_cat for L5RhZ. This means that a significant portion of the Rh is substituted in the bulk of the pyrochlore and is not available during the reduction reaction, as expected.

Figure 5.4. Temperature Programmed Reduction of freshly calcined LZ, L2RhZ, L5RhZ pyrochlores.
TPR profiles obtained in this study are similar to the ones observed by Haynes et al [19]. The peak observed for LZ in our study shows two types of reducing species, one at 490°C and the other at 580°C. Whereas, the one observed by Haynes et al [19], for LZ has a single peak at 527°C. This difference in the reduction peaks could be due to the difference in the hydrogen concentration in the two TPR procedures. The concentration of the gas used for TPR in the work by Haynes et al [19], was 5% H₂/Ar and the one used in this work was higher 10% H₂/Ar keeping the same ramp rate and flow rate. Higher partial pressure of the reducing gas in the present work resulted in a faster reduction reaction, allowing a distinction to be made between reduction peaks that were not visible in the Haynes et al. [19] study. The single broad peak observed by Haynes et al., thus appeared as a double peak in the present work. The deconvoluted TPR profiles of LZ, L2RhZ, and L5RhZ pyrochlores are shown in Figure 5.5 (a), (b), and (c) respectively (these figures differ in y-axis scale).

![TPR Profiles](image)

Figure 5.5. Deconvoluted TPR profiles of freshly calcined (a) LZ, (b) L2RhZ, and (c) L5RhZ.
(Figure 5.5 continued)
Figure 5.5 (a) shows that the LZ reduction peaks involve the reduction of four species. XPS results show that La and Zr are present in +3 and +4 oxidation states respectively in the pyrochlore structure. Peaks at 490°C and 580°C could be due to the reduction of La\(^{+3}\) and Zr\(^{+4}\) species [31]. The lower temperature peaks at 396°C and 430°C (not visible in Figure 5.4 due to the y-axis scale) could be due to the reduction of partially co-ordinated lanthanum or zirconium cations at the surface. Hoang et al [31], conducted TPR of the ZrO\(_2\) support and lanthana promoted zirconia structure (La\(_2\)O\(_3\)-ZrO\(_2\)). They observed a reduction peak at 574°C for ZrO\(_2\) and at 554°C for La\(_2\)O\(_3\)-ZrO\(_2\) [31]. The high temperature peaks at 490°C and 580°C can be attributed to the reduction of La\(_2\)O\(_3\)-ZrO\(_2\) and ZrO\(_2\) phase respectively [31]. In Figure 5.5 (b), L2RhZ has a small peak at 280°C appears to be due to the reduction of a weakly interacting Rh species [19]. The intensity of this peak is very low and thus this reducing species could not be accurately determined and deconvoluted during the analysis of the XPS peaks. Peak at 375°C and 394°C can be assigned to the reduction of Rh with varying degrees of interaction with oxygen and neighboring atoms in the bulk of pyrochlores. The 394°C peak could also be due to the reduction of some lanthanum zirconate species reducing at 396°C as seen in Figure 5.5 (a). As mentioned earlier, the lanthanum zirconate is reduced at 430°C and 490°C [see Figure 5.5 (a)]. The peak at 455°C [in Figure 5.5 (b)] could be due to the reduction of these lanthanum zirconate species which have different level of interaction with the neighboring metals due to Rh substitution in the pyrochlores structure compared to unsubstituted LZ pyrochlore.

Deconvoluted TPR peaks for L5RhZ [Figure 5.5 (c)] shows that there are peaks at 352°C, 396°C, and 416°C. The 352°C peak is likely be due to the reduction of Rh\(^{6+}\) species as observed in XPS results. The 396°C and 416°C peaks can be assigned to the reduction of bulk Rh with varying interaction with the pyrochlore structure. These species reducing at 396°C and 416°C
have similar oxidation states and thus could not be distinctly determined during XPS analysis. Some portion of the 396°C peak could be due to the reduction of the lanthanum zirconates as seen in Figure 5.5 (a). The high temperature peaks at 500°C and 570°C is primarily due to the reduction of the same lanthanum and zirconium species as seen in Figure 5.5 (a).

There are some apparent differences in the oxidized species observed in the TPR results and the XPS results. This is because the fresh catalysts, after calcination at 1000°C for 8 hours as the final step in the synthesis process, were pretreated prior to the TPR in flowing oxygen up to 950°C, whereas the catalysts used for XPS were not pretreated, although they were also calcined at 1000°C for 8h. It is clear from the above deconvoluted TPR peaks that no peak can be assigned solely to the reduction of a particular metal species. Lanthanum zirconate reduction peaks overlap with reduction peaks for Rh in the pyrochlore. Thus, quantification of the percentage of Rh reduction in these pyrochlores cannot be performed using TPR.

5.3.4. Temperature Programmed Surface Reaction (TPSR)

TPSR was performed on LZ, L2RhZ, and L5RhZ and the product composition is plotted in Figure 5.6 (a, b, and c respectively) as a function of temperature. For L2RhZ [Figure 5.6 (b)], there is no CO or H₂ formation observed until ~490°C, but over L5RhZ [Figure 5.6 (c)] product formation begins at ~410°C. Small but measurable water formation is observed over both the catalysts after light-off, which suggests that the RWGS takes place over both the catalysts up to ~700°C. Assuming the rate determining step is the breaking of the C-H bond in CH₄ to form CHₓ surface species [32], and that this step occurs over Rh sites [33], the L5RhZ, which has more surface Rh sites (shown by XPS and TPR), enhances CH₄ activation and accelerates the reforming reaction rate compared to L2RhZ. This faster reaction rate over L5RhZ results in a lower light-off temperature i.e., 410°C, compared to 490°C for L2RhZ.
Figure 5.6. TPSR plots for (a) LZ, (b) L2RhZ, and (c) L5RhZ at in the temperature range 50°C - 900°C at 1 atm and GHSV = 48,000 mL g<sub>cat</sub> h<sup>-1</sup>.
5.3.5. Temperature Effects on Activity

Effect on CH₄ conversion (X_{CH₄}): Figure 5.7 shows the conversion of CH₄ (X_{CH₄}) for all three catalysts at each temperature as a function of time. The values on the right hand y-axis show the thermodynamic equilibrium values at that particular temperature. X_{CH₄} over LZ pyrochlores was between 0.5% and 0.8%, and was constant at all temperatures. This lower conversion is due to absence of any catalytically active Rh site on the surface of the LZ pyrochlore.

The catalysts do not reach equilibrium at these temperatures. For the two Rh-containing catalysts, X_{CH₄} increases with time. This increase could be attributed to in-situ reduction of the catalyst by CH₄. The catalysts used in this study were not reduced as a part of pre-treatment before conducting the reaction. As a result, the catalysts are likely initially reduced in-situ by CH₄ then reduced by CO and H₂ as they are formed [21]. However, this in-situ reduction by CO
and H\(_2\) could be slower than that in H\(_2\)-TPR due to lower concentration of H\(_2\) during reaction. Ashcroft et al [21], proposed this in-situ reduction in their study of DRM over Eu\(_2\)Ir\(_2\)O\(_7\) pyrochlores [21]. In-situ reduction of the catalyst would increase the number of available active metal sites with time thus increasing the conversion of CH\(_4\) with time-on-stream.

![Figure 5.7](image)

Figure 5.7. CH\(_4\) Conversion for LZ, L2RhZ and L5RhZ pyrochlores at 550°C, 575°C, and 600°C at 1atm and GHSV = 48,000 mL g\(_{\text{cat}}\)\(^{-1}\) h\(^{-1}\). The values on the right hand y-axis show the thermodynamic equilibrium values at that particular temperature as obtained from equilibrium calculations.

Iglesia and co-workers [32, 34] demonstrated that the rate of methane consumption on Rh/Al\(_2\)O\(_3\) is first order in CH\(_4\) concentration, and is independent of CO\(_2\) concentration i.e., \(r_{\text{CH}_4} = kP_{\text{CH}_4}\). They also demonstrated that the active site for DRM is Rh site and the lack of any significant activity for the LZ catalyst shows that Rh sites are required to catalyze this reaction. The TPR and XPS results show that L5RhZ has more active Rh on the surface compared to L2RhZ and LZ. Thus it would be expected that L5RhZ will have higher X\(_{\text{CH}_4}\) than L2RhZ and
LZ, which is what Figure 5.7 shows. This is consistent with the results of Verykios et al [35], who showed that during DRM, breaking of CH\textsubscript{4} to CH\textsubscript{x} (x = 1-3) on the Rh sites is the slow step in the reaction mechanism and determines the overall kinetics of the reaction over Rh/Al\textsubscript{2}O\textsubscript{3}. Thus higher metal loading would kinetically favor the activation of methane and DRM.

Effect on CO\textsubscript{2} conversion (X\textsubscript{CO2}): The conversion of CO\textsubscript{2} (X\textsubscript{CO2}) as a function of time for these catalysts is shown in Figure 5.8. The average X\textsubscript{CO2} for LZ was insignificant and independent of temperature. X\textsubscript{CO2} for L5RhZ is substantially greater than that for L2RhZ at all temperatures.

![Figure 5.8. CO\textsubscript{2} Conversion for LZ, L2RhZ and L5RhZ pyrochlores at 550°C, 575°C, and 600°C at 1 atm and GHSV = 48,000 mL g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1}. The values on the right hand y-axis show the thermodynamic equilibrium values at that particular temperature as obtained from equilibrium calculations.](image-url)

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For L2RhZ, the experimental $X_{CO_2}$ value at 550°C is constant with time at ~18%, which is substantially lower than the equilibrium value of 44.7% [see Figure 5.8]. When the temperature is further increased to 575°C and 600°C, the experimental $X_{CO_2}$ for L2RhZ increases with time, and reaches a value close to equilibrium at 575°C and greater than equilibrium value of 47.5% at 600°C after 200 min on stream. For L5RhZ, the experimental $X_{CO_2}$ increases slightly with time at all temperatures, and is consistently greater than equilibrium values at all temperatures except 550°C, where it is ~41% versus equilibrium of 44.7%. Equilibrium values of $X_{CH_4}$ and $X_{CO_2}$ were computed by considering C(s) as one product. Thermodynamically, C(s) formation is significant at these temperatures and the conversion of $CO_2$ is limited. It appears that carbon formation is kinetically limited on these catalysts, (as will be seen in the later $H_2/CO$ ratio results) compared to DRM and the reverse water gas shift (RWGS), allowing $X_{CO_2}$ to be greater than the thermodynamic equilibrium values calculated when C(s) is included in the calculation.

Previous studies show that $CO_2$ is activated by the support to form carbonate species and not by the active metal during DRM over conventional supported catalysts such as Rh/Al$_2$O$_3$ and Rh/La$_2$O$_3$ [33, 35-37]. Verykios and co-workers[35] while comparing Ni/La$_2$O$_3$ and Ni/Al$_2$O$_3$ catalysts for DRM showed that in the presence of La$_2$O$_3$; activation of $CO_2$ occurs via formation of La$_2$O$_2$CO$_3$. They proposed that the basic nature of La$_2$O$_3$ assists in the activation of $CO_2$ in the presence of surface CH$_x$ species on the metal or the metal support interface. It can be postulated that, in our case, the lanthanum zirconate assists in the activation of $CO_2$ to form adsorbed carbonate species. The adsorbed carbonate species are then reduced to form CO by the adsorbed CH$_x$ species formed on the Rh sites [35, 37, 38]. In case of LZ pyrochlore, there is no activation of CH$_4$ molecule since there are no Rh sites, thus reduction of $CO_2$ is limited at all temperatures,
consistent with the results in Figure 5.8. If CH₇ species enhance the reduction of CO₂ to CO, it would be expected that X₇CO₂ for L5RhZ will be greater than L2RhZ. The experimental results are in agreement with this hypothesis; X₇CO₂ is greater for L5RhZ than for L2RhZ [Figure 5.8].

Effect on H₂/CO ratio: The H₂/CO ratio plots for the three catalysts at 550°C, 575°C, and 600°C are shown in Figure 5.9. The H₂/CO ratio for LZ pyrochlore was found to be close to 0.05 at all bed temperatures which is negligible and was constant throughout the time on stream. The H₂/CO ratio for L5RhZ was considerably greater than for L2RhZ at all reaction temperatures [see Figure 5.9].

![Graph showing H₂/CO ratio](image)

**Figure 5.9.** H₂/CO ratio for LZ, L2RhZ and L5RhZ pyrochlores at 550°C, 575°C, and 600°C at 1atm and GHSV = 48,000 mL g⁻¹ h⁻¹. The values on the right hand y-axis show the thermodynamic equilibrium values at that particular temperature as obtained from equilibrium calculations.
The product stream consisted mainly of H₂ and CO, with a consistently lower H₂/CO ratio than equilibrium at all temperatures. As mentioned earlier, thermodynamic calculations show that equilibrium amounts of C(s) are significant at these conditions. High levels of carbon formation would limit the formation of CO and thus increase equilibrium H₂/CO ratio. However, it can be postulated that the rate of carbon formation on these catalysts is kinetically limited, favoring DRM and RWGS. DRM results in the H₂/CO ratio of unity but due to the simultaneous occurrence of RWGS, the H₂/CO ratio drops below equilibrium. Thus comparing the H₂/CO ratio for L₂RhZ and L₅RhZ; the H₂/CO ratio of L₅RhZ is consistently greater and closer to unity than L₂RhZ. This suggests greater rate of DRM than RWGS over L₅RhZ compared to L₂RhZ. Thus, increasing Rh substitution helps in limiting simultaneous reactions like RWGS and favors DRM.

The H₂/CO ratio for L₂RhZ increases with time, particularly at 575°C and 600°C suggesting increase in the rate of DRM compared to RWGS. A similar increasing trend was also observed for the conversion of CH₄ (see Figure 5.7), suggesting that the rate of DRM reaction increases with that of the activation of CH₄.

5.3.6. Characterization of the Spent Catalyst

5.3.6.1. TPO (Carbon Burn-off) of the Spent Catalysts

Immediately after performing DRM over these three catalysts, the spent catalysts were subjected to in-situ TPO. The CO₂ signal during TPO of spent catalysts tested at 550°C, 575°C, and 600°C is plotted in Figure 5.10, Figure 5.11, and Figure 5.12 respectively. The amount of carbon formed during the reaction was quantified and is summarized in Table 5.3. The total amount of carbon formed over L₅RhZ is roughly half of the amount of carbon formed over L₂RhZ in each experiment.
Table 5.3. Summary of the carbon formed over the catalysts during the time on stream.

<table>
<thead>
<tr>
<th>Bed Temperature (°C)</th>
<th>Carbon formed (g_{carbon}/g_{catalyst})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LZ</td>
</tr>
<tr>
<td>550</td>
<td>0.014</td>
</tr>
<tr>
<td>575</td>
<td>0.012</td>
</tr>
<tr>
<td>600</td>
<td>0.009</td>
</tr>
</tbody>
</table>

A general mechanism can be postulated based on activation of CH$_4$ molecule on metallic sites to produce adsorbed CH$_x$ species (x=1-3) [33]. These CH$_x$ species can be further reduced to surface carbon on the metal sites, which can react with CO$_2$ (DRM), or form surface carbon, leading to deactivation [37]. The TPO results (Figure 5.10-Figure 5.12) show that although there was carbon deposited on all three catalysts, there was no observable decrease in activity with time on stream, up to 200 min, likely due to the slow axial growth of the deactivated portion of the catalyst bed.

Catalyst spent at 550°C: TPO profile for the catalyst spent at 550°C [Figure 5.10] shows that for LZ, a single broad peak was observed at 130°C. This peak at ~100-130°C is presumably due to the oxidation of the carbon with a relatively high H/C ratio [39]. For L2RhZ, single broad peak was observed at 625°C. This broad peak overlaps other small peaks at higher temperatures of 750°C and 900°C. This suggests that there are at least two more forms of carbon formed over L2RhZ during the reaction. The peak at 625°C is attributed to the oxidation of dehydrogenated form of carbon deposited on or near the metal site [22].

The higher temperatures that are overlapped by the 625 °C peak could be due to oxidation of less reactive carbon species or the graphitic form of carbon which could be present away from the Rh site [22, 40]. TPO profile for L5RhZ shows a single identifiable peak at 650°C attributed to dehydrogenated form of carbon which is very similar to the 625°C peak observed over L2RhZ. A shoulder was observed for L5RhZ at 830°C. This shoulder is most likely due to the oxidation
of the less reactive graphitic carbon which is similar to that observed for L2RhZ at higher temperatures. Peaks at 750ºC and 900ºC (for L2RhZ) are not observed for L5RhZ; this could be due the greater surface coverage of Rh on L5RhZ compared to L2RZ.

Figure 5.10. TPO profile for the catalysts spent at 550ºC, GHSV = 48,000 mL g<sub>cat</sub> h<sup>-1</sup> at 1atm.

Catalyst spent at 575ºC: Figure 5.11 shows the TPO profile for the catalyst spent at 575ºC for the three catalysts. The unsubstituted LZ pyrochlore shows a single broad oxidation peak at 140ºC. This peak is most likely due to the oxidation of reactive hydrogenated polymeric carbon with greater H/C ratio compared to the high temperature carbon. This peak at 140ºC is similar to the one observed over LZ spent at 550ºC (see Figure 5.10). There were four types of oxidation peaks observed for L2RhZ, indicating formation of a corresponding number of different species of surface carbon. The peak at 130 ºC could be due to the reactive form of carbon with a high H/C ratio as seen on the LZ pyrochlore. The 240ºC peak could be attributed to carbon with H/C ratio lower than that corresponding to the peak at 140ºC. It could also be the
same carbon as 140°C but situated away from the surface metal [39]. Thus, the peak at 660°C may be attributed to hydrogenated carbon deposited on the metal atom while the 850°C peak could be due to the oxidation of highly unsaturated carbon deposited over the non-active sites (i.e., lanthanum zirconate in our case) or further away from the Rh site. Peaks observed for L5RhZ are at 230°C, 680°C and 830°C which are similar to the ones observed for L2RhZ. The species of the carbon oxidized at these temperatures would be qualitatively the same as those oxidized over L2RhZ.

Figure 5.11. TPO profile for the catalysts spent at 575°C, GHSV = 48,000 mL g\textsubscript{cat} -1 h\textsuperscript{-1} at 1atm.

Catalyst spent at 600°C: TPO profile for LZ pyrochlores spent at 600°C [shown in Figure 5.12] shows a peak at 140 °C which is similar to the peaks observed over LZ spent at 550°C [see Figure 5.10] and 575°C [see Figure 5.11]. L2RhZ TPO profile shows a very small peak at 270°C followed by a large peak at 710°C. The peak at 270°C is due to the oxidation of hydrogenated carbon which is qualitatively similar to the 240°C peak for L2RhZ in Figure 5.11. The peak at 710°C could be due to the dehydrogenation of the carbon formed further away from the active...
metal site which is oxidized at high temperatures. The graphitic nature of the carbon oxidized at 710°C could be similar to the one observed in the superimposed peaks at 750°C, and 900°C in Figure 5.10 for L2RhZ. The TPO profile for L5RhZ has a small hump at 280°C which is similar to the 270°C peak for L2RhZ in the same plot. There is a very small peak observed at 730°C which could be assigned to the same species as seen over the L2RhZ at 710°C. A peak at 800°C is observed for L5RhZ which was not seen over L2RhZ, this could be due to the deposition of dehydrogenated or graphitized carbon which is not in the proximity of the metallic site [40].

![TPO profile](image)

Figure 5.12. TPO profile for the catalysts spent at 600°C, GHSV = 48,000 mL g\textsubscript{cat}^{-1} h\textsuperscript{-1} at 1 atm.

5.3.6.2. XRD of the Spent Catalyst from DRM and TPO

The diffraction pattern of the spent LZ and L2RhZ pyrochlores resembled the pattern for the fresh catalyst (thus not shown here). There was no apparent shift in the peaks for La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} or formation of any perovskite phase observed for LZ and L2RhZ. This shows that LZ and L2RhZ pyrochlores maintained their structure (La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}) after catalyzing the reaction under reducing reforming condition at these temperatures.
However, for L5RhZ spent catalysts, there was a peak observed at about 32° which could be assigned to the formation of a separate perovskite (LaRhO₃) phase. The magnified image of the XRD pattern for 27°-34° is shown in Figure 5.13; this plot shows clearly the formation of the perovskite peak at these reaction temperatures. This peak (LaRhO₃) was also observed in the fresh L5RhZ catalysts but it was not as prominent compared to the other La₂Zr₂O₇ peaks. After subjecting the catalysts to the reducing reaction conditions followed by oxidation, this particular peak for LaRhO₃ at 32° becomes apparent.

Figure 5.13. Plot of the XRD pattern for the L5RhZ pyrochlores spent for DRM at 500°C, 575°C, and 600°C with GHSV = 48,000 mL g⁻¹ h⁻¹ at 1atm followed by TPO showing in particular the formation of the LaRhO₃ perovskite phase.

5.3.6.3. TPR by H₂ of the Spent Catalysts from DRM and TPO

To study the changes in the reducibility of LZ and of Rh in the L2RhZ and L5RhZ pyrochlores, TPR was conducted on each spent catalyst after (a) DRM at different temperatures and (b) TPO. The TPR plots obtained from these spent catalysts are compared to the plots of the freshly calcined catalysts for L2RhZ and L5RhZ in Figure 5.14 (a), and (b) respectively.
Figure 5.14. Temperature Programmed Reduction by H$_2$ of the catalysts spent for DRM at different temperatures and TPO (a) L2RhZ, and (b) L5RhZ. Reduction conducted from 50°C-950°C ramping at 5°C/min.
A qualitative and quantitative change was observed in the reduction profiles of L2RhZ pyrochlore [see Figure 5.14 (a)]. The fresh catalyst had a reduction peak at 380ºC which is shifted consistently to a lower temperature in the reduction profiles of the spent catalysts, suggesting a slight increase in the reducibility of Rh in the pyrochlore structure. When the reaction temperature was 600ºC; there was a low temperature peak observed at 170ºC and a shoulder at 315ºC, which was not seen in the other L2RhZ profiles. These peaks could be attributed to Rh that is less strongly bound to the pyrochlore structure which developed after DRM/TPO conditions. The quantitative increase in the H₂ consumption after DRM/TPO could be attributed partly to the reduction of the lanthanum zirconate at 570ºC and reduction of Rh at lower temperatures.

A comparison of the reduction profiles for fresh L5RhZ and those spent after DRM/TPO is shown in Figure 5.14 (b). For the spent L5RhZ pyrochlores; a low temperature reduction peak was observed at 130ºC which was absent in the profile of fresh L5RhZ. In the TPR study by Haynes, et.al; [19] a reduction peak at 136ºC for Rh/Al₂O₃ was attributed to the reduction of supported Rh with weaker interaction with the support. This suggests that Rh that was substituted in the pyrochlore structure during calcination; apparently comes out of the structure to the surface of the pyrochlore as a result of the DRM/TPO reactions. This surface Rh is similar to the Rh observed on the supported Rh/Al₂O₃ catalysts in terms of the reducibility [41]. There was a continuous increase observed in the quantity of the H₂ consumed during reduction for L5RhZ [see Figure 5.14 (b)] as for L2RhZ [Figure 5.14 (a)]. This increase in the H₂ consumption is partly due to the increase in the reduction of the lanthanum zirconate at 500ºC and partly due to the reduction of Rh metal that interacted less strongly with the pyrochlore structure.
The temperature of reduction of spent LZ did not change significantly as compared to the reduction of the fresh LZ. The TPR profiles of the fresh catalyst and the spent catalysts are not shown here due to the similarity between them and lack of any additional insight. The H$_2$ consumption for the reduction of the spent catalyst is in direct proportion to the temperature at which the DRM reaction was conducted. Because the DRM reaction conditions are extremely reducing, this may have caused some of the Rh to destabilize from the bulk of the crystal and diffuse to the surface of the catalyst. As the Rh loading increased, the maximum capacity of the pyrochlore structure for Rh at the B site was exceeded, causing Rh atoms to break the coordination with the neighboring La, Zr, Rh, and O atoms in the bulk and move to the surface and form weakly bonded Rh, with a reducibility comparable to supported Rh catalysts.

5.3.6.4. XRD of the Spent Catalysts from DRM Followed by TPO and TPR

![Image of XRD patterns for L5RhZ pyrochlores spent for DRM at 500ºC, 575ºC, and 600ºC with GHSV = 48,000 mL g$^{-1}$ h$^{-1}$ at 1 atm followed by TPO and TPR up to 950ºC showing in particular that the LaRhO$_3$ perovskite peak vanishes after TPR.](image-url)
After conducting TPR on the spent L5RhZ pyrochlore, the changes in their crystalline structure was studied by conducting XRD over these catalysts. We are not aware of any paper in the literature discussing these series of experiments over pyrochlores for DRM. The diffraction pattern of these reduced L5RhZ pyrochlores did not show the presence of perovskite (LaRhO$_3$) phase [in Figure 5.15]. The observable perovskite phase (LaRhO$_3$) that was formed in the L5RhZ pyrochlore after the TPO of the spent catalysts, appears to be reduced by TPR to amorphous form which could not be detected by the X-rays during diffraction.

5.4. Conclusion

The XRD studies of the freshly calcined pyrochlores show a LaRhO$_3$ peak for L5RhZ pyrochlore, possibly due to the higher Rh loading which led to separation of the excess Rh into the perovskite phase. XPS shows that rhodium is present primarily as Rh$^{+3}$ species on the surface of L2RhZ and L5RhZ and that there was no major local surface aggregation due to higher concentration of Rh on the surface of L5RhZ. TPR results of the fresh catalysts show that the total reducibility of the pyrochlores (mg H$_2$ consumed/g$_{cat}$) increased with increasing Rh substitution. The conversion of CH$_4$ and CO$_2$ and the resultant product H$_2$/CO ratio over a series of substituted lanthanum zirconate pyrochlores increased with Rh loading and reaction temperature. The TPO of the catalysts after DRM show that carbon formation decreases with an increase in Rh loading and increasing reaction temperature. The post reaction XRD plots show that there was no apparent change observed in the LZ and L2RhZ structures. However, for spent L5RhZ, the higher Rh loading could have caused the excess metal to separate out as a perovskite phase. When these spent L5RhZ pyrochlores were subjected to TPR after the TPO, the reduction temperature of the Rh was lower than that of the freshly calcined catalysts and there was also an observable increase in the H$_2$ consumption. This was attributed to the diffusion of Rh metal from
the bulk of the structure to the surface. However, the XRD pattern of the reduced spent L5RhZ pyrochlore did not show a perovskite phase, likely because the LaRhO₃ phase was reduced to some non-crystalline form. This result is novel and gives an insight into the behavior of Rh in the pyrochlore structure under alternating reducing (DRM and TPR) and oxidizing conditions. To our knowledge, this disappearance of perovskite (LaRhO₃) phase by alternative oxidation and reduction treatment has not been reported in the literature particularly for pyrochlores catalyzing DRM.

5.5. References


Chapter 6 : Dry Reforming of Methane over Rh Substituted La$_2$Zr$_2$O$_7$ Pyrochlores. I) Study of Catalytic Active Sites for CH$_4$ Activation

6.1. Introduction

Activation of methane is an active topic of research and it is important to study the catalysis of methane reforming reactions in order to develop an efficient process to utilize this important resource. Although methane is typically reformed by reacting it with steam, CO$_2$ reforming can also be used to produce synthesis gas (of H$_2$/CO $\leq$ 1) which can later be selectively converted to oxygenates like methanol or to higher hydrocarbons [1-5].

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H_{298K} = +59.1 \text{ kcal/mol}
\]

Activation of CH$_4$ is a crucial step in DRM mechanism [6-8]. However, there is no consensus in the literature on the mechanism of activation of CH$_4$ on catalytic sites, even on the same metal. For example, Luntz, et al [9] and Wei, et al [10] proposed that on Pt and Pd [11] clusters the activation of CH$_4$ occurs by direct decomposition where all C-H bonds simultaneously dissociate resulting in C$_{(s)}$ and evolution of H$_2$$_{(g)}$. However, theoretical calculations by Seets, et.al [12] suggest activation of CH$_4$ by formation of reactive intermediates like formates or CH$_x$ species. Yamaguchi, et al [11], observed that activation of the C-H bond in CH$_4$ is structure sensitive and its rate increases with decreasing particle size of the Pd clusters.

For DRM, the activity decreases in the order Ru, Rh $>$ Ir $>$ Ni, Pt, Pd $>$ Co $>$ Fe, Cu [13], with noble metals showing higher activity and greater resistance to deactivation by carbon deposition [14-16]. The activity of Rh is about ten times of that of Ni catalysts [17] and appears to deactivate less rapidly [18]. DRM has been widely studied on various catalysts however, we are aware of no papers in the literature in which substituted pyrochlores have been studied for DRM other than those reported by our group [19-21]. Pyrochlores are crystalline thermally stable
ternary metal oxides based on the fluorite structure with a cubic unit cell and general formula of $A_2B_2O_7$. The A-site is usually a large cation (typically rare earth elements) and the B-site cation has a smaller radius (usually transition metal) [22].

These materials have two important properties that make them interesting for this reaction. The first is oxygen ion conductivity. Vacancies at the O sites, created during synthesis, facilitate oxygen ion migration which minimizes carbon deposition formed by CH$_4$ dissociation [23]. The second is the ability to isomorphically substitute catalytically active transition metals into the B site, where they do not sinter at the high temperatures of DRM. These transition metals are the primary active sites for activation of CH$_4$ in the DRM reaction [24]. Candidate catalytically active transition metals for B-site substitution include Ru, Rh, and Pt [19, 20]. The most closely related paper for DRM over pyrochlores is by Ashcroft, et.al [25] who studied Eu$_2$Ir$_2$O$_7$ for DRM. However, the pyrochlore structure decomposed to Eu$_2$O$_3$ and Ir under DRM conditions above 340°C.

Here, we report a systematic study of the active sites and kinetics of DRM on two Rh-substituted lanthanum zirconate [LZ] pyrochlores: 2wt% [L2RhZ] and 5wt% [L5RhZ]. Specifically, we examine CH$_4$ activation and its role in the mechanism of the DRM. A detailed characterization and activity study of these materials has been reported in our earlier work [21] where we confirm the formation of the pyrochlore phase and substitution of Rh at the B-site.

Here, the process of CH$_4$ activation as a function of temperature and Rh substitution in the pyrochlore structure was studied by means of CH$_4$ temperature programmed reduction (CH$_4$ TPR). The role of CH$_4$ in the rate limiting step in DRM mechanism is examined by studying the CH$_4$/CD$_4$ kinetic isotope effect. The elementary steps involved in the mechanism were studied
by transient pulsing of CH$_4$ and CO$_2$ with an Ar tracer. Kinetic rate models based on postulated mechanisms were validated by statistically fitting the kinetic data obtained over L2RhZ and L5RhZ pyrochlore catalysts.

6.2. Experimental Section

6.2.1. Catalyst Synthesis

The LZ, L2RhZ, and L5RhZ pyrochlores studied in this work were prepared by the modified Pechini sol-gel method [26]. The metal salts of lanthanum nitrate hexahydrate [La(NO$_3$)$_3$.6H$_2$O] (GFS Chemicals, 99.9%), zirconium oxynitrate [ZrO(NO$_3$)$_2$.xH$_2$O] (Alfa Aesar, 99.9%), and rhodium nitrate [Rh(NO$_3$)$_3$.2H$_2$O] (Alfa Aesar, 99.9%) were used as precursors. Anhydrous citric acid (C$_{6}$H$_{8}$O$_{7}$) and ethylene glycol (C$_2$H$_6$O$_2$) were used as complexing and polymerizing agents, respectively. The metal salts in required stoichiometric amounts were dissolved separately in 50 ml deionized water. The metal solutions were then combined in a larger beaker with continuous stirring. Aqueous solution of citric acid (CA) with molar CA to metal ion ratio as 1.2 was added to the metal solution beaker. The mixture was heated to 70°C and then ethylene glycol was added with molar ratio of ethylene glycol to CA as 1:1. The solution was stirred for several hours until a clear viscous gel remained in the beaker. The gel was further transferred to a heating mantle and heated to 130°C to promote the polyesterification reaction. This resulted in an amorphous polyester-type resin. This resin was collected and calcined at 1000°C for 8 h to form pyrochlore catalyst.

6.2.2. H$_2$ Pulse Chemisorption

The total amount of Rh accessible on the surface of the pyrochlores was determined by H$_2$ pulse chemisorption. Before chemisorbing H$_2$, the catalysts were first reduced at 900°C for 30 min in flowing 5% H$_2$/Ar then cooled to 50°C in flowing He. Then 0.5377 mL of 5% H$_2$/Ar was
pulsed over the catalyst until the surface of the catalyst was saturated with dissociated H₂. The dispersion was calculated by using the stoichiometric ratio of H₂: metal as 1:2.

6.2.3. Activation Energies

The rates of CH₄ and CO₂ consumption were performed in an AMI-200 lab-scale fixed bed reactor with the catalyst held in place by quartz wool. The composition of reactant gases used for the reaction was 10 mole% CO₂/He (99.999% pure) and 10 mole% CH₄/He (99.999% pure). The catalysts were mixed/diluted with α-alumina with ratio pyrochlore: alumina=1:10 so that the total mass of mixture was 110 mg. The flow rate of each reactant was 20 mL/min. The temperature range was carefully selected to limit the reactant conversion below 15% to minimize temperature and concentration gradients across the catalyst bed. The activation barrier of CH₄ and CO₂ was determined by monitoring the rates of consumption of CH₄ and CO₂ in the on-line Ametek quadrapole mass spectrometer at the selected temperatures. Because the activity of L₅RhZ was higher than L₂RhZ [21], the temperature range chosen for L₂RhZ (585 – 605°C) was higher than that for L₅RhZ (520 – 560°C) to limit the conversion in both cases and to minimize any effects of concentration/temperature gradients across the catalyst bed. Blank reactor runs were also conducted to confirm the inert nature of the alumina and quartz wool.

6.2.4. Transient Pulsing

In this work we use single pulse format (SPF) where a single pulse of known volume of CH₄/Ar is introduced in the He carrier gas and the time dependence of the product pulse was determined with Ar as tracer. The transient pulsing experiments were conducted in a non-steady state reaction system comprised of a Diffuse Reflectance Infra-red Fourier Transform Spectroscopy (DRIFTS) cell connected to an 8-port valve. The valve was fitted with a loop of 0.5 mL which was used to pulse the reactant mixture over the catalyst in the DRIFTS cell. The
catalysts were first reduced in 4% H₂/He at 550°C for 30 min and then flushed with He. The experimental sequence of pulsing used to study L2RhZ and L5RhZ catalysts at 550°C was 10%CH₄/2%Ar/bal He → 10%CO₂/2%Ar/bal He → 10%CH₄/2%Ar/bal He. Here He was used as the carrier gas continuously flowing over the catalyst and mixture of 10%CH₄/2%Ar/bal He or 10%CO₂/2%Ar/bal He was pulsed into the continuous stream of He. The product formation and the tailing process of each pulse was analyzed separately and designated here as CH₄/Ar pulse 1 → CO₂/Ar pulse 2 → CH₄/Ar pulse 3. The unreacted reactant and the products formed from the pulse were analyzed in an on-line Ametek quadrapole mass spectrometer (MS).

After introducing the first CH₄/Ar pulse, the catalyst was flushed in He for 10 mins before a pulse of CO₂/Ar was introduced, which was then followed by 10 min He flushing. Then another pulse of CH₄/Ar was introduced and the product stream was evaluated to study the intermediate steps occurring in the process of CH₄ activation. The masses analyzed were: H₂ (1), CH₄ (15), H₂O (18), CO (28), Ar (40), and CO₂ (44). The NIST web-book suggests that CO₂ has a ~10% (of mass 44) intensity at mass 28. This information was used to correct the concentration of CO formed during all the experiments described in this work.

6.2.5. Temperature Programmed Reduction (TPR) by CH₄

This characterization method was used to study the reducibility of the pyrochlore structure. For this purpose, about 50 mg of catalyst was dried at 200°C in He. The catalyst bed was then subjected to reduction by 10% CH₄/He flowing at 30 mL/min and the temperature was ramped from 40°C to 950°C at the ramp rate of 5°C/min. This experiment was conducted in the same equipment as used in section 6.2.3. The product stream during the CH₄ TPR was analyzed using the mass spectrometer (MS) connected to the reactor outlet.
6.2.6. **CH₄/CD₄ Kinetic Isotope Effect**

Deuterium kinetic isotope effect was studied by using 10 mole% of CD₄/He (99.99% pure), the reactor, analytical system unit and CH₄/He and CO₂/He gas compositions is same as mentioned in the Arrhenius plot (Section 6.2.3). Before testing for DRM, the catalysts were reduced in 4% H₂/He by ramping from 25°C to 600°C and maintaining isothermal conditions at 600°C for 30 min then purged in He for 15 min. For testing the change in the rate of consumption of CH₄ and CD₄, alternate cycles of CH₄/CO₂/He and CD₄/CO₂/He of 30 min each were performed on L2RhZ and L5RhZ.

6.2.7. **Kinetic Rate Modeling**

The kinetic data for testing the validity of the rate expressions was obtained in the same lab-scale reactor using the same catalyst dilution ratio as explained above. The partial pressure dependence of the rate of consumption of CH₄ and CO₂ was determined by keeping partial pressure of one reactant (CH₄ or CO₂) constant at 0.05 atm and varying that of the other (CO₂ or CH₄) as 0.03, 0.035, 0.04, and 0.045 atm (balance He). These set of experiments were performed at 570°C, 590°C, and 610°C for L2RhZ and at 520°C, 540°C, and 560°C for L5RhZ. The conversion of the reactants was kept below 15%, so as to approach differential conditions.

6.3. **Results and Discussion**

6.3.1. **H₂ Pulse Chemisorption**

The apparent dispersions of Rh on L2RhZ and L5RhZ are 6.6% and 6.4% respectively, as measured by H₂ pulse chemisorption. However, it is important to acknowledge that because surface sites other than Rh can chemisorb hydrogen, the true Rh dispersion is difficult to measure.
using this or related techniques, such as CO pulse chemisorption. Factors that complicate the measurement of Rh dispersion using these techniques include:

i. ensemble effects of the metal that may change the nature of the adsorption site, so that it is impossible to assign a specific H-metal stoichiometry to a pulse chemisorption result,

ii. electronic interactions between the Rh and other metals in the pyrochlore, which could change the hydrogen binding properties of these sites,

iii. changes in the hydrogen adsorption kinetics due to structure sensitivity [27], which renders H$_2$ pulse chemisorption inappropriate for determining the actual dispersion of Rh on the surface of these multi-metallic pyrochlore catalysts.

There are a number of recent examples of this ambiguity [28-30], which show that the adsorption of H$_2$ on a bimetallic catalyst is strongly affected by the neighboring atoms on the surface and hence sites with different co-ordinations have different adsorption characteristics. This would logically be true of the pyrochlores as well because Rh is substituted in the pyrochlore lattice.

6.3.2. Activation Energies

The apparent activation energies for the rates of CH$_4$ and CO$_2$ disappearance calculated from an Arrhenius plot for L2RhZ and L5RhZ are shown in Figure 6.1. Table 6.1 shows the apparent activation energies for both CH$_4$ and CO$_2$ reactions. The activation energy for CH$_4$ is greater than that for CO$_2$ on both catalysts, which agrees well with the results reported in the literature [13, 31, 32]. The activation energies for CH$_4$ and CO$_2$ are significantly lower on L5RhZ than L2RhZ, suggesting a different type of catalytically active site on L5RhZ than on L2RhZ. The activation energies for L5RhZ are essentially equal to those reported for Rh
(0.5%)/Al₂O₃-La₂O₃-BaO [33], indicating catalytically similar active sites on these two materials. This is not the case for L2RhZ, which has higher activation energies, suggesting quite different sites on this catalyst.

Figure 6.1. Arrhenius plot for CH₄ and CO₂ consumption over (a) L2RhZ, (b) L5RhZ. Data obtained at different temperature range (x-axis) at 1 atm with 10% CH₄/He and 10% CO₂/He at 20 mL/min each.
Table 6.1. Summary of the activation energies calculated in this work and its comparison to that reported in the literature.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Apparent activation energy (kcal/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH₄</td>
<td>CO₂</td>
</tr>
<tr>
<td>L2RhZ</td>
<td>34.2±0.4</td>
<td>27±0.2</td>
</tr>
<tr>
<td>L5RhZ</td>
<td>21.8±0.2</td>
<td>18.7±0.1</td>
</tr>
<tr>
<td>Rh (0.6%)/La₂O₃(27%)-SiO₂</td>
<td>14.7</td>
<td>11.8</td>
</tr>
<tr>
<td>Rh (0.5%)/Al₂O₃-La₂O₃-BaO</td>
<td>22</td>
<td>19.28</td>
</tr>
</tbody>
</table>

The higher activation energies for CH₄ (compared to CO₂) on both L2RhZ and L5RhZ show that the activation of CH₄ is a slower step than the activation of CO₂ on both catalysts. A previous study on Ni/La₂O₃ and BaO promoted catalysts suggests that basic sites on these catalysts activate the mildly acidic CO₂ [35]. Zhang and Verykios [36] suggest that the presence of basic surface La-O sites catalyze the conversion of CO₂ to lanthanum oxy-carbonates (La₂O₂CO₃), which decreases the apparent activation energy for CO₂ conversion so that the activation of CH₄ is a relatively slower reaction step.

6.3.3. Transient Pulsing

Studying the steady-state reaction provides useful information, but does not allow insight that can be gained by transient pulsing. In these SPF experiments, the CH₄ pulse is followed by a CO₂ pulse and the time-dependent reaction products are measured (details in Section 6.2.4). This gives insight into the chemisorption of, diffusion of the chemisorbed species between different active sites, reaction between the chemisorbed species, and desorption of the products. Detecting the chemisorbed surface species and studying their interaction with the catalytic active sites is essential in understanding the overall mechanistic scheme of the reaction. The non-steady state reaction setup allowed rapid pulsing of known volume and composition of gas mixture over the catalyst. The pulsing could be followed by He flushing without any pressure drop across the catalyst bed which resulted in tailing pulse type response of the product stream. The rate at which the pulses exit the reactor, the shape of the response pulse curve with respect to that of the
Ar tracer, the relative product yields is a function of diffusion, adsorption, reaction selectivity and desorption of the gas over the catalyst surface [37]. These transient experiments can elucidate the details of the surface reaction intermediates, provided the intermediate reactions are not undetectably fast [8, 37, 38].

Figure 6.2 and Figure 6.3 show the response of the pulse scheme CH₄/Ar pulse 1 → CO₂/Ar pulse 2 → CH₄/Ar pulse 3 for L2RhZ and L5RhZ respectively. For each pulse the reactant gas mixture was pulsed at t=0 (x-axis), however there was a slight delay in the appearance of the unreacted reactant and Ar tracer in the MS signal [Figure 6.2 (a), and Figure 6.3 (a)] due to the dead volume between the reactor bed and the MS. The MS signal was then normalized so that the normalized intensities represent the time dependent response and not the actual product yield [Figure 6.2 (b), and Figure 6.3 (b)]. The Ar tracer is inert, so that the yield on Ar was almost 100% in all pulses and it diffused through the catalyst bed without significant interaction with the catalytic surface. To confirm the inactivity of Ar with the catalyst surface, a blank experiment was conducted with exact same conditions but using quartz wool instead of the catalyst. The normalized response of Ar pulse from the blank was exactly the same as that on L2RhZ and L5RhZ, confirming that the interaction of Ar with the catalyst surface was insignificant.

L2RhZ, CH₄ pulse 1: The MS signal response for the three consecutive pulses over L2RhZ is shown in Figure 6.2 (a) and the normalized pulse response in Figure 6.2 (b). During CH₄/Ar pulse 1, the MS signal [Figure 6.2 (a)] shows response pulses for significant amounts of H₂, CO, unreacted CH₄, Ar, and negligible amounts of CO₂. Quantification of the MS signal suggests that about 55% of CH₄ was converted to primarily CO and H₂ (and an insignificant amount of CO₂) during the CH₄/Ar pulse 1 [Table 6.2]. The H₂ formed during this pulse was
about 83.1% of the theoretical value calculated from CH$_4$ conversion. A carbon balance suggests that only 53.1% of the carbon from CH$_4$ activation could be accounted by formation of CO and CO$_2$. Thus CO and CO$_2$ are formed by the reaction between surface carbon and lattice oxygen, as found in the CH$_4$-TPR test [Figure 6.4] which is discussed later in Section 6.3.4. During DRM, carbon deposition is primarily due to decomposition of CH$_4$ [39, 40]. The remaining carbon that could not be accounted in CO and CO$_2$ formation, is likely solid surface carbon that remains on the catalyst after all the product gases have exited the reactor bed. Normalized response for the components formed during the CH$_4$ pulse 1 can be compared to the response for Ar.

First, it is important to note that the residence time distribution of the gas in the catalyst bed is dependent on (a) the interaction (adsorption/desorption) of the gas with the catalyst, and on (b) the gas diffusivity [37, 41]. Thus if there is no interaction of the gas with the catalyst, the gases will exit the reactor in the order of decreasing diffusivities i.e., increasing molecular weights. In the case of diffusion controlled pulse response, the order of gas exiting the reactor would be H$_2$, CH$_4$, CO, Ar, and lastly CO$_2$. Any change in this order would be due to interaction of the gas with the catalyst surface. For normalized CH$_4$ pulse 1 [Figure 6.2 (b)], CH$_4$ is observed to exit the reactor faster than Ar, this could be attributed to greater diffusivity of CH$_4$ compared to Ar. Molecules of CO and H$_2$ are much smaller (thus greater diffusivity) than Ar and would be expected to exit before Ar. However, the response for CO and H$_2$ was observed to be much slower than Ar response. This is because either, CO and H$_2$ both interact strongly with the catalyst surface, or the rate of reaction forming CO and H$_2$ is much slower than diffusion of Ar. It is important to note that the response curve for CO is quite close to that of H$_2$, suggesting that CO and H$_2$ are formed at the same time, presumably from a common surface reaction.
L2RhZ CO₂ pulse 2: There are two possible mechanisms for activation of CH₄; direct dissociation [9, 42], in which all four C-H bonds are cleaved to produce a surface carbon, and precursor mediated activation [12], in which CH₄ forms adsorbed intermediates like CHₓ or formates. During CO₂ pulse 2, the MS signal showed no traces of CH₄ and H₂ [Figure 6.2 (a)]. This suggests that there were no CHₓ, adsorbed formates or adsorbed H₂ intermediates present on the catalyst from the previous CH₄/Ar pulse 1. This would mean that activation of CH₄ is by direct dissociation mechanism over these pyrochlores, where it decomposes completely to C(s) and H₂. About 33.7% of the CO₂ is converted during the CO₂ pulse 2, but only 19.1% of the CO₂ converted resulted in CO formation [Table 6.2]. The rest of the CO₂ likely forms surface carbonates. The normalized response for CO₂ in pulse 2 suggests simultaneous exit of CO and
CO₂ which is slower than diffusion of Ar [Figure 6.2 (b)]. This suggests that CO is a product of either the reduction of CO₂ or the oxidation of surface carbon by CO₂ or both. The next CH₄ pulse (pulse 3 below) provides insight into the mechanism of the formation of CO and oxidation of the surface carbon.

L2RhZ CH₄ pulse 3: The MS signal intensity for H₂ in CH₄ pulse 3 is smaller than in CH₄ pulse 1 [Figure 6.2 (a)]. Quantification suggests that only 48.1% of CH₄ was converted in CH₄ pulse 3 as opposed to 55% in CH₄ pulse 1 [Table 6.2], possibly due to carbon blocking the active sites during CH₄ pulse 1. The H₂ selectivity however, remains essentially the same at 81.3% in CH₄ pulse 3 (compared to 83.1% in CH₄ pulse 1). Carbon balance suggests that there was an increase in the amount of CO formed during the CH₄ pulse 3 compared to the CH₄ pulse 1. About 64% of the carbon converted in CH₄ could be accounted for by the formation of CO and small amounts of CO₂. The carbon in CO and CO₂ could be from the CH₄ activated in CH₄ pulse 3, reduction of the carbonates formed during CO₂ pulse 2, and oxidation of the carbon formed during CH₄ pulse 1. It is important to note that carbon yield and formation of CO in the CH₄ pulses is significantly greater than the CO₂ pulse. This suggests that the presence of H₂ has a positive effect on the formation of CO.

Consider the normalized CH₄ pulse 3 to understand the role of H₂ in CO formation [Figure 6.2 (b)]. H₂ and CO exit the reactor simultaneously inspite of the large differences in their molecular diffusivities, suggesting that both H₂ and CO are produced in a slow surface reaction [43]. Based on this it can be postulated that the H₂ formed from dissociation of CH₄ does not desorb immediately but reacts with the oxygen associated with either surface carbonates or with the pyrochlore lattice to form H₂O. If this H₂ bonds with the carbonate oxygen, it would reduce the carbonates to CO and if it reacts with the lattice oxygen, it would reduce the
pyrochlore [See section 6.3.4]. This H₂O then oxidizes the carbon formed from CH₄ activation (C(s) + H₂O → CO + H₂), liberating CO and H₂ simultaneously. Osaki, et al [44] observed the same trend of delayed H₂ and CO response over Ni/SiO₂ catalyts and proposed that oxidation of carbon by H₂O is the rate limiting step in the mechanism. This step of carbon oxidation by H₂O over pyrochlores here must be a slow step in order to cause a delay in the response of H₂ and CO with respect to Ar [45]. The presence of strong CH₄/CD₄ isotope effect (as will be seen later) results suggest that carbon oxidation step is not rate-determining, but is slow enough to be detected in the transient pulse experiments. Oxidation of surface carbon is a crucial step in the DRM mechanism and is greatly influenced by the activation of CH₄.

<table>
<thead>
<tr>
<th>Pulse</th>
<th>L2RhZ</th>
<th>L5RhZ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH₄/CO₂ Conversion (%)</td>
<td>H₂ yield ‡</td>
</tr>
<tr>
<td>CH₄ pulse 1</td>
<td>55</td>
<td>83.1</td>
</tr>
<tr>
<td>CO₂ pulse 2</td>
<td>33.7</td>
<td>-</td>
</tr>
<tr>
<td>CH₄ pulse 3</td>
<td>48.1</td>
<td>81.3</td>
</tr>
</tbody>
</table>

‡ – (moles of CO or CO₂ formed/moles of CH₄ converted) x 100
† – (moles of CO₂ + CO formed/moles of CH₄ converted) x 100
§ – (moles of H₂ formed/(2 x moles of CH₄ converted)) x 100

L5RhZ CH₄ pulse 1: The process of methane activation appears to be occurring to a greater extent on the L5RhZ compared to the L2RhZ due to greater Rh content of the catalyst. The MS signal for CH₄ pulse 1 over L5RhZ [Figure 6.3 (a)] suggests significant amounts of formation of H₂ and CO. In addition, CO₂ formation is an order of magnitude greater than that over L2RhZ. During this pulse 64.3% of CH₄ was converted which is greater than that (55%) observed over L2RhZ. The experimental H₂ produced is about 82.5% of the theoretical value.
calculated from the CH₄ conversion [Table 6.2]. The carbon balance computed from CO and CO₂ formation accounts for about 61.8% of the carbon reacted in CH₄ pulse 1. The remaining carbon likely remains on the catalyst as solid adsorbed carbon, C(s). The carbon balance is greater for L5RhZ (61.8%) compared to L2RhZ (53.1%). The normalized response suggests that the CH₄ response is faster than the Ar response [Figure 6.3 (b)]. H₂ and CO formation are simultaneous, similar to what was observed in L2RhZ CH₄ pulse 1. This could be due to oxidation of the surface carbon by H₂ via H₂O formation with the pyrochlore lattice oxygen. The response for CO₂ is slower than CO and H₂; also there is a shift in the peak of CO₂. The resulting CO₂ response curve has a higher residence time over the catalyst than any other component. This could be either due to lower diffusivity or increased interaction with the catalyst surface. The response of CO₂ during the blank experiment was observed to be much faster than the CO₂ response over L5RhZ; thus the delay in the CO₂ response curve could be a strong function of primarily the interaction/slow surface reaction [46] and not the lower diffusivity value of CO₂. The fact that the peak for CO₂ appears later than the peak for CO and H₂, suggests that CO₂ might be formed from further oxidation of CO. A delay in the response curve would also mean that the catalyst has strong CO₂ adsorbing sites, which increases the residence time over the catalyst [37].

L5RhZ CO₂ pulse 2: The CO₂ pulse 2 for L5RhZ [Figure 6.3] is qualitatively and quantitatively very similar to that observed for L2RhZ [Figure 6.2]. Conversion of CO₂ was about 32.7% and no H₂ and CH₄ were observed in the MS signal suggesting the absence of any CHₓ or H₂ species on the surface. Thus CH₄ activates on L5RhZ by direct dissociation mechanism forming C(s) and H₂. About 22% of the converted CO₂ resulted in the formation of CO; the remaining 78% of the converted CO₂ presumably results in carbonate formation over the
catalyst but could not be completely reduced to CO due to absence of H₂. The normalized response of CO is accompanied by that of CO₂, suggesting that this limited amount of CO is formed either from the reduction of CO₂ or from the oxidation of C(s) formed in the CH₄ pulse 1.

Figure 6.3. Pulse response for scheme CH₄/Ar → CO₂/Ar → CH₄/Ar for L5RhZ, (a) mass spec signal response, (b) normalized pulse response.

L5RhZ CH₄ pulse 3: During the CH₄ pulse 3, the CH₄ conversion dropped to 58.8% compared to 64.3% in CH₄ pulse 1. As the carbon balance during CH₄ pulse 1 suggested substantial carbon formation, this presumably blocked the active sites and resulted in lower CH₄ activation. The H₂ yield was 83% which is nearly the same as that in the CH₄ pulse 1 [Table 6.2]. The carbon balance improved in CH₄ pulse 3 to about 68.8% as compared to 61.8% for CH₄ pulse 1. Some of the carbonates formed during CO₂ pulse 2 were reduced to CO during CH₄ pulse 3 which resulted in an improved carbon balance. The normalized response for CH₄, H₂ and CO during CH₄ pulse 3 is very similar to that during CH₄ pulse 1. Simultaneous exit of H₂ and
CO suggests oxidation of the surface carbon by H\textsubscript{2}O. However, there is a difference in the normalized CO\textsubscript{2} response during the two CH\textsubscript{4} pulses. The CO\textsubscript{2} normalized response during CH\textsubscript{4} pulse 3 is delayed compared to CH\textsubscript{4} pulse 1, likely due to lower diffusivity of CO\textsubscript{2}. However, there are multiple peaks observed in pulse 3. The multiple peaks suggest multiple reactions with varying rates leading to formation of CO\textsubscript{2} [37]. The broadness of the peak suggests the presence of different types of CO\textsubscript{2} adsorbing sites on the catalyst surface, as reported by others [46, 47]. For L5RhZ, the mechanism of CH\textsubscript{4} activation and product formation during CH\textsubscript{4} pulse 1 differs from that during CH\textsubscript{4} pulse 3 as seen by the difference in the CO\textsubscript{2} response curve. This difference could also be present for the L2RhZ but was not clearly apparent due to limited CO\textsubscript{2} formation.

Increased CH\textsubscript{4} conversion over L5RhZ compared to L2RhZ suggests that the active site for CH\textsubscript{4} is Rh. Also L5RhZ showed better carbon balance numbers suggesting that Rh plays an important role in oxidation of the surface carbon. Considering that the activation of CO\textsubscript{2} is primarily by La sites on the pyrochlore surface [48-50], the oxidation of surface carbon could be occurring at the Rh-La interface. This is in agreement with the transient experiments where L5RhZ having higher surface Rh concentration had higher carbon oxidation rate as seen by higher carbon balance. This greater number of Rh-La interfacial sites on L5RhZ compared to L2RhZ leads to greater rates of oxidation of the surface carbon.

6.3.4. Temperature Programmed Reduction (TPR) by CH\textsubscript{4}

The lattice oxygen in the pyrochlore crystals is believed to be reactive towards surface carbon [26, 51], especially at the high temperatures of interest here. CH\textsubscript{4}-TPR was used to study the reactivity of the lattice oxygen in the pyrochlore structure. During this reduction process, CH\textsubscript{4} is thought to adsorb dissociatively forming C(s) and H\textsubscript{2}. The reactive lattice oxygen from
the pyrochlore crystal then oxidizes the surface carbon atom forming mostly CO but some CO$_2$. Figure 6.4 shows the formation of H$_2$, CO and CO$_2$ during TPR by CH$_4$ of the freshly calcined (a) L2RhZ, and (b) L5RhZ. MS signal showed that there was very significant amount of H$_2$ formed at the exact same temperature as CO during the CH$_4$-TPR experiment. This suggests a mechanism in which H$_2$ reacts with the lattice oxygen to produce H$_2$O, which then oxidizes the surface carbon forming CO and H$_2$ simultaneously, as explained in the transient experiments. However, no observable signal for H$_2$O was observed in the MS during the experiment.

![Figure 6.4](image)

**Figure 6.4.** TPR by CH$_4$ of freshly calcined (a) L2RhZ, (b) L5RhZ from 50°C - 950°C at the ramp rate of 5°C/min. [ISO represents that the conditions were isothermal at 950°C for 30 min]. The plot of each catalyst differs in y-axis scale.
CH₄-TPR of L₂RhZ shows that CO and H₂ forms at 570°C [Figure 6.4 (a)] and a small but measurable quantity of CO₂ was also formed. The total CO formed was 48 mg CO/g cat with 12 mg CO₂/g cat of CO₂, corresponding to 36.7 mg O/g cat. For L₅RhZ, the peak temperature of CO formation was 415°C with a shoulder at 330°C, which is much lower than that for L₂RhZ pyrochlores [Figure 6.4 (b)]. The formation of CO (98 mg CO/g cat) and CO₂ (13 mg CO₂/g cat) was
greater for L5RhZ compared to L2RhZ pyrochlores. The total amount of O reacting from the lattice of L5RhZ was 60.4 mgO/g\text{cat} which is greater than L2RhZ. The summary of the quantification of reactive oxygen for each catalyst is shown in Table 6.3.

Table 6.3. Summary of the reactive oxygen from the lattice of the pyrochlores.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Amount of CO formed (mg\text{CO}/g\text{cat})</th>
<th>Amount of CO\textsubscript{2} formed (mg\text{CO}_2/g\text{cat})</th>
<th>Amount of reactive lattice O (mgO/g\text{cat})</th>
<th>Percentage of the total lattice oxygen reacted (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L2RhZ</td>
<td>48</td>
<td>12</td>
<td>36.7</td>
<td>17.4</td>
</tr>
<tr>
<td>L5RhZ</td>
<td>98</td>
<td>13</td>
<td>60.4</td>
<td>27.7</td>
</tr>
</tbody>
</table>

There are two further differences in the CH\textsubscript{4}-TPR results for these two catalysts. First, although both show multiple peaks, the lowest significant TPR peak temperature for the L5RhZ (415°C versus 570°C for the L2RhZ) suggests greater lattice oxygen reactivity in the L5RhZ, assuming the reactivity of the surface carbon formed by CH\textsubscript{4} decomposition is similar on both catalysts. Second, there are three higher temperature peaks for the L2RhZ (655, 770 and 950°C), suggesting that there are different species of reactive oxygen within the lattice. These oxygen species have different activation energies for diffusion to the surface of the pyrochlore where they oxidize the carbon formed from the activation of CH\textsubscript{4}. Hence there are different temperatures for formation of CO and CO\textsubscript{2}. These different oxygen species are a characteristic of the metal substitution in the pyrochlore structure. Higher Rh substitution results in lower activation barriers for the diffusion of reactive lattice oxygen to the surface. On the L5RhZ, there are two high temperature peaks (882°C and 950°C). The 882°C peak does not match any of those on the L2RhZ, indicating a distinct type of reducibility on this catalyst. When isothermal conditions (950°C) were maintained for 35 min (ISO-isothermal part on the temperature axis in Figure 6.4) in flowing CH\textsubscript{4}, the CO signal did not return back to the baseline. If CH\textsubscript{4} flow was continued at this temperature for longer duration then, over a period of time, the lattice oxygen
would eventually deplete, and CO formation would end. Although this process is evident in the results shown in Figure 6.4, 35 min was not enough for the lattice oxygen, activated at 950°C, to be depleted completely, the CO signal did not drop back to the baseline.

6.3.5. CH₄/CD₄ Kinetic Isotope Effect

Apparent activation energies [Table 6.1] show that CH₄ dissociation is the rate limiting step during DRM on these catalysts. In order to verify the expected rate limiting C-H bond cleavage in DRM, the CH₄/CD₄ kinetic isotope effect was studied. In this experiment the rate of consumption of CH₄ and CO₂ was measured before and after switching CH₄ to CD₄. Figure 6.5 and Figure 6.6 show the changes in conversion of CH₄, CD₄, and CO₂ over L2RhZ and L5RhZ respectively, when CH₄ is switched with CD₄ and then back to CH₄. During the first 30 min cycle (i.e., t = 0-30 min) of CH₄/CO₂ at 600°C, significant CH₄ and CO₂ conversion [Figure 6.5 and Figure 6.6] was observed, as expected. When CH₄ was switched with CD₄ in the next cycle a strong deuterium isotope effect was apparent, where the CD₄ conversion at the time of switch (t = 30 min) was about 15% for L2RhZ and 30% for L5RhZ and dropped to 0% and 10% respectively by the end of 30 min (i.e., t = 60 min) cycle. The CO₂ conversion during this cycle (t = 30-60 min) was lower as compared to that during the first cycle (t = 0-30 min) for both catalysts suggesting that deuterium had a strong isotope effect on CO₂ conversion as well. When the reaction mixture was switched back to CH₄/CO₂ (t = 60-90 min), the catalysts regained their first-cycle activity. In the next cycle (t = 90-120 min) when CH₄ was switched again with CD₄, the exact same decay of CD₄ conversion with time was observed as in the first switch (t = 30-60 min); with CD₄ conversion gradually decreasing during the 30 min cycle.
Increasing the temperature from 600°C to 620°C resulted in an increase in the CH₄ and CO₂ conversion (t = 120-150 min) and the same isotope effect was observed for both the catalysts [Figure 6.5 and Figure 6.6]. Finally, the conditions of the first cycle were repeated (600°C) and showed no deactivation of the catalyst over the 180 min of the previous cycles.
Figure 6.6. CH₄/CD₄ kinetic isotope effect on (a) CH₄/CD₄ conversion, and (b) CO₂ conversion, observed in alternating cycles of CH₄/CO₂ and CD₄/CO₂ for L5RhZ.

The conversion of CH₄/CD₄ and CO₂ over L5RhZ was greater than L2RhZ in all cycles and no conversion was observed over non-substituted LZ pyrochlores. The XPS results reported earlier [21] suggest that the surface concentration of Rh on L5RhZ is twice of that on L2RhZ. Linic, et al.,[52] performed DFT calculations and found that the activation barrier for CH₄ on
terrace sites is higher from that on stepped sites and that uncoordinated metals sites assists in C-H bond activation. Since the active site for CH₄ activation is the Rh metal, the difference in CH₄ conversion is attributed to greater Rh surface concentration and presumably greater number of stepped sites on L5RhZ pyrochlores compared to L2RhZ. In the first cycle, CH₄ was switched with CD₄ and the CD₄ conversion gradually drops and reaches a substantially low value by the end of the cycle, consistent with the hypothesis that breaking the C-H bond in methane is rate-limiting. In the early part of the CD₄+CO₂ cycle, CD₄ adsorbs on the Rh sites causing a high apparent CD₄ conversion even though it is not reacting. As time progresses, the slow dissociation rate of CD₄ prevents the turnover of the CD₄ molecule and active sites are gradually saturated with CD₄. This gradual saturation of the Rh sites causes a decrease in the further adsorption of CD₄ and results in a corresponding gradual drop in the apparent CD₄ conversion. When the CD₄ is switched back with CH₄, a significant amount of CD₄ from the previous cycle desorbs and leaves the reactor along with the products of the succeeding CH₄ cycle. All of CD₄ that is adsorbed does not dissociate due to slow dissociation rate and is replaced by CH₄ during the CH₄ cycle.

Higher activity of L5RhZ than L2RhZ could be due to the difference in the mechanism of activation or the kinetics (activation energy and CH₄ TPR) of CH₄/CD₄ activation over the two pyrochlores. Breaking of the C-H or C-D bond in the rate limiting step should result in an isotope effect factor (k_{CH₄/CD₄}) value of >1 [53]. In this case, due to a time dependent decrease in the CD₄ conversion for L2RhZ and L5RhZ, no single kinetic isotope effect factor could be calculated. However, it is evident from the CH₄/CD₄ conversion profiles that the conversion of CD₄ is consistently lower than CH₄ conversion and k_{CH₄/CD₄} is >1 at all times. Due to the lower vibrational frequency of CD₄, it is less reactive than CH₄ [52, 53] and the clear (though
(qualitative) isotope effect shows that the rate limiting step involves the dissociation of the C-H (D) bond [52-54]. Au, et al. [53] observed that over Ni/SiO₂ deuterium (CD₄) isotope had no effect on CO₂ conversion and the effect was less prominent of CO formation; thus they proposed that the activation of CO₂ is independent of the activation rate of CH₄ for Ni/SiO₂. However, in the work presented here, a strong deuterium isotope effect is observed in the CO₂ conversion suggesting that the activation of CH₄ and formation of H₂ is essential for the conversion or reduction of CO₂. This dependence of CO₂ reduction on H₂ is in agreement with the transient (section 6.3.3) and CH₄ TPR (section 6.3.4) results reported previously in this paper.

6.3.6. Mechanism and Kinetic Rate Modeling

*Reaction mechanism:* We are not aware of any literature on the mechanism of the DRM reaction over Rh-pyrochlore catalysts. Thus, literature based on catalysts containing Rh, La₂O₃ and ZrO₂ as components have been used here to postulate possible mechanistic steps occurring during DRM and tested by kinetic rate modeling in this study. Richardson, et.al [17], showed that a Langmuir-Hinshelwood redox model fit the data obtained over 0.5% Rh/Al₂O₃ catalyst in the temperature range of 600-700°C at 1 atm. Nakamura, et.al [55], showed that simultaneous occurrence of RWGS is significant and that the H₂O formed by RWGS oxidizes the C(s) formed from dissociative adsorption of CH₄ over Rh/Al₂O₃ catalysts. Dissociation of CO₂ was the rate limiting step in the work by Nakamura [55]. However, Quiroga, et.al [56], showed similar reaction mechanism with dissociative adsorption of CH₄, molecular adsorption of CO₂, but the reaction between the two was direct and without formation of H₂O unlike the model proposed by Nakamura, et.al [55]. The oxidation of the surface carbon with adsorbed CO₂ was the rate limiting step in the model by Quiroga, et.al [56]. Munera, et.al [57] suggested a dual site mechanism over Rh/La₂O₃ where CH₄ dissociates over Rh and CO₂ reacts with La₂O₃ to form
surface carbonates, which then react with the C(s) at the metal-support interface to form CO. Munera, et al [57] proposed dissociation of CH$_4$ to adsorbed C(s) and H$_2$, and oxidation of the C(s) by La-oxycarbonates as the rate limiting step.

The most crucial step in DRM, which is also repeatedly reported to be the rate limiting step, is the activation of CH$_4$ [58, 59]. Mechanistic rate models with dissociation of CH$_4$ as the rate limiting step were observed to fit the kinetic data of Souza, et al [31] Erdohelyi, et al [32], Verykios, et al [36] and Mark, et al [60]. However, Zhang, et al [61], and O’Connor, et al [62], suggest that dissociation of the CO$_2$ and oxidation of the surface carbon are the slow steps in the DRM mechanism. Kinetic study by Wei and Iglesia [63, 64] over Ni/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ catalysts showed that the overall rate of DRM or steam reforming (SR) is first order in CH$_4$, i.e., $r=k \cdot P_{CH_4}$, and is independent of the partial pressure of the co-reactant. However, studies by Munera, et.al [34, 57], Gallego, et.al [65], Verykios, et.al [66], Carrara, et.al [67] suggest fractional order dependence on CO$_2$ for La$_2$O$_3$ based catalysts.

Based on the mechanistic work in the literature, a series of kinetically significant steps, with one of the steps being rate limiting, is postulated here. This mechanistic sequence was then used to derive the mathematical kinetic rate expressions. The assumptions of the kinteically significant steps were based on theoretical kinetic models such as Eley-Rideal, Langmuir-Hinshelwood (single and dual site) mechanisms. Various possibilities of rate limiting steps, including dissociation of the C-H bond in CH$_4$, dissociation of C-O bond in CO$_2$, oxidation of C formed from dissociation of CH$_4$ were assumed. The combinations of the theoretical models, kinetically significant steps and possible rate limiting step resulted in a matrix of eleven kinetic rate models, out of which only two were were statistically valid for the Rh substituted pyrochlores studied in this work.
The fitting parameters obtained from these two models had (a) positive values, (b) 95% confidence intervals that did not include zero, (c) adsorption constants decreasing with increasing temperature, (d) and the rate constants increased with increasing temperature.

The reaction sequence for the two kinetic models that resulted in a statistically valid fit to the kinetic data is:

\[
\begin{align*}
\text{CH}_4 + S_1 & \rightleftharpoons \text{CH}_4S_1 \quad (1) \\
\text{CH}_4S_1 & \rightleftharpoons \text{C-S}_1 + 2\text{H}_2 \quad (2) \\
\text{CO}_2 + S_2 & \rightleftharpoons \text{CO}_2S_2 \quad (3) \\
\text{CO}_2S_2 & \rightleftharpoons \text{CO} + \text{O-S}_2 \quad (4) \\
\text{H}_2 + \text{O-S}_2 & \rightleftharpoons \text{H}_2\text{O} + S_2 \quad (5) \\
\text{C-S}_1 + \text{H}_2\text{O} & \rightleftharpoons \text{CO} + \text{H}_2 + S_1 \quad (6)
\end{align*}
\]

The proposed mechanism is a dual site mechanism, where CH\textsubscript{4} activates on S\textsubscript{1} (Rh site) and CO\textsubscript{2} on S\textsubscript{2} (a surface La-O). Activation of CH\textsubscript{4} results in surface carbon which is then oxidized by carbonates formed from activation of CO\textsubscript{2}. The two rate models were derived using this mechanism sequence, but differed in the rate limiting step assumption. In the first model (designated – Dual site [1]) the irreversible dissociation of CH\textsubscript{4} (eqn (2)) was assumed to be the rate limiting step and in the second one (designated – Dual site [2]) the dissociation of CO\textsubscript{2} (eqn (4)) was assumed to be irreversible and rate limiting. The mechanism that resulted in a statistically valid fit for the kinetic data assumes oxidation of the surface carbon by H\textsubscript{2}O, formed by the reaction of H\textsubscript{2} and adsorbed carbonates. Of the eleven models tested, only two resulted in statistically valid fits meeting criteria (a-d) above. Comparison of these two reaction models to the results presented in the previous sections can be used to determine the most likely mechanism.
Kinetic rate modeling: The two models giving a valid statistical fit had the same mechanistic sequence but differed in the assumed rate limiting step i.e., either dissociation of CO\(_2\) or dissociation of CH\(_4\). The kinetics isotope effect results [section 6.3.5 above] clearly showed a strong deuterium isotope effect when CH\(_4\) was replaced with CD\(_4\). Presence of alkaline and alkaline earth metals like La, Mg, Ce, Ca, Sr adds to the basicity of the catalysts which helps in activation of mildly acidic CO\(_2\) and accelerates the rate of carbonate formation, consistent with the literature [33, 35, 38, 49, 68]. The presence of La-O on the L2RhZ and L5RhZ surface increases the rate of CO\(_2\) activation to form carbonates. These results suggest that the rate limiting step is the activation of CH\(_4\) or, in other words, dissociation of the C-H bond in CH\(_4\).

Oxidation of the carbon formed from CH\(_4\) activation is an important step. From the transient experiments [Section 6.3.3] and CH\(_4\) TPR [Section 6.3.4], it was observed that the surface carbon is oxidized by the carbonates via H\(_2\)O formation. This is the step assumed in the postulated mechanism. Thus the most probable DRM mechanism over L2RhZ and L5RhZ would be the Dual site [1] mechanism i.e., steps (1-6) and step (2) as an irreversible rate limiting step.

The rate expression derived for the proposed mechanistic sequence is given in eqn (7). Using this expression and the kinetic data, the adsorption and rate constants giving the best statistical fit were determined.

\[
  r_{CH_4} = \frac{k_2K_1P_{CH_4}}{(1 + K_1P_{CH_4} + \frac{P_{CO}P_{H_2}}{K_6P_{H_2O}})} \\
  P_{H_2O} = \frac{K_3K_4K_5P_{H_2}P_{CO_2}}{P_{CO}} \tag{7}
\]

The statistical fitting parameters \(K_1, k_2, K_3-K_6\) determined by fitting the kinetic data for L2RhZ and L5RhZ to the above rate expression are shown in Table 6.4. The parameter were estimated by using the function minimization Marquardt’s algorithm [56]. Here, \(K_1\) and \(K_3\) are
adsorption constants for the adsorption of CH₄ and CO₂ respectively. The rate constant for the rate limiting dissociation of CH₄ is given by k₂, other constants K₄-K₆ are equilibrium constants for the steps 4-6. Note that for large values of K₆ (reaction of steam with surface carbon) and small values of K₁ (adsorption of CH₄, step 1), the rate becomes first order in methane, as observed on other catalysts reported in the literature [10, 11, 63, 64].

Table 6.4. Summary of the statistical fitting parameters for L2RhZ and L5RhZ obtained by fitting the kinetic data to the derived rate expression. (Values ± 95% confidence interval)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>L2RhZ</th>
<th>L5RhZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₁ (atm⁻¹) x 10⁻²</td>
<td>11.6 ± 1.8</td>
<td>10.3 ± 1.4</td>
</tr>
<tr>
<td>k₂ (mol s⁻¹ g⁻¹) x 10⁻⁴</td>
<td>6.7 ± 3.1</td>
<td>16.1 ± 4.9</td>
</tr>
<tr>
<td>K₃ (atm⁻¹) x 10⁻³</td>
<td>857 ± 2.4</td>
<td>808 ± 15.9</td>
</tr>
<tr>
<td>K₄ (atm) x 10⁻³</td>
<td>762 ± 2.1</td>
<td>718 ± 14.1</td>
</tr>
<tr>
<td>K₅ x 10⁻³</td>
<td>666 ± 1.89</td>
<td>628 ± 12.4</td>
</tr>
<tr>
<td>K₆ (atm) x 10⁻³</td>
<td>571 ± 1.6</td>
<td>538 ± 10.6</td>
</tr>
</tbody>
</table>

The parity plots [Figure 6.7] for L2RhZ and L5RhZ show reasonable agreement of the predicted reaction rate of CH₄ consumption and the experimental reaction rate, over both L2RhZ compared to L5RhZ based on the adjusted R² values. It can be concluded that a Langmuir-Hinshelwood dual site mechanism with dissociative adsorption of CH₄ as the rate-limiting step is consistent with the kinetic measurements, and also with the results of the transient and pulsing results. Further, methane activation appears to take place on the Rh sites while CO₂ activation takes place on the surface La-O sites. Differences in the rates of the DRM reaction on the two catalysts are due to differences in the nature of the surface Rh sites. Specifically, the L5RhZ contains surface Rh sites that activate CH₄ via a lower energy transition state (Eapp = 21.8 kcal/mol) than L2RhZ (Eapp = 34.2 kcal/mol).
Figure 6.7. Statistical fit of the postulated kinetic model showing the comparison of the rate predicted by the model to the experimental rate for (a) L2RhZ, and (b) L5RhZ.
6.4. Conclusion

The dry reforming of methane (DRM) on two lanthanum zirconate pyrochlores containing different levels of rhodium substitution shows significantly different kinetic behavior. The different levels of rhodium (2% and 5%) produced catalytically different materials, likely due to different degrees of substitution of Rh in the lattice and different concentrations and types of rhodium on the surface, as measured by CH$_4$-TPR and kinetic measurements. Increasing the Rh content facilitates CH$_4$ activation by decreasing the apparent activation energy for CH$_4$, clearly suggesting a difference in the nature of surface rhodium sites on the two catalysts. Increasing the Rh content also increases the oxygen reactivity, as measured by CH$_4$-TPR, and thus the reducibility of the pyrochlore.

The primary site for activation and dissociation of CH$_4$ molecule is the Rh surface site, as shown by isotope studies in which there is a direct correlation between the CH$_4$ (CD$_4$) conversion and the Rh content of the catalyst. A strong deuterium kinetic isotope effect was apparent on the CH$_4$ and CO$_2$ conversion suggesting that dissociation of C-H (D) bond is the rate limiting step in DRM process over both pyrochlores. A correspondingly strong deuterium isotope effect on CO$_2$ conversion indicates that the activation of CH$_4$ (or the products formed from CH$_4$ activation) is essential for conversion of CO$_2$. This mechanistic step is elucidated by transient experiments where H$_2$ from CH$_4$ reacts with the carbonates formed from CO$_2$, reducing them to CO, resulting in simultaneous formation of H$_2$ and CO. Absence of H$_2$ would cause a decrease in the CO$_2$ conversion, as observed in the isotope effect results. The delayed response in H$_2$ and CO relative to Ar suggests (a) a slower rate of formation of CO and H$_2$, and (b) simultaneous formation of H$_2$ and CO.
The activation of CH$_4$ over the pyrochlores reported here is by direct dissociation mechanism to form C(s) and H$_2$ as shown by the absence of any CH$_x$ species during the CO$_2$ pulse of the transient experiments. Activation of CO$_2$ presumably takes place on the La site and CH$_4$ on the Rh site; this suggests that the oxidation of C(s) could be occurring at the Rh-La interface. The higher surface Rh concentration on L5RhZ compared to L2RhZ (as shown by CH$_4$-TPR), would produce a greater number of Rh-La interfacial sites at which surface carbon would be oxidized. This is in agreement with the carbon balance obtained during the transient pulse experiments. The kinetic data are consistent with a Langmuir-Hinshelwood dual site mechanism over both L2RhZ and L5RhZ pyrochlores. This is the first time in the literature that the kinetics of DRM has been reported on pyrochlore catalysts.

6.5. References


Chapter 7: Dry Reforming of Methane over Rh Substituted La$_2$Zr$_2$O$_7$ Pyrochlores. II) Study of Catalytic Active Sites for CO$_2$ Activation and Intermediate Mechanistic Steps.

7.1. Introduction

Dry reforming of methane (DRM) has received considerable attention in recent years due to its ability to utilize two most abundant green-house gases (CH$_4$ and CO$_2$) and produce industrially important synthesis gas (CO and H$_2$) mixture [1, 2]. This syngas can be used for production of both liquid hydrocarbons by Fischer-Tropsch and higher value oxygenates [3]. In the past decade other methane reforming processes like steam reforming of methane (SRM), partial oxidation of methane (POM), autothermal reforming of methane (ARM) have been investigated. These processes differ in the final H$_2$/CO product ratio and energetics. From among these reforming processes, DRM is shown to have lower operating cost under some conditions [4]. However, DRM has certain disadvantages like its high endothermicity, requiring high reaction temperatures (~900°C) to attain equilibrium conversions, and deactivation by carbon deposition and sintering [5]. Thus there is a need to develop catalysts that will resist deactivation due to sintering at temperatures as high as 900°C and decrease carbon formation during DRM [6].

A balance between formation and oxidation of surface carbon is necessary for DRM catalyst stability. There are several ways to increase deactivation resistance, such as increasing and maintaining the dispersion of the active metal on the support in order to decrease the ensemble size necessary for carbon deposition coking [2, 3, 7]. Another way to improve the oxidation rate of surface carbon is to increase the concentration of an oxidizing agent like CO$_2$ on the catalyst surface [8]. Since CO$_2$ is mildly acidic in nature, increasing the basicity of the catalyst will increase the activation of CO$_2$ and decrease carbon formation [9, 10]. Increasing the surface basicity of the catalyst has helped in increasing the CO production over Rh/La$_2$O$_3$ compared to
Rh/SiO$_2$ [11]. Addition of basic promoters like La$_2$O$_3$, CeO$_2$ and alkaline earth metal oxides like MgO, CaO, BaO help in activation of CO$_2$ and thus increase the availability of reactive oxygen for oxidation of surface carbon [5, 12-16]. Basic promoters also increase the dispersion of the active metal, reducing surface carbon formation [10].

A catalyst with inherent basicity that is also stable at the demanding conditions of DRM, and which also has sites for CH$_4$ activation is required. One such material is the lanthanum zirconate pyrochlore, a class of ternary metal oxides of general formula A$_2$B$_2$O$_7$ with the A-site occupied by a trivalent basic rare earth metal like La and the B-site occupied by tetravalent transition metal like Zr. Pyrochlores are extremely structurally stable at the required high DRM temperatures. They also resist carbon deposition due to their inherent lattice oxygen conductivity [17-22]. Here, we report results of DRM on three catalysts; lanthanum zirconate pyrochlore [La$_2$Zr$_2$O$_7$, designated LZ], and two LZ catalysts in which Rh is substituted at the B-site at two levels, 2 wt% [L2RhZ] and 5wt% [L5RhZ]. A detailed study of characterization, DRM activity and CH$_4$ activation steps have been reported in our previous work [22]. This work has shown that the presence of La on the surface of the pyrochlores enhances its ability to activate CO$_2$ to form La-oxycarbonates which can further be differentiated into separate surface structures, depending on their structural orientation. The catalytic performance of different phases of oxycarbonates formed on pyrochlores are studied by means of in-situ FTIR and in-situ XPS in order to understand the role of carbonates in DRM on L2RhZ and L5RhZ pyrochlores. The reactivity of the different forms of carbonates is determined by transient pulsing of CH$_4$ over the pre-adsorbed carbonates and following the changes in their IR spectra, which shows clear differences in active versus spectator oxycarbonates.
7.2. Experimental Section

7.2.1. *In-situ* FTIR and Transient Pulsing

The details of the catalyst synthesis, characterization and activity study has been reported earlier in our previous study of these materials [22]. In this work the *in-situ* Fourier Transform Infra-Red (FTIR) spectra were collected with a Thermo Electron Nexus 670 spectrometer using a liquid N₂ cooled MCT detector and a Diffuse Reflectance Infra-red Fourier Transform Spectroscopy (DRIFTS) cell from Pike Technologies. KBr beamsplitter was used to obtain spectra in the wavenumber range of 4000-500 cm⁻¹. Prior to the collection of the spectra, the catalysts (LZ, L₂RhZ, and L₅RhZ) were reduced in flowing 4% H₂/He (20mL/min) by ramping the temperature from 25°C to 550°C and maintaining isothermal conditions at 550°C for 30 min. The reduced catalysts were then flushed in He for 15 min to remove the gas phase H₂ and prepare the surface of the catalyst for background collection. The DRIFTS cell was connected to an 8-port valve which allowed rapid switching between gases without interrupting the continuous He carrier gas flow and thus avoiding any pressure drop across the cell. The valve was fitted with a loop of 0.5 cm³, allowing injection of known concentration of reactant gas pulse in the continuous He flow. After background collection at 550°C, the catalysts were treated in flowing 10% CO₂/He (20 mL/min) mixture for 15 minutes and then flushed in He for 15 min. This resulted in adsorption of CO₂ and formation of carbonate on the catalysts and the gas phase CO₂ was later removed by He flushing.

These carbonates were then reacted with 10% CH₄/He which was pulsed by using the 0.5 cm³ loop fitted with the 8-port valve attached to the DRIFTS cell. A total of 10 pulses of 10% CH₄/He separated by a time gap of 10 min were injected in the continuous He flow over the CO₂ treated catalysts. After 10 pulses, the catalysts were again treated in flowing 10% CO₂/He
(20mL/min) for 15 min and was followed by He flush for 15 min. Series spectra was collected throughout the pre-adsorption of CO₂, 10 pulses of CH₄, and re-adsorption of CO₂ with resolution of 4 cm⁻¹.

The DRIFTS cell was connected to an on-line mass spectrometer where the product stream from the pulses could be analyzed continuously. The masses analyzed were; H₂ (1), CH₄ (15), H₂O (18), CO (28), Ar (40), and CO₂ (44). The NIST web-book suggests that CO₂ has a ~10% (of mass 44) intensity at mass 28. This information was used to correct the concentration of CO formed during all the experiments described in this work.

7.2.2. In-situ X-Ray Photoelectron Spectroscopy (XPS)

The elemental electronic states of the catalyst surface were investigated using in situ XPS under different gas exposures and temperature. The measurements were carried out on a Physical Electronics (PHI) spectrometer model 590. The photoelectron kinetic energy was measured by OmniFocus III spherical capacitance analyzer (SCA). Magnesium anode was used as the source of X-ray radiation (MgKα : 1253.6 eV). The pressure in the analysis chamber was maintained between 10⁻⁸ to 10⁻⁹ Torr during measurements. The binding energies were corrected utilizing the reference binding energy (BE) of adventitious carbon C₁s at 284.8 eV. The spectra from the regions related to Zr₃d, La₃d, and Rh₃d core levels were recorded and analyzed. The XPS analysis chamber is attached to a reaction chamber through a gate valve. The sample was mounted on a heat-controlled arm that can go up to 600°C and can move between these chambers.

The treatment given to the catalysts in the XPS chamber was designed so as to replicate the in-situ FTIR experimental treatment. The freshly calcined catalysts were first loaded in the sample chamber and were placed in position using a double sided tape. XPS spectra of the freshly
calcined catalyst was collected at 10^9 torr and at room temperature. The catalyst was then heated to 550°C under vacuum and was dosed with 1.4x10^5 Langmuir (i.e., 5x10^-5 torr for 2715 sec and 1L =10^-6 torr*1 sec) of H_2. The chamber was then vacuumed so as to remove the H_2. The catalyst was then dosed with 5.9x10^4 Langmuir of CO_2 maintaining the temperature at 550°C. The chamber was then vacuumed and XPS spectra this catalyst surface treated in CO_2 were collected. The catalyst was not exposed to atmospheric air at any point of time during the in-situ XPS experiment. The spectra of the CO_2 treated catalyst was then compared to that of the fresh catalyst so as to study the change in the oxidation state of the surface metals as a result of CO_2 treatment. These results were then correlated with the in-situ FTIR results to study the active site for activation of CO_2 on these pyrochlore catalyst. The obtained XPS peaks were deconvoluted by subtracting Shirley background and performing peak fitting with a symmetric Gauss-Lorentz sum function.

7.3. Results and Discussion

7.3.1. Theory of La-oxycarbonates (La_2O_2CO_3)

Lanthanum oxycarbonates are polymeric complexes built up of slabs forming layer-type structures [23] of La_2O_2^{2+} and CO_3^{2-} ions formed from the chemisorption of mildly acidic CO_2 by basic La_2O_3 sites; La_2O_3 + CO_2 → La_2O_2CO_3 [24]. Depending on the positioning of the La_2O_2^{2+} ions in the complex, three different crystalline polymorphs type I, Ia and II are defined [Figure 7.1] [25]. Characterization of these structures shows that there are no weight changes during type-I → type-Ia → type-II transformations, confirming their polymorphic nature [23].
Figure 7.1. Representation of the orientation of carbonate (CO$_3^{2-}$) ions in (a) type I, (b) type Ia, and (c) type II phases of La-oxide. The corners are represent La atoms and the O associated with La is not shown. Adapted from [23].

Type-I form of La-oxycarbonates are square layers [Figure 7.1] of (La$_2$O$_2^{2+}$)$_n$ separated by CO$_3^{2-}$ ions and arrangement of the (La$_2$O$_2^{2+}$)$_n$ layers result in a tetragonal crystalline form and type-Ia form is the monoclinic distortion of type-I [26]. Type-II carbonate are hexagonal unit cell crystallites found in A-form sesquioxides with more than one local coordination of La [23, 26].

Formation of these three polymorphs is a function of the carbonation temperature, presence of H$_2$O as an impurity, and the heating/cooling rate [27]. A detailed study of formation of carbonates as a function of different pre-treatments is reported by Irusta, et al [25]. These are the types of La-
oxycarbonates that have been reported to be formed on La$_2$O$_3$ supports. Thus, it is important to acknowledge the possibility of minor differences in the La-oxycarbonates formed on lanthanum zirconate pyrochlores.

7.3.2. **In-situ FTIR and Transient Pulsing**

7.3.2.1. Adsorbed La-oxycarbonates

*In-situ* FTIR studies carried out on CO$_2$ treated LZ, L2RhZ, and L5RhZ [Figure 7.2] show strong CO$_2$ chemisorption bands in the range 1000-1600 cm$^{-1}$ corresponding to the formation of La-oxycarbonates [8]. Spectra in Figure 7.2 are obtained after 15 min of CO$_2$ flow followed by 15 min of He flush to purge all the gas phase CO$_2$, leaving only the strongly adsorbed species on the surface. For determining the likelihood of adsorption of CO$_2$ on La$_2$O$_3$ and ZrO$_2$, La$_2$O$_3$ and ZrO$_2$ standards were used and the FTIR spectra for CO$_2$ adsorption was studied on these oxides. No adsorbed CO$_2$/carbonate species were observed on ZrO$_2$, but strong adsorption bands were observed for La$_2$O$_3$, suggesting that La-O is the active site for activation of CO$_2$ on the lanthanum zirconate pyrochlores. However, it is important to acknowledge that there could be a difference in the surface sites over La$_2$O$_3$ and that over LZ, L2RhZ, and L5RhZ pyrochlores. Although ZrO$_2$ did not show any activation of CO$_2$, the presence of Zr in the pyrochlore structure could contribute to the formation of carbonates due to the difference in the structure of oxides like La$_2$O$_3$ or ZrO$_2$ and the pyrochlores.

The carbonate bands (1100-1600 cm$^{-1}$) for all three catalysts show a two-fold splitting, suggesting more than one polymorph of carbonate [28-30]. Carbonate (CO$_3^{2-}$) is a non-linear molecule and thus it should have 3n-6 (i.e., 6) modes of vibration, however, due to the degeneracy of the modes and overlap with absorption bands of other surface species, not all modes of carbonate vibrations are apparent in the spectra [26]. For LZ [Figure 7.2 (a)], peaks at 1066 and
1349 cm$^{-1}$ correspond to the presence of type-Ia polymorph of La-oxycarbonate [23, 25, 27]. The band at 1066 cm$^{-1}$ corresponds to the symmetrical stretching mode of vibration, this mode is infrared inactive for the free ion but is active for crystalline complexes [23]. The distinct appearance of 1066 cm$^{-1}$ bands suggests that the carbonate is a part of the crystalline monoclinic tetragonal type-Ia structure and is closely associated with the La ion. The peak at 1511 cm$^{-1}$ correspond to the $v_3$ vibration of CO$_3^{2-}$ associated with the type-II form of oxycarbonate [28]. Taylor, et al [27] reported the presence of type-Ia at 1363 cm$^{-1}$ and type-II form of oxycarbonate at 1499 cm$^{-1}$ for La$_2$O$_3$. The shift in the peaks could be assigned to the difference in the surface sites on LZ compared to that on La$_2$O$_3$. Taylor et al. [27], also report the presence of bands in the range of 500-1000 cm$^{-1}$ for La$_2$O$_3$ supports, however, these bands are infrared inactive (no change in the dipole moment of the molecule) for the pyrochlores reported here. This suggests a difference in the coordination or bonding of the La ions on LZ (and other reported pyrochlores) as compared to that over La$_2$O$_3$. A shoulder at 1573 cm$^{-1}$ could be assigned to presence of formates which is confirmed by the presence of C-H stretching bands at 2834 cm$^{-1}$ [31-34]. A small peak at 2163 cm$^{-1}$ is due to the presence of weakly adsorbed CO which is ionic in nature as the band is at a higher wavenumber as reported in the literature [31, 35-37]. There are negative bands at 3631 and 3652 cm$^{-1}$ which correspond to stretching frequencies of the hydroxyl (O-H) species [23, 25, 31, 34, 38]. The negative absorbance peaks suggest that there were chemisorbed hydroxyl species present on LZ after reduction with H$_2$ and were accounted for in the background spectra. However, after reaction with CO$_2$ these hydroxyls are consumed to form formate species, a negative peak for these wavenumbers [31]. The ionic CO observed at 2163 cm$^{-1}$ could be a part of the formate species due to the reduction of CO$_2$ by the surface hydroxyls [31, 35].
Figure 7.2. FTIR spectra after 15 min of CO₂/He flow → 15 min of He flush over reduced (a) LZ, (b) L2RhZ, (c) L5RhZ.
The FTIR spectra for L2RhZ [Figure 7.2 (b)] shows type-Ia oxycarbonate peaks at 1068 cm\(^{-1}\) and 1367 cm\(^{-1}\) [32]. Presence of Rh in the structure, changes the electronic structure of the type-Ia oxycarbonates and adds an ionic character, causing it to shift to a higher wavenumber compared to LZ. Type-II oxycarbonate appears on L2RhZ at wavenumber 1509 cm\(^{-1}\) which corresponds to that formed over LZ at 1511 cm\(^{-1}\). Small shoulder at 1745 cm\(^{-1}\) corresponds to the carbonyl group (\(\text{C}=\text{O}\)) of the bidentate carbonate species [8, 31]. There are no C-H stretching or hydroxyls bands observed over L2RhZ, unlike LZ. This is because presence of Rh on the surface inhibits the hydration of the catalyst as reported by Irusta, et al [25], over Rh/La\(_2\)O\(_3\). The carbonate species observed over L5RhZ [Figure 7.2 (c)] are very similar to that observed over L2RhZ with type-Ia at 1072 and 1373, type-II at 1498 cm\(^{-1}\). Heating of type-I oxycarbonate in air above 500°C results in monoclinic distortion of type-I to form type-Ia [23, 28]. Since the experimental conditions reported in this work are at 550°C, there is presence of only two
polymorphs of oxycarbonates (type-Ia and II) and no type-I is observed. There is a clear
difference between the wavenumbers of the carbonates on the non-substituted LZ and the Rh
substituted pyrochlores. This could be due to the fact that the electronegativity of Rh (2.28) is
greater than that of La (1.1) and Zr (1.33), which has an effect on the coordination of the electron
rich carbonates species with the lattice.

7.3.2.2. Reactive La-oxycarbonates

From among the different types of oxycarbonates present on the surface of these
pyrochlores discussed above, it is important to distinguish the reactive oxycarbonate species from
the spectator ones in order to understand the mechanistic role of oxycarbonates in DRM. The
FTIR spectra for freshly adsorbed oxycarbonates are compared to FTIR spectra after 10 pulses of
CH$_4$/He. This would help identify the change in the surface species as a result of CH$_4$/He pulses.
Following the 10 pulses of CH$_4$/He, the catalysts were again treated in flowing CO$_2$ to study its
readsoorption and study the changes, if any, in the oxycarbonate re-formation. The comparison of
spectra for freshly adsorbed oxycarbonates [discussed in section 7.3.2.1], oxycarbonates after 10
CH$_4$/He pulses and readsoorption of oxycarbonates are shown in Figure 7.3 (a), (b), and (c) for LZ,
L2RhZ, and L5RhZ, respectively. For LZ [Figure 7.3 (a)], there is no apparent change in the
spectra after 10$^{th}$ CH$_4$ pulse compared to the adsorbed CO$_2$ spectra. Due to the absence of Rh in
LZ, no CH$_4$ could react with the carbonates, as discussed in section 7.3.2.3. The spectra for re-
adsorbed CO$_2$ (after 10$^{th}$ CH$_4$ pulse) is identical to that of CO$_2$ adsorbed before the catalyst was
pulsed with CH$_4$ suggesting the inactivity of LZ towards DRM, conforming results previously
reported [22].
Mass spectrometer analysis of the effluent gas showed that there was consumption of CH$_4$ observed during CH$_4$/He pulsing over adsorbed oxycarbonates for L2RhZ and L5RhZ which will be discussed later in section 7.3.2.3. Substitution of Rh on the B-site of the pyrochlore results in the formation of active sites that are not present in LZ. After pulsing CH$_4$ over the adsorbed oxycarbonates over L2RhZ and L5RhZ there were significant changes in spectra and a clear distinction between the spectator and reactive species was achieved.

For L2RhZ [Figure 7.3 (b)], peaks at 1068, 1367, and 1745 cm$^{-1}$ are spectator species which do not change in wavenumber or absorbance as a result of CH$_4$ pulse and upon readsorption of CO$_2$. However, the 1509 cm$^{-1}$ peak corresponding to adsorbed CO$_2$, decreases significantly after the 10$^{th}$ CH$_4$ pulse. This peak reappears in identical form upon readsorption of CO$_2$, suggesting that the oxycarbonates identical to the freshly adsorbed carbonates are re-formed.

![Figure 7.3. FTIR spectra comparing the changes in the carbonates as a result of CH$_4$ pulses over (a) LZ, (b) L2RhZ, and (c) L5RhZ.](image)
(Figure 7.3 continued)

(b) Absorbance (a.u.)

- readsorbing CO$_2$
- after 10$^{th}$ CH$_4$ pulse
- adsorbed CO$_2$

Wavenumber (cm$^{-1}$)

(c) Absorbance (a.u.)

- readsorbing CO$_2$
- after 10$^{th}$ CH$_4$ pulse
- adsorbed CO$_2$

Wavenumber (cm$^{-1}$)

Key:
- 1509
- 1367
- 1068
- 1498
- 1373
- 1745
- 1866
- 1072
- 1749
Table 7.1 shows that the ratio of the absorbance of oxycarbonate peaks at 1367:1509 cm$^{-1}$ over L2RhZ and the closely related 1373:1498 cm$^{-1}$ peaks L5RhZ are essentially the same, indicating that the same oxycarbonate species is reacting with CH$_4$ on both catalysts. For L5RhZ [Figure 7.3 (c)], species corresponding to 1072, 1373, 1749 cm$^{-1}$ are the spectator species and 1498 cm$^{-1}$ species is dynamic [Table 7.1].

Table 7.1. Summary of the change in the ratio of the absorbance of type-Ia peak to that of type-II peak as a result of CH$_4$ pulses and CO$_2$ readsorption for L2RhZ and L5RhZ.

<table>
<thead>
<tr>
<th>Catalyst/Treatment</th>
<th>Adsorbed CO$_2$</th>
<th>After 10$^{th}$ CH$_4$ pulse</th>
<th>Readsorbing CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L2RhZ</td>
<td>Ratio of peak 1367:1509</td>
<td>1.26</td>
<td>8.71</td>
</tr>
<tr>
<td>L5RhZ</td>
<td>Ratio of peak 1373:1498</td>
<td>1.3</td>
<td>8.05</td>
</tr>
</tbody>
</table>

There is a significant change in the peak absorbance observed over both L2RhZ and L5RhZ after CH$_4$ pulses. The ratio of type-Ia to type-II for L2RhZ increase from 1.26 to 8.71 and for L5RhZ from 1.3 to 8.05, suggesting a significant decrease in the population of type-II oxycarbonates. This absorbance is regained after readsorption of CO$_2$ where the ratio increases from 8.71 to 1.04 for L2RhZ and from 8.05 to 1.06 for L5RhZ [Table 7.1], suggesting reformation of the type-II oxycarbonates on both catalysts. The reactive oxycarbonates at 1509 cm$^{-1}$ for L2RhZ and 1498 cm$^{-1}$ for L5RhZ are attributed to type-II oxycarbonates. These type-II oxycarbonates were also formed over LZ at 1511 cm$^{-1}$ but were spectator species in that case. This confirms that the presence of Rh increases the reactivity of the type-II species.

It can be postulated that the type-II oxycarbonates are formed irrespective of the presence of Rh but only those at the Rh-La interface are reactive with CH$_4$. Since the type-II oxycarbonates (1509 cm$^{-1}$ for L2RhZ and 1498 cm$^{-1}$ for L5RhZ) change only in absorbance and not in wavenumber after pulses, these type of sites are decreasing in number over the surface but are
structurally the same throughout the CH₄ pulsing sequence. This is also in agreement with the fact that the ratios of these peaks in Table 7.1 are the same before and after CH₄ pulse. Type-I or Ia oxycarbonates, even if present on the Rh-La interface are inactive towards DRM. There is a small peak at 1866 cm⁻¹ for L2RhZ and L5RhZ, this is attributed to bridge adsorbed CO [39-42] which can be formed from the oxidation of carbon produced by activation of pulsed CH₄ or from reduction of the oxycarbonates [32-34, 43]. There were no C-H stretching bands observed at about 2800 cm⁻¹ for L2RhZ and L5RhZ, suggesting that there was dissociative adsorption of CH₄ and no CHₓ species existed on the surface long enough to be detected by FTIR. This agrees with work previously reported in the literature [44, 45] and our study on CH₄ activation over L2RhZ and L5RhZ [Chapter 6].

7.3.2.3. Product Formation During Transient Pulsing

Treating the catalysts in flowing CO₂/He led to the formation of strongly adsorbed carbonates which were studied by FTIR in section 7.3.2.1. These carbonates were then reacted with transient pulses of 10% CH₄/He. The MS signals of the H₂ and CO produced by the reaction of CH₄ and adsorbed carbonates showed changes as a function of CH₄ pulse number [Figure 7.4 (a) and (b)]. As expected, the consumption of CH₄ is greatest during the first pulse for both the pyrochlores and decreases in subsequent pulses. The pulses were quantified and the moles of unreacted CH₄ were used to compute the conversion of CH₄ during each pulse. The quantified moles of H₂ and CO formed as a function of pulse number are shown in Figure 7.5 (a) and (b), and % CH₄ converted as a function of pulse number is shown in Figure 7.5 (c).

The CH₄ conversion decreases linearly with pulse number for both L2RhZ and L5RhZ. This drop in the CH₄ conversion corresponds directly with a similar linear decrease in the moles of H₂ and CO formed from pulse 1 to pulse 10, with L5RhZ producing more H₂ and CO than
L2RhZ. XPS results reported earlier [22] show a greater surface concentration of Rh on L5RhZ compared to L2RhZ. This means there are more Rh-La interfacial sites over L5RhZ than L2RhZ. Since Rh is the active site for CH$_4$ activation and Rh-La interface is the active site for oxidation of surface carbon [section 7.3.2.2], the greater rate of consumption of CH$_4$ (and formation of H$_2$ and CO) is likely due to greater number of available Rh-La sites on L5RhZ. The H$_2$ formed during these pulses originates exclusively from CH$_4$. However, the CO could be formed either from the oxidation of the carbon (formed from CH$_4$ activation) or from the reduction of the oxycarbonates, or both.

![Figure 7.4. MS signal showing the changes in the product composition as a function of CH$_4$ pulse number over carbonates adsorbed on (a) L2RhZ, and (b) L5RhZ. [The horizontal line denotes the height of the highest peak of the respective product.]](image)
With increasing pulse number, there is a decrease in the concentration of the reactive oxycarbonates at the interface resulting in carbon build-up on the catalyst. Thus a decrease in the CH$_4$ conversion with pulse number [Figure 7.5] could be attributed to both the exhaustion of the oxidizing carbonates around the Rh-La interface, and blocking of the active sites due to carbon build-up on Rh.
Figure 7.5. Quantification of pulses showing (a) moles of H$_2$ formed, (b) moles of CO formed, and (c) % CH$_4$ conversion as a function of CH$_4$ pulse number. These pulse number corresponds to the scheme shown in Figure 7.4.
The formation of CO [Figure 7.5 (b)] shows an initial rise from pulse 1-2 and a linear decrease thereafter from pulse 2-10. The amount of CO formed during the CH₄ pulses is a function of the concentration of carbon (from CH₄ activation) and carbonates (from CO₂ activation) on the catalyst. The observed effect on CO formation is the net result of two processes—the formation of carbon from CH₄ activation and the oxidation of this carbon by oxycarbonates from CO₂ activation. During the first CH₄ pulse, the carbon formed from activation of CH₄ appears to be rapidly oxidized, but with some small amount carbon left on the surface. During the second pulse additional carbon is formed from CH₄, which is also oxidized along with carbon from the first pulse by a sufficient population of adjacent oxycarbonates, resulting in an
observed increase in CO formation. However, in the subsequent pulses, carbon is formed on the catalyst and the oxycarbonates are being exhausted. Both these factors could be limiting the formation of CO and activation of CH\textsubscript{4}, hence decreasing its conversion with increasing pulse number.

7.3.3. *In-situ* X-ray Photoelectron Spectroscopy (XPS)

*In-situ* XPS was performed to be able to compare the sites for activation of CO\textsubscript{2} with the FTIR results. The catalyst pretreatment in the *in-situ* chamber was designed to closely match the FTIR experiment. Since the IR spectra for L2RhZ and L5RhZ were observed to be similar for CO\textsubscript{2} activation, the *in-situ* XPS results only for L5RhZ are reported here. Detection of Rh on the surface of L2RhZ is very difficult resulting in an extremely low signal to noise ratio making peak fitting potentially inconclusive. Deconvolution and peak fitting is more definitive on L5RhZ due to greater surface concentration of Rh compared to L2RhZ [22], and hence only L5RhZ results are presented here.

In Figure 7.6 the XPS spectra for La 3d, Zr 3d, and Rh 3d regions of fresh L5RhZ catalyst is compared to that of L5RhZ treated in CO\textsubscript{2} *in-situ*. The La 3d core line [Figure 7.6] of “fresh” L5RhZ shows La 3d\textsubscript{5/2} at 834.1 eV and La 3d\textsubscript{3/2} at 851 eV, these correspond to the presence of trivalent La (La\textsuperscript{3+}) on the fresh L5RhZ surface [46-48]. The spin-orbit splitting of the 3d\textsubscript{5/2} and 3d\textsubscript{3/2} orbitals was found to be about 16.9 eV which is agreement with the literature [47-49]. The 3d core line peaks are accompanied by satellite peaks 3d’\textsubscript{5/2} at 837.9 eV and 3d’\textsubscript{3/2} at 855 eV that are in close proximity to the main 3d\textsubscript{5/2} and 3d\textsubscript{3/2} peaks [48, 50, 51] which confirm the presence of the La\textsuperscript{3+} state. These satellite peaks are formed due to the transfer of electron from oxygen from the La\textsubscript{2}O\textsubscript{3} type species to the initially empty 4f orbital of La [47, 49]. The “reacted with CO\textsubscript{2}” La 3d spectra show an increase in the binding energy as compared to the “fresh” spectra. This
increase in the binding energy is due to the in-situ CO\textsubscript{2} treatment of L5RhZ. As reported in the FTIR results [section 7.3.2.1] that activation of CO\textsubscript{2} results in the formation of La-oxycarbonates (La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3}) due to the basic nature of the La-O sites. Due to the presence of the highly electronegative carbonate (CO\textsubscript{3}\textsuperscript{2-}) ions in close proximity to the La\textsuperscript{3+} ions, there appears to be a shift in the La 3d binding energy to a higher value compared to the fresh spectra. This shift is observed in both, 3d\textsubscript{5/2} and 3d\textsubscript{3/2} (main peaks as well as satellite peaks) while maintaining the spin-orbit splitting value of 16.9 eV, suggesting that the shift in the binding energy is legitimate and is due to the change in the electronic orientation around the La ions due to the presence of carbonate ions.

The Zr 3d level spectrum of the fresh L5RhZ was also compared to the CO\textsubscript{2} treated spectrum [Figure 7.6 (b)] to study the changes in the Zr oxidation state as a result of carbonate formation. The Zr 3d\textsubscript{5/2} and 3d\textsubscript{3/2} for the fresh L5RhZ appear at 181.6 and 183.9 eV which is a representation of the presence of the tetravalent Zr (Zr\textsuperscript{4+}) on the L5RhZ surface [52-54]. The spin-orbit splitting between 3d\textsubscript{5/2} and 3d\textsubscript{3/2} is about 2.3 eV which is in agreement with the reported literature [55-57]. When the fresh Zr 3d spectra is compared to the one reacted with CO\textsubscript{2}, there is a clear shift observed in the binding energies, suggesting that the even though the active site for CO\textsubscript{2} activation is La-O, the presence of carbonates has its effect on the electronic orientation of Zr site which is co-ordinated with La in the pyrochlore structure. The binding energies for La 3d and Zr 3d may differ by ±0.3eV from the ones reported in the literature, this could be due to the changes in the electronic structure of La and Zr that must have taken place after their substitution into the pyrochlore structure and also due to partial substitution of Rh on the Zr site. However, the shifts in the binding energies during the experiment are due to the reaction with CO\textsubscript{2}. 

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Figure 7.6. *In-situ* XPS spectra comparing the (a) La 3d, (b) Zr 3d, and (c) Rh 3d region of the freshly calcined L5RhZ with the ones reacted with CO$_2$ *in-situ*. 
The Rh 3d core level spectra for the fresh and CO$_2$ reacted L5RhZ is compared in Figure 7.6 (c). The XPS signal for Rh 3d for both fresh and reacted in CO$_2$ is very noisy with a very low signal to noise ratio. This is due to the fact that the majority of the Rh is substituted in the bulk of the pyrochlore catalyst and with few Rh sites on the surface [18, 21, 22]. To attain information from the Rh 3d spectra, the spectra was mathematically smoothed to perform peak fitting. The fresh catalyst shows the presence of 3d$_{5/2}$ at 309.5 eV and 3d$_{3/2}$ at 314.3 eV which corresponds to the Rh$^{3+}$ oxidation state [58-61]. The ratio of 3d$_{5/2}$ to 3d$_{3/2}$ peak area was set to 3:2. During the in-situ pretreatment, the catalysts were reduced in H$_2$ at 550°C before reacting it with CO$_2$ which is why Rh is in Rh$^0$ (3d$_{5/2}$ at 307.5 eV and 3d$_{3/2}$ at 312.3 eV) state for “Reacted with CO$_2$” catalyst. Apart from the Rh$^0$ (307.5 eV) species in the CO$_2$ reacted catalyst, there is a small proportion of...
Rh$^{+3}$ species with 3d$_{5/2}$ at 309.1 and 3d$_{3/2}$ at 313.9 eV. This could be some Rh$^{+3}$ which was not reduced due to low H$_2$ pressure in the in-situ reaction chamber. The reaction with CO$_2$ may have created some partially oxidized Rh on the surface but due to a low signal to noise ratio effective deconvolution could not be achieved.

### 7.3.4. Summary of the DRM Reaction Mechanism

A detailed characterization and activity study of L2RhZ and L5RhZ has been reported in our previous work [22]. The characterization results suggested higher surface coverage of Rh on L5RhZ compared to L2RhZ. Also, CH$_4$ and CO$_2$ conversion was observed to be greater for L5RhZ than L2RhZ as suggested by the activity results. To study the catalytic active sites responsible for dissociation of CH$_4$ and its oxidation to CO, a detailed study of the activation of CH$_4$ was conducted and is reported [Chapter 6]. That study showed strong deuterium (CH$_4$/CD$_4$) isotope effect suggesting that breaking of the C-H bond in CH$_4$ is the rate-limiting step. CH$_4$ is activated on Rh sites on both catalysts, although these sites appear to be different on L2RhZ compared to L5RhZ.

Based on our previous work and the results reported here, a sequence of mechanistic steps for DRM over Rh substituted pyrochlores can be derived. The most important step in the DRM mechanism is the activation of CH$_4$ which occurs solely on the Rh site in L2RhZ and L5RhZ [Step 1 in Figure 7.7]. Activation of CH$_4$ occurs via dissociative adsorption [Step 2 in Figure 7.7] as suggested by the absence of the C-H stretching bands in the IR spectra during the CH$_4$ pulsing experiment [section 7.3.2.2] and as seen in the literature [62, 63]. The dissociation of the C-H bond is also the rate-limiting step as seen from our previous study which showed that the rate of CH$_4$ consumption exhibited a strong deuterium isotope effect. This was also confirmed by the fact that the activation energy for the rate of CH$_4$ consumption was greater than that for CO$_2$.
suggesting slower kinetics for activation of CH₄. This rate-limiting dissociative adsorption of CH₄ results in the formation of and surface carbon and hydrogen. The activation of mildly acidic CO₂ occurs at the La-O sites which result in the formation of the La-oxycarbonates (La₂O₂CO₃) [Step 3 and 4 in Figure 7.7].

In our previous study we pulsed CH₄/Ar mixture over reduced L2RhZ and L5RhZ catalysts and observed that the simultaneous evolution of H₂ and CO was much slower than the evolution of Ar. Because CO and H₂ are smaller molecules and have greater diffusivity compared to Ar, a delay in their response compared to Ar suggests that H₂ and CO are formed in the same
surface reaction which occurs at a rate slower than the diffusion of Ar. This observation suggests that hydrogen (formed from the activation of CH$_4$ on the Rh site) reacts with the adsorbed La-oxycarbonates [Step 5 in Figure 7.7], perhaps by diffusion from Rh to the La-Rh interface, forming H$_2$O and reducing carbonates to CO. This H$_2$O later reacts with the surface carbon at the La-Rh interface evolving CO and H$_2$ simultaneously [Steps 6 and 7 in Figure 7.7].

Since H$_2$ and CO are observed to evolve much later than Ar, either the surface diffusion of H$_2$ or the oxidation of surface carbon is a slow step. This delay in the formation of H$_2$ and CO compared to Ar could also be due to slow activation of CH$_4$, which is a rate-limiting step. Since CH$_4$ and Ar are pulsed simultaneously, a slow CH$_4$ dissociation would result in slower formation of H$_2$ and thus a further delay in the H$_2$O formation and subsequent oxidation of carbon. Oxidation of the surface carbon via H$_2$O formation is an important step in understanding the mechanism of DRM over these pyrochlores. In our previous rate modeling work, a dual-site mechanism was consistent with our kinetic data. These two types of sites that are responsible for activation of CH$_4$ and CO$_2$ have been clearly identified as Rh and La respectively. Hence the previously reported reaction mechanism can be restated as follows:

\[
\begin{align*}
\text{CH}_4 + \text{Rh} & \rightleftharpoons \text{CH}_4\text{-Rh} \quad (1) \\
\text{CH}_4\text{-Rh} & \rightarrow \text{C-Rh} + 2\text{H}_2 \quad (2) \text{...rate limiting step} \\
\text{CO}_2 + \text{La}_2\text{O}_3 & \rightleftharpoons \text{La}_2\text{O}_2\text{CO}_3 \quad (3) \\
\text{La}_2\text{O}_2\text{CO}_3 + \text{H}_2 & \rightleftharpoons \text{La}_2\text{O}_3 + \text{CO} + \text{H}_2\text{O} \quad (4) \\
\text{C-Rh} + \text{H}_2\text{O} & \rightleftharpoons \text{CO} + \text{H}_2 + \text{Rh} \quad (5)
\end{align*}
\]
7.4. Conclusion

The FTIR results on CO\textsubscript{2} adsorption and CH\textsubscript{4} transient pulsing suggest a dual-site mechanism for DRM over Rh-substituted lanthanum-zirconate pyrochlores, where CH\textsubscript{4} and CO\textsubscript{2} are activated on fundamentally different sites. The activation of mildly acidic CO\textsubscript{2} occurs at the basic La-O sites and these sites are very similar on LZ, L2RhZ and L5RhZ as seen in the FTIR results. The CO\textsubscript{2} is activated and converted to 3 polymorphic forms of La-oxycarbonates; type I, Ia and II, which differ in orientation of the La and carbonate ions. While CO\textsubscript{2} is activated on La-O site, CH\textsubscript{4} is activated on Rh site since no CH\textsubscript{4} conversion was observed for CH\textsubscript{4} transient pulses over LZ. The difference in the FTIR spectra for adsorbed La-oxycarbonates before and after CH\textsubscript{4} pulses clearly shows that only type-II oxycarbonate is the reactive species while type I and Ia are spectator species. Since these oxycarbonates act as oxygen suppliers in oxidizing the surface carbon during DRM, distinction between spectator and reactive oxycarbonates is important in limiting carbon formation.

Since it is well known in the literature that the lattice oxygen of pyrochlore materials is reactive; the oxygen from oxycarbonates/CO\textsubscript{2} could also be interchangeable with the lattice oxygen of the pyrochlores, however, this could not be confirmed from in the present work. Since the carbon is formed from activation CH\textsubscript{4} at the Rh site and CO\textsubscript{2} is activated by La-O, oxidation of the surface carbon perhaps occurs at the Rh-La interfacial sites. Thus increase in the Rh-La interfacial sites would increase the rate of carbon oxidation and help in resisting deactivation due to carbon formation. These results are first set of mechanistic study reported for DRM over pyrochlores.
7.5. References


Chapter 8 : Conclusions and Future Work

8.1. Conclusions

8.1.1. Role of Rh, Ru and Pt

Activation of CH$_4$ is the most important step in DRM mechanism and is also the rate limiting step as seen by the CH$_4$/CD$_4$ kinetic isotope effect, hence to increase the rate of occurrence of DRM on a catalyst, it is important to determine the kinetics of and active site for CH$_4$ activation. The transient pulsing, activity studies showed significant increase in CH$_4$ conversion over L2RhZ, L5RhZ, LPtZ, and LRuZ, whereas no conversion was observed for LZ, suggesting that the active site for CH$_4$ activation is the Rh (Ru or Pt) site.

Activation of CH$_4$ occurs via direct dissociation mechanism on the noble metal resulting in formation of C(s) and H$_2$. This C(s) has to be oxidized and removed from the catalyst surface in order to avoid catalyst deactivation. This suggests that the primary role of Rh, Ru and Pt in the pyrochlore structure is to dissociate CH$_4$ which determines the overall rate of DRM and begins the mechanistic cycle.

8.1.2. Role of La and Zr in the Pyrochlore Structure

Since DRM occurs at high temperatures, it is essential that the catalyst is structurally stable at such high temperatures and avoid deactivation due to sintering. For pyrochlore structure to be stable it is essential that the ratio of the A-site to B-site ion is between 1.4 and 1.8 [1-4]. The ratio of La$^{+3}$ (co-ordination no: 8) and Zr$^{+4}$ (co-ordination no: 6) is 1.61. Thus the combination of La and Zr provides structural stability and helps in maintaining the A$_2$B$_2$O$_7$ framework even at temperatures as high as 800-1000°C.
The primary source of oxygen for oxidation of C(s) formed from dissociation of CH₄ is CO₂. Hence the activation of CO₂ is crucial for maintaining long term activity of the catalyst. Due to mildly acidic nature of CO₂, having La which is basic in nature helps in efficient and fast activation of CO₂. La activates CO₂ from gas phase and converts it to La-oxycarbonates. These La-oxycarbonates then undergo reduction and simultaneously oxidize C(s) to form CO. As reported in Chapter 6 and Chapter 7, the oxidation of C(s) and reduction of La-oxycarbonates takes place in the presence of H₂ (which is formed during CH₄ dissociation) and at the La-Rh interfacial site. Thus La plays an important role in maintaining stable DRM activity of the catalyst.

8.2. Future Work

8.2.1. Studying the Role of the Lattice Oxygen

The lattice oxygen of pyrochlores is reactive towards C(s) as seen in CH₄ TPR results in Chapter 6. Although the primary source of oxygen for C(s) oxidation in CO₂, the lattice oxygen acts as a secondary source which increases the resistance of the catalyst towards deactivation due to carbon formation. It would be interesting to study the role of lattice oxygen in the DRM mechanism. A DRM reaction study with isotopically labelled C¹⁸O₂ and CH₄ should result in H₂ and C¹⁸O. Thus if the pyrochlore lattice oxygen (which is ¹⁶O) is reactive or interchangeable with ¹⁸O from C¹⁸O₂, there would be formation of C¹⁶O. Quantification of C¹⁶O (if any) would suggest the extent to which pyrochlore lattice oxygen takes part in DRM mechanism. Performing CH₄ and C¹⁸O₂ DRM reaction at different temperatures would suggest the changes in the reactivity of lattice oxygen as a function of temperature.
A comparative study between the catalyst spent during CH\(_4\)/C\(^{18}\)O\(_2\) DRM and CH\(_4\)/C\(^{16}\)O\(_2\) DRM could be characterized by XRD to see if the \(^{18}\)O has resulted in any change in the lattice parameter. TPO of the spent catalysts would suggest the changes in the reactivity of the surface carbon formed as a result of C\(^{18}\)O\(_2\) in the reactant DRM feed. Understanding the role lattice oxygen plays is crucial in enhancing the resistance of pyrochlores towards carbon formation and hence maintaining the catalytic activity for prolonged period of time under DRM conditions.

8.2.2. Study Using Labelled Carbon in CO\(_2\) or CH\(_4\)

The primary source of carbon which leads to deactivation is CH\(_4\) [5-7]. This surface carbon formed from CH\(_4\) dissociation is oxidized to CO in the presence of H\(_2\) and La-oxycarbonates. However, what percentage of C(s) formed from CH\(_4\) stays unoxidized and what amount gets oxidized to CO was not clear from the studies reported here. Also, no claim could be made about the relative rates of CO formation from oxidation of carbon and reduction of carbonates.

These issues could be addressed by performing transient experiments (similar to those performed in Chapter 6) with labelled \(^{13}\)CH\(_4\) and \(^{12}\)CO\(_2\) with Ar as a tracer gas. Labelling the carbon will result in \(^{13}\)CO (by oxidation of \(^{13}\)CH\(_4\)) and \(^{12}\)CO (by reduction of \(^{12}\)CO\(_2\) or La-oxycarbonates) which would help in quantifying the selectivity of CH\(_4\) towards CO and C(s). Also the changes in the selectivity could be studied as a function of temperature. Monitoring the difference (if any) in the \(^{13}\)CO and \(^{12}\)CO response would suggest if the oxidation of carbon (to \(^{13}\)CO) is faster/slower than reduction of carbonates (to \(^{12}\)CO). The results obtained in this work and the proposed experiments will later be used by computational researchers to build a micro-kinetic model of DRM over pyrochlores.
8.3. References


Appendix A : CO₂ Reforming of CH₄ over Ru-substituted Pyrochlore Catalysts: Effects of Temperature and Reactant Feed Ratio

A.1. Introduction

Dry reforming of CH₄ (DRM) has received considerable attention in the recent years as a means of utilizing carbon-free energy sources such as solar or wind to capture or transport this clean energy in the form of CO and H₂. A major limitation of DRM is catalyst deactivation [1], which has generally been attributed to either sintering of the active metal or carbon formation on active sites of the catalyst [2, 3]. Deactivation due to carbon formation on metallic sites is generally thought to be caused by either CH₄ decomposition and/or the Boudouard reaction (CO disproportionation) [1]. Depending on the reaction conditions and the reactant composition, carbon build-up can be thermodynamically favorable, and must be kinetically limited [4]. Decomposition of CH₄ is favored at high temperatures whereas Boudouard reaction is favored at low temperatures [2, 3]. To thermodynamically limit carbon formation, DRM at a CH₄/CO₂ ratio less than 1 has to be operated at T >800 °C [1, 4]. Carbon deposition also depends on the active metal [5]. In general, the noble metals (Rh, Ru, Pt, Pd, Ir) have been shown to be more resistant towards deactivation by carbon than non-noble metals such as Ni [6]. At the same time, the limited availability and higher cost of these metals prohibit their commercial application. Ni is the preferred catalyst for dry reforming due to its lower cost. However, Ni based catalysts are prone to rapid deactivation due to carbon formation [1]. It has been proposed that metal oxide supports having strong Lewis basicity help to reduce deactivation due to carbon formation [7].

Pyrochlores have the empirical formula $A_2B_2O_7$ where “A” is a rare-earth element, and “B” is a transition element. These pyrochlores have a defect fluorite structure and possess ordered cations (A and B), oxygen anions (O) and vacancies (O'), with the A site, B site, O site, and O' site occupying the 16d, 16c, 48f, and 8b sites, respectively [8]. Substitution of metals at the A and B sites in certain pyrochlore formulations yields a refractory material that is stable at temperatures greater than 2000°C [9], retaining relatively large specific surface areas even at these extreme conditions [10]. This resistance to thermal deactivation, coupled with the isomorphous substitution of catalytically active metals within the structure, suggests the possibility that these materials may be suitable for CH$_4$ reforming. For example, we have recently reported DRM on structurally-stable lanthanum-zirconate ($La_2Zr_2O_7$) pyrochlore with partial substitution of Ni for Zr, Rh for Zr, and Ca for La sites [11].

We are aware of only one reported study of pyrochlores for DRM. Ashcroft et al. [12], carried out DRM on a europium iridate ($Eu_2Ir_2O_7$) and found that this pyrochlore was unstable at 590°C and 660°C. At these conditions the pyrochlore structure was lost, forming Eu$_2$O$_3$ and Ir metal.

Here, we report the activity of a Sr- and Ru-substituted $La_{1.97}Sr_{0.03}Ru_{0.05}Zr_{1.95}O_7$ (LSRuZ) pyrochlore catalyst for DRM. While Sr was substituted on La sites, Ru was substituted into the Zr site. Commercially available 0.5 wt% Ru/Al$_2$O$_3$ was used as a comparison to the pyrochlore catalyst. The effect of temperature and CH$_4$/CO$_2$ inlet feed ratio on the yield of products on both catalysts is reported. Characterization of catalyst powders using TPR, XRD, and XPS was performed to investigate physical and chemical properties of the materials and relate them to activity.
A.2. Experimental Section

A.2.1. Catalyst Preparation

All the catalysts were prepared by a modified Pechini method as described elsewhere [13]. A flow-chart showing the preparation steps is shown in Figure A.1. The commercial catalyst (0.5 % Ru/Al₂O₃) was purchased from Strem Chemicals and used as supplied.

![Flow chart showing the synthesis of pyrochlore catalyst.](image)

Figure A.1. Flow chart showing the synthesis of pyrochlore catalyst.

A.2.2. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

Bulk elemental composition was determined using ICP-OES on a Perkin Elmer 2000 DV instrument. Samples were first quantitatively weighed in a Teflon bottle. Five mL of aqua regia
was added to each sample and allowed to sit overnight, loosely capped. Five mL of HF was then added to each sample, heated until complete dissolution at ~ 95°C. Samples were brought to 100 mL with DI water.

A.2.3. X-ray Diffraction (XRD)

XRD analysis of the freshly synthesized pyrochlore catalyst and the baseline 0.5 wt% Ru/Al₂O₃ catalyst was performed using a Bruker/Siemens D5000 system. The system had a ceramic X-ray tube with Cu Kα radiation operating at a wave length of 1.54184 Å. The tube operated at a voltage of 40 kV with a current of 30 mA. Angle of divergence slit for the incident X-ray beam was set to 1° and the antiscatter slit was set at 0.5°. Analysis was performed over a 2θ range from 10° to 80° at a sweep rate of 0.020° /min. All the spectra were analyzed by Jade (v. 9).

A.2.4. Energy Dispersive X-ray Analysis (EDX)

EDX spectra of the sample were obtained on the catalyst samples along with SEM images. Each sample was sputter-coated with gold for about 5 minutes to improve conductivity which gives a sharper image and a better resolution. After the particles were imaged, they were analyzed by EDX to determine the composition of elements present in each catalyst.

A.2.5. X-ray Photoelectron Spectroscopy (XPS)

XPS spectra was obtained on a Kratos Axis-165 X-ray photoelectron spectrometer using Al Kα radiation (1486.6 eV), which was operated at 15 kV and 10 mA. The base pressure of the UHV analysis chamber was maintained at 10⁻⁹ torr to allow high quality spectra being acquired. For XPS measurements, the pass energy of the analyzer was fixed at 40 eV for high resolution scanning. Spectra were obtained for the C 1s, O 1s, La 3d, Sr 3d, Zr 3d, Ru 3p, Ru 3d, and Al 2p
regions. In each case, the binding energy (BE) and the area of the corresponding peaks were measured. In the deconvolution process, a Shirley background was subtracted before the peak fitting with a symmetric Gauss-Lorentz sum function was performed. Due to the overlapping of Ru 3d_{3/2} line with C 1s line, the referencing of the binding energy (BE) scale would not be reliable if the C 1s line (284.6 eV) is used as a traditional procedure. For this reason, the La 3d signal at 833.4 eV (La_2O_3) and the Al 2p signal at 74.6 eV (Al_2O_3) were taken as reference for the LSRuZ and 0.5% Ru/Al_2O_3 respectively.

**A.2.6. Temperature Programmed Reduction (TPR)**

Temperature programmed reduction of the catalysts was conducted in an AMI 200 (Altamira instruments, Pittsburgh, PA) fixed bed reactor. For each run, 100 mg of catalyst was loaded into the quarter inch quartz tube. TPR was performed on LSRuZ pyrochlore and the 0.5% Ru/Al_2O_3 catalyst. Before starting the TPR, samples were first treated in O_2 to remove any surface carbonates or impurities left during their synthesis. For this treatment, the temperature was ramped from ambient (ca. 35°C) to 750°C at a rate of 20°C/min in 5% O_2/He with a flow rate of 20 mL/min. The sample was then purged with pure He (flow rate 20 mL/min) for 15 min, and then cooled to room temperature in He. Next, the sample was exposed to a mixture of 10% H_2/Ar flowing at 30 mL/min with a temperature ramping from 50°C to 750°C at 5°C/min. It was held at 750°C for 30 minutes and then cooled to room temperature.

The amount of metal reduced in pyrochlores and the baseline catalyst was quantified using silver oxide (Ag_2O) standards. A known quantity of Ag_2O was reduced under similar conditions as the catalysts. From stoichiometric calculations, the amount of H_2 required for reduction of the given amount of Ag_2O was determined.
A.2.7. Kinetic Measurements

CO\textsubscript{2} was reacted with CH\textsubscript{4} in an AMI-200 lab-scale fixed bed reactor. The reactant gases were 10\% (by mol) of CO\textsubscript{2}/He and 10\% (by mol) of CH\textsubscript{4}/He. The effect of temperature on DRM was measured at 635°C, 735°C, and 835°C with an equimolar reactant feed rate of 15 mL/min of each of the reactant gases to give a constant total gas space velocity of 18,000 mL g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1}. The effect of feed molar ratio (CH\textsubscript{4}:CO\textsubscript{2}) on the reaction was examined for three reactant molar ratios (CH\textsubscript{4}:CO\textsubscript{2}) – 1:2, 1:1 and 2:1 at 785°C maintaining a constant space velocity of 18,000 mL g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1}. For each run, 100 mg of catalyst was loaded in the U-tube reactor. The catalysts were not reduced before performing any experiment because the extremely reducing conditions during dry reforming should lead to the reduction of catalysts. Before each experiment, the catalyst was treated with He flowing at 20 mL/min at 150°C for 30 min to remove any surface moisture. After this step, the bed was cooled to room temperature. Next, the catalyst was ramped in 5\% O\textsubscript{2}/He at a flow rate of 20 mL/min up to 700°C with the ramp rate of 20°C/min to oxidize any surface carbonates species or other impurities left-over from the synthesis process. The catalyst was then cooled/heated to the desired bed temperatures (i.e., 635°C, 735°C or 835°C) under flowing He at 20 mL/min. After flowing He for 20 min, the reactants at desired flow rates were introduced in the reactor. After each run in which the catalysts were tested for the effect of CH\textsubscript{4}:CO\textsubscript{2} feed ratio, each catalyst was immediately subjected to in situ temperature programmed oxidation (TPO) to characterize the carbon formed during the reaction. During this experiment, the catalyst-bed was first cooled down to room temperature under pure He flowing at 30 mL/min and then ramped from room temperature to 950°C under a gas mixture of 5\%O\textsubscript{2}/He flowing at 40 mL/min. All the TPO spectra were recorded in an on-line mass spectrometer (MS, Dycor ProMaxion, Ametek Process Instruments) located down-stream of the reactor.
A.3. Results and Discussion

A.3.1. Kinetic Measurements

Table A.1 summarizes the results from ICP-OES showing the compositions of LSRuZ and 0.5%Ru/Al₂O₃ catalysts.

Table A.1. Elemental composition of catalyst samples

<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>Wt. % La</th>
<th>Wt. % Sr</th>
<th>Wt. % Ru</th>
<th>Wt. % Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSRuZ</td>
<td>47.70</td>
<td>0.46</td>
<td>0.85</td>
<td>32.26</td>
</tr>
<tr>
<td>Ru/Al₂O₃</td>
<td>-</td>
<td>-</td>
<td>0.35</td>
<td>-</td>
</tr>
</tbody>
</table>

The amount of Ru for both catalysts obtained from Table A.1 was used to calibrate the thermal conductivity detector which was used to quantify the amount of H₂ consumed during temperature programmed reduction.

A.3.2. XRD Studies of the Fresh Catalyst

The XRD pattern of the fresh LSRuZ catalyst is plotted in Figure A.2. Peaks for the La₂Zr₂O₇ crystalline phase confirm the presence of face-centered cubic unit cell pyrochlore structure. Diffraction peaks for Ru metal substituted in the structure were not detected, likely due to the low metal loading and the substitution of dispersed Ru atoms within the pyrochlore structure. Haynes, et al [14], also conducted XRD experiments on a similar LSRuZ pyrochlore synthesized by the same method used here.

In addition to the expected lanthanum-zirconate peaks, the diffraction pattern for their catalyst showed the presence of peaks at 33°, 65°, and 74° which were attributed to a defect SrZrO₃ perovskite phase. These perovskite peaks were not observed in our catalyst (Figure A.2) which had the molecular formula La₁.97Sr₀.03Ru₀.05Zr₁.95O₇. The reason for the absence of these peaks is the higher Sr loading (La₁.5Sr₀.5Ru₀.05Zr₁.95O₇) in the pyrochlore used by Haynes et al.
The pyrochlore structure has a limited capacity for accommodating Sr in the crystal lattice. If Sr is in excess of this limit, it can form a separate SrZrO$_3$ perovskite phase during calcination. The Sr loading in our catalyst is lower than the maximum capacity of the lanthanum-zirconate structure and we do not observe a perovskite phase.

![XRD spectra of fresh LSRuZ pyrochlore catalyst](image)

Figure A.2. XRD spectra of fresh LSRuZ pyrochlore catalyst

A.3.3. SEM-EDX

Area-averaged elemental composition of the catalyst was determined by EDX as shown in Figure A.3.
Figure A.3. Figure showing EDX spectra for (a) 0.5% Ru/Al₂O₃, and (b) LSRuZ pyrochlore catalyst. Both spectra were acquired on fresh catalyst samples.

EDX analysis for the 0.5% Ru/Al₂O₃ catalyst (Figure A.3 (a)) shows three peaks for oxygen, aluminum, and gold, respectively. Peak for gold was visible since the sample was sputter-coated with Au to increase the conductivity of the sample before recording the images. Similar to the alumina catalyst, peaks for the main constituents, in this case La, Zr, O, and Au, were seen for during the EDX analysis of the pyrochlore, as shown in Figure A.3 (b). Ru and Au have similar k-line energies; this may be the reason why Ru could not be distinctly observed in either sample.

A.3.4. XPS Results

XPS was used to determine the oxidation state of the active metal in LSRuZ and 0.5% Ru/Al₂O₃ catalysts. It is important to note that the chemical state of a given element can be significantly affected by the surrounding chemical environment. Figure A.4 (a), (b) and (c) represent the Ru 3d spectra obtained from LSRuZ, the 0.5% Ru/Al₂O₃, and the 3p spectra for Ru in LSRuZ catalyst, respectively. In all the profiles a careful deconvolution of the XPS spectra was performed.
Figure A.4. XPS spectra of fresh catalysts: a) LSRuZ – Ru 3d region, b) 0.5% Ru/Al₂O₃ – Ru 3d region, and c) LSRuZ – Ru 3p region.
Figure A.4 (a) shows the calibrated and deconvoluted spectra of Ru 3d and C 1s peaks of LSRuZ. The C 1s peak positioned at 284.8 eV is related to adventitious carbon. The C 1s spectra also exhibits peaks at 286.9 and 288.7 eV that were attributed to carbonaceous species associated with oxygen and/or hydrogen [16]. According to literature, Ru 3d spectrum is comprised of an unresolved 3d_{5/2}-3d_{3/2} doublet with a splitting of ca. 4.14 eV [16, 17]. Although RuO_3 or higher oxidation states of Ru may have 3d_{5/2} peaks in the range from 283~285 eV, the lack of a splitting 3d_{3/2} peak suggest that this is not the case here. The only Ru species identified is Ru^{4+} (RuO_2), which is assigned to a weak peak at 281.3 eV [16, 18]. Additional XPS investigation [Figure A.4 (c)] regarding the Ru 3p spectrum also supports this conclusion. In the B.E. range of 459.5-468.5 eV, the Ru 3p peaks are fitted with a Ru^{4+} line at 464.1 eV and Ru^0 line at 461.5 eV [19, 20]. As indicated in Table A.2 which shows the relative ratio of different Ru species in the catalysts, freshly calcined pyrochlore catalyst is rich in RuO_2 species and deficient in Ru^0. The low Ru^0 contribution to Ru_{total} also explains why Ru^0 species could not be identified in the 3d spectra,
considering the C 1s line was too strong to extract the Ru signal. Figure A.4 (b) presents the Ru 3d and C 1s peaks of 0.5% Ru/Al$_2$O$_3$. Unlike the LSRuZ sample, the Ru signal of 0.5% Ru/Al$_2$O$_3$ was stronger. Two sets of Ru peaks with Ru 3d$_{5/2}$ line at 281.0 eV and 282.5 eV can be assigned to Ru$^{4+}$ (RuO$_2$) and Ru$^{n+}$ (RuO$_3$ or RuO$_4$), respectively [17].

However, the 0.5% Ru/Al$_2$O$_3$ catalyst did not have Ru$^0$ on the surface, showing that Ru was present in a stable oxide form on the surface in this catalyst.

Table A.2. XPS relative atomic ratios of different Ru species

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ru$^0$/Ru$_{total}$ (%)</th>
<th>Ru$^{4+}$/Ru$_{total}$ (%)</th>
<th>Ru$^{n+}$/Ru$_{total}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSRuZ</td>
<td>8</td>
<td>92</td>
<td>0</td>
</tr>
<tr>
<td>0.5% Ru/Al$_2$O$_3$</td>
<td>0</td>
<td>56</td>
<td>44</td>
</tr>
</tbody>
</table>

Table A.3 compares the bulk Ru concentrations obtained by ICP-MS (Table A.1) and the surface concentration from XPS for the two catalysts.

Table A.3. Ru concentration (mass %) obtained by different methods

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Method for obtaining Ru Concentration (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical Concentration*</td>
</tr>
<tr>
<td>LSRuZ</td>
<td>1</td>
</tr>
<tr>
<td>0.5% Ru/Al$_2$O$_3$</td>
<td>0.5</td>
</tr>
</tbody>
</table>

*Denotes the desired loading amount.

As expected, the surface Ru% obtained from XPS analysis for LSRuZ was much lower (~0.1%) than the bulk concentration consistent with a structure in which the Ru resides primarily within the lattice at depths not detectable by XPS (>15nm from surface). For the 0.5% Ru/Al$_2$O$_3$, the surface concentration is somewhat greater than that based on the bulk, consistent with a morphology in which clusters of Ru are supported on the oxide surface.
A.3.5. Temperature Programmed Reduction (TPR) Studies

The TPR profiles of LSRuZ pyrochlore and 0.5% Ru/Al₂O₃ are shown in Figure A.5. For 0.5% Ru/Al₂O₃, a low temperature peak is observed at 140°C, which is due to the reduction of RuO₂ and other RuOₓ species to Ru metal [15]. Results from XPS showed that the RuOₓ species may correspond to RuO₂, RuO₃ and/or RuO₄ for the 0.5% Ru/Al₂O₃. The peaks at 470°C and 550°C are due to the reduction of the bulk Ru atoms with varying degrees of interaction with the alumina support. In a previous TPR study by Canu et al [21] on Ru/SiO₂, Ru/Al₂O₃, and Ru/CeO₂-ZrO₂ catalysts, similar small peaks were observed from 400-800 °C and these peaks were assigned to the reduction of the oxide support. This could well be the case in the 0.5% Ru/Al₂O₃ catalyst studied here where the two peaks at 470°C and 550°C could be a contribution of the reduction of Ru atoms and the support itself. On the other hand, the TPR of the pyrochlore catalyst shows a single reduction peak at 280°C. This peak is due to the reduction of the surface Ru species which are accessible to the reducing gas, but which are strongly bound to oxygen in the pyrochlore lattice. The TPR profile of the LSRuZ pyrochlore studied by Haynes, et al [14] showed a peak for reducible Ru species at 182°C. They assigned this peak to the reduction of Ru substituted into the B-site of the pyrochlore structure.

In the pyrochlore structure, Ru in the bulk would be coordinated with 6 oxygen atoms, and for surface Ru the coordination would be anywhere between 0-5. Thus the reduction peak of surface Ru in their study was attributed to the reduction of RuO₆₋ₓ (x = 1-5) to Ru⁰. However, in our study the XPS result suggests that the surface Ru for LSRuZ is mainly RuO₂ which is reduced to Ru⁰ during TPR. It is important to note that the difference in the Sr loading may also cause a difference in the reduction temperatures observed on otherwise similar pyrocholes reported by both Haynes, et al [14] and our work here. This difference in the Sr loading might
have caused the difference in the coordination number of the metal atom in the two structures and caused the observed difference in the reduction behavior of the surface metal atoms of the two pyrochlores. Unlike the 0.5% Ru/Al₂O₃ catalyst where most of the Ru atoms are on the surface, pyrochlores are defect fluorites with substantial amount of metal substituted into the bulk rather than on the surface. Thus, the amount of Ru reduced during TPR of LSRuZ would be less than Ru/Al₂O₃. This is supported by the TPR results. Assuming that all the Ru is present as RuO₂, only 21.6% of the total Ru-metal in the pyrochlore catalyst was reduced compared to 81.3% of Ru reduced in the 0.5% Ru/Al₂O₃.

Figure A.5. TPR spectra of fresh LSRuZ pyrochlore and baseline catalyst.

A.3.6. Kinetic Investigations

A.3.6.1. Effects of Temperature

The apparent CH₄ and CO₂ conversions for the LSRuZ pyrochlore and 0.5% Ru/Al₂O₃ catalyst with time on stream (TOS) are shown in Figure A.6.
Figure A.6. Conversion profile for (a) CO\textsubscript{2} (X\textsubscript{CO\textsubscript{2}}) for 0.5\% Ru/Al\textsubscript{2}O\textsubscript{3} catalyst and LSRuZ, and (b) CH\textsubscript{4} (X\textsubscript{CH\textsubscript{4}}) for 0.5\% Ru/Al\textsubscript{2}O\textsubscript{3} catalyst and LSRuZ at 635 °C, 735 °C, and 835 °C at 1 atm and a space velocity of 18,000 mL g\textsubscript{cat}^{-1} h\textsuperscript{-1}. Data for LSRuZ is shown with filled symbols and 0.5\% Ru/Al\textsubscript{2}O\textsubscript{3} catalyst is shown with empty symbols. Thermodynamic equilibrium conversions of the respective reactant at that particular temperature are displayed on the Y-axis to the right. Equilibrium values were calculated using HSC chemistry 7.1 software at P=1 atm. Equilibrium calculations were carried out using as initial composition of CH\textsubscript{4}:CO\textsubscript{2}=1:1 allowing H\textsubscript{2}, CO, H\textsubscript{2}O, and C\textsubscript{(s)} as products.
CO₂ conversion. The X\textsubscript{CO₂} [Figure A.6 (a)] and X\textsubscript{CH₄} [Figure A.6 (b)] profiles show that both catalysts have similar initial activities at each of the three reaction temperatures. At 635°C and 735°C, the equilibrium X\textsubscript{CO₂} values are 50% and 75% respectively which are lower than the final experimental X\textsubscript{CO₂} values for the two catalysts at those temperatures. Further, equilibrium calculations show that the H₂/CO ratios at 635°C and 735°C are 2.4 and 1.3 respectively. But experimentally, the H₂/CO values were found to be 0.8 and 0.9 for LSRuZ and for 0.5% Ru/Al\textsubscript{2}O\textsubscript{3} [figures not shown here] they were found to be 0.82 and 0.9 at 635°C and 735°C respectively, and did not change with time. These significantly lower experimental H₂/CO ratios compared to the equilibrium values, coupled with the significantly greater experimental X\textsubscript{CO₂} compared to the equilibrium X\textsubscript{CO₂} suggests that the relative rate of the RWGS reaction is significantly greater than the competing reactions on both catalysts at these temperatures. At 835°C, the experimental and thermodynamic equilibrium values are equal within experimental error, and there is no significant difference in X\textsubscript{CO₂} between the two catalysts.

CH₄ conversion. The X\textsubscript{CH₄} [Figure A.6 (b)] at 635°C showed decreasing trend with time for 0.5% Ru/Al\textsubscript{2}O\textsubscript{3}. The decrease in conversion could be due to the loss of active metallic sites due to carbon deposition, likely by encapsulation rather than filament growth [22]. The values for X\textsubscript{CH₄} at 735°C and 835°C are near equilibrium for both the catalysts and there is no observable deactivation over this 7 h run.

A.3.6.2. Effects of Reactant Feed Ratio

The effect of CH₄:CO₂ ratio on X\textsubscript{CH₄}, X\textsubscript{CO₂}, and H₂/CO ratio for LSRuZ and 0.5% Ru/Al\textsubscript{2}O\textsubscript{3} at 785°C is shown in Figure A.7 (a-c), respectively, and the values have been summarized in Table A.4. Two thermodynamic calculations at inlet reactant ratios of 1:2, 1:1,
and 2:1 were performed. In the first calculation, solid carbon was allowed as one of the products (Eq\textsuperscript{n1}), while in the second, no solid carbon was allowed (Eq\textsuperscript{n2}). In both cases, the reactants/products included only gas phase CH\textsubscript{4}, CO\textsubscript{2}, CO, H\textsubscript{2}O, and H\textsubscript{2}. A comparison of the experimental results and these equilibrium calculations are shown in Table A.4 and Figure A.7.

Table A.4. Experimental conversion of reactants for 0.5% Ru/Al\textsubscript{2}O\textsubscript{3} and LSRuZ and the equilibrium values for the respective reactant feed ratios \textsuperscript{a}.

<table>
<thead>
<tr>
<th>CH\textsubscript{4}:CO\textsubscript{2} Ratio</th>
<th>0.5% Ru/Al\textsubscript{2}O\textsubscript{3}</th>
<th>LSRuZ</th>
<th>0.5% Ru/Al\textsubscript{2}O\textsubscript{3}</th>
<th>LSRuZ</th>
<th>With C(s) Eq\textsuperscript{n1}</th>
<th>Without C(s) Eq\textsuperscript{n1}</th>
<th>With C(s) Eq\textsuperscript{n2}</th>
<th>Without C(s) Eq\textsuperscript{n2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>97.3</td>
<td>95.0</td>
<td>98.5</td>
<td>98.7</td>
<td>98.0</td>
<td>85.0</td>
<td>88.0</td>
<td>97.0</td>
</tr>
<tr>
<td>1:2</td>
<td>98.2</td>
<td>98.5</td>
<td>69.1</td>
<td>63.1</td>
<td>99.0</td>
<td>99.1</td>
<td>66</td>
<td>68.5</td>
</tr>
<tr>
<td>2:1</td>
<td>60.2</td>
<td>58.1</td>
<td>99.5</td>
<td>99.2</td>
<td>90.0</td>
<td>50.0</td>
<td>90.0</td>
<td>99.9</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Experimental values are based on the average of values recorded for 200 min. on stream at 785 °C and space velocity of 18,000 mL g\textsubscript{(cat)}\textsuperscript{-1} h\textsuperscript{-1} (see Figure A.7). All the simulations were performed using HSC Chemistry 7.1. Equilibrium calculations were carried out as a free energy minimization at 785 °C, 1 bar; using an initial composition of CH\textsubscript{4}:CO\textsubscript{2}=1:1, 1:2, and 2:1, allowing H\textsubscript{2}, CO, H\textsubscript{2}O, (and C(s) in one case; designated Eq\textsuperscript{n1}) as products. Eq\textsuperscript{n2} corresponds to the same calculation without C(s) as a product.

Effect on CH\textsubscript{4} conversion. Figure A.7 (a) shows that at an equimolar reactant feed ratio (i.e., CH\textsubscript{4}:CO\textsubscript{2} = 1:1), LSRuZ and 0.5% Ru/Al\textsubscript{2}O\textsubscript{3} catalysts had near equilibrium X\textsubscript{CH4} values, when C(s) is allowed (Eq\textsuperscript{n1}; see Table A.4). For CH\textsubscript{4}:CO\textsubscript{2} = 1:1, the mean X\textsubscript{CH4} for 0.5% Ru/Al\textsubscript{2}O\textsubscript{3} (97.3%) was slightly greater than X\textsubscript{CH4} for LSRuZ (95.0%). At this 1:1 CH\textsubscript{4}:CO\textsubscript{2} ratio, 0.5% Ru/Al\textsubscript{2}O\textsubscript{3} catalyst is operating at near-equilibrium conversion (98.0 %; as calculated with solid carbon; Eq\textsuperscript{n1}; Table A.4), while X\textsubscript{CH4} for the LSRuZ is slightly less. This small but significant difference in the two catalysts could be due to methane decomposition on 0.5% Ru/Al\textsubscript{2}O\textsubscript{3}, forming C(s) on the surface, to a greater extent than on LSRuZ. However, this did not result in any observable deactivation, at least over the time scale of this experiment. For CH\textsubscript{4}:CO\textsubscript{2} = 1:2, X\textsubscript{CH4} for both catalysts is constant with time and near the equilibrium values of
99.0% (Eq\textsuperscript{m} 1) and 99.1% (Eq\textsuperscript{m} 2), which are essentially equal whether C(s) is allowed or not (Table A.4). For CH\textsubscript{4}:CO\textsubscript{2} = 2:1, experimental X\textsubscript{CH4} for both catalysts was lower than equilibrium when C(s) is included in the calculation (Eq\textsuperscript{m} 1), but higher than when C(s) was not included (Eq\textsuperscript{m} 2; Table A.4). Higher experimental X\textsubscript{CH4} in comparison with Eq\textsuperscript{m} 2 (w/o carbon) values suggest that there is considerable amount of C(s) deposited during the course of the reaction on both catalysts. However, in neither case was there any deactivation over this 200 min experiment.

Effect on CO\textsubscript{2} conversion. For 2:1 and 1:1 CH\textsubscript{4}:CO\textsubscript{2} ratios, the CO\textsubscript{2} conversion is near equilibrium without C(s) for both catalysts, and does not change with time. For CH\textsubscript{4}:CO\textsubscript{2} = 1:2, there is an increase in X\textsubscript{CO2} for LSRuZ from 60.0% to 63.0% over 200 min. For 0.5% Ru/Al\textsubscript{2}O\textsubscript{3}, X\textsubscript{CO2} increased from an initial value of 63.0% to the Eq\textsuperscript{m} 1 value of 71.0% after 200 min, suggesting an increase in the relative rate of the RWGS with time on this catalyst.

![Figure A.7. Profiles for (a) Conversion of CH\textsubscript{4} (X\textsubscript{CH4}), (b) Conversion of CO\textsubscript{2} (X\textsubscript{CO2}) and (c) H\textsubscript{2}/CO ratio for LSRuZ and 0.5% Ru/Al\textsubscript{2}O\textsubscript{3} catalyst at constant GHSV of 18,000 mL g\textsuperscript{(cat)}\textsuperscript{-1} h\textsuperscript{-1} and CH\textsubscript{4}:CO\textsubscript{2} ratio of 1:1, 1:2 and 2:1 at 785 °C and P = 1 bar. Equilibrium calculations were carried out using as initial composition of CH\textsubscript{4}:CO\textsubscript{2} = 1:1 allowing H\textsubscript{2}, CO, H\textsubscript{2}O, and C\textsubscript{(s)} as products.](image-url)
(Figure A.7 continued)

**Figure A.7 (b)**

- **CO₂ Conversion (XCO₂)**
  - **Eqm (2:1) = 92%**
  - **Eqm (1:1) = 88%**
  - **Eqm (1:2) = 66%**

**Figure A.7 (c)**

- **H₂/CO ratio**
  - **Eqm (2:1) = 2.22**
  - **Eqm (1:1) = 1.12**
  - **Eqm (1:2) = 0.7**
Effect on H₂/CO ratio. Figure A.7 (c) shows the H₂/CO ratio in the product gas as a function of time at each of the three CH₄:CO₂ inlet reactant ratios at 785°C. For CH₄:CO₂ = 1:1, the measured H₂/CO ratios for both catalysts are essentially equal, constant with time, and far below equilibrium when C(s) is included in the equilibrium calculation. Figure A.7 (a) shows that for the 0.5% Ru/Al₂O₃ catalyst, X₇H₄ was slightly greater (97.3%), than for LSRuZ (95.0%). This is likely due to somewhat greater rate of CH₄ decomposition on 0.5% Ru/Al₂O₃. With increasing X₇H₄ it would be expected that there should be a corresponding increase in the H₂/CO ratio. However, the constant H₂/CO ratio for 0.5% Ru/Al₂O₃ suggests that: 1) either H₂ was simultaneously consumed in some other reaction, or 2) CO was produced from some other reaction taking place simultaneously with DRM. In this case, it appears that RWGS is continuously consuming H₂, limiting the increase in the H₂/CO ratio during the reaction. However if the RWGS reaction were solely responsible for this observation, one would expect an increase in CO₂ consumption with time on stream, which is not the case here since CO₂ conversion was constant during the reaction [Figure A.7 (b)]. This indicates that along with DRM and RWGS, the Boudouard reaction, which produces CO₂, is taking place:

\[2CO \leftrightarrow CO₂ + C(s)\]

This also explains the reason why both the conversion of CO₂ and H₂/CO ratio are relatively constant with time on stream.

For CH₄:CO₂ = 1:2, H₂/CO ratio for LSRuZ is greater than 0.5% Ru/Al₂O₃, however, X₇CH₄ is the same for both catalysts, and X₇CO₂ is lower for LSRuZ compared to 0.5% Ru/Al₂O₃, meaning that LSRuZ kinetically inhibited the RWGS to a greater extent compared to 0.5% Ru/Al₂O₃. For CH₄:CO₂ = 2:1, H₂/CO ratio for LSRuZ is essentially the same as 0.5% Ru/Al₂O₃.
However, at these conditions, $X_{\text{CH}_4}$ and $X_{\text{CO}_2}$ for 0.5% Ru/Al$_2$O$_3$ were higher than LSRuZ. This increase in CH$_4$ consumption at a constant H$_2$/CO ratio suggests occurrence of RWGS to a greater extent on 0.5% Ru/Al$_2$O$_3$ compared to LSRuZ. Increased CH$_4$ consumption would also result in carbon deposition.

**A.3.6.3. Effects of Surface Carbon on Equilibrium Conversion**

The equilibrium values in Figure A.7 are calculated based on gas-phase compositions of the reactants and expected products by considering solid carbon, C(s), as one of the products of the reaction. A corresponding calculation can be made in which C(s) is excluded in the equilibrium calculations, and only gas phase products allowed in the calculation. Table A.4 shows the experimental and the calculated equilibrium values for CH$_4$ and CO$_2$ conversion for the different CH$_4$:CO$_2$ ratios. Inclusion of C(s) as a separate phase in these calculations has no significant effect on $X_{\text{CH}_4}$ except for CH$_4$:CO$_2 = 2:1$, where significant carbon formation is thermodynamically favored, with the equilibrium $X_{\text{CH}_4}$ decreasing from 90.0% to 50.0% if C(s) is excluded. Assuming elemental carbon is at least qualitatively representative of carbon that forms on the catalyst, the results in Table A.4 clearly suggest that the formation of carbon accounts for the fact that the experimental values of $X_{\text{CH}_4}$ for both catalysts at CH$_4$:CO$_2 = 2:1$ (60.2% for 0.5% Ru/Al$_2$O$_3$ and 58.1% for LSRuZ) are greater than the equilibrium value of 50% when C(s) is not allowed in the equilibrium calculation. These results suggest further that carbon formation is kinetically limited by both the catalysts during the course of the reaction. The small difference between the experimental value of $X_{\text{CH}_4}$ for 0.5% Ru/Al$_2$O$_3$ (60.2%) and LSRuZ (58.1%), suggests that the LSRuZ is kinetically inhibiting carbon formation to a slightly greater extent than 0.5% Ru/Al$_2$O$_3$. This hypothesis is supported by the temperature programmed oxidation (TPO) results (section A.3.7.1).
A.3.7. Characterization of Spent Catalysts

A.3.7.1. Carbon Deposition by TPO of the Spent Catalysts

Equilibrium carbon formation: Figure A.8 shows the equilibrium amounts of solid, elemental carbon [C(s)] at different CH₄:CO₂ feed ratios. Carbon formation is thermodynamically favored at all CH₄:CO₂ ratios at temperatures below ~750°C. However, above ~750°C, carbon is not favored when the inlet ratio is CH₄:CO₂ = 1:2.

![Equilibrium carbon formation plot](image)

Figure A.8. Plot for equilibrium amount of solid elemental carbon, C(s), as a function of temperature as simulated by HSC chemistry 7.1. These values were computed by taking the initial molar ratios to be CH₄:CO₂ = 1:1, 1:2, and 2:1 at 1 atm and varying temperature from 0-1000°C. The results in Figure A.7 are at 785°C.
The amount of carbon formed over the catalysts is normalized with respect to the weight of the reducible Ru metal as measured by TPR. From TPR profiles of the fresh catalysts [see Figure A.5], the amount of Ru accessible to H\textsubscript{2} is 81.3\% for 0.5\% Ru/Al\textsubscript{2}O\textsubscript{3} and 21.6\% for LSRuZ (1\% Ru). From this result it can be inferred that the weight of Ru exposed per weight of catalyst is 0.406 g\textsubscript{Ru} / g\textsubscript{cat} for 0.5\% Ru/Al\textsubscript{2}O\textsubscript{3} and 0.21 g\textsubscript{Ru} / g\textsubscript{cat} for LSRuZ. As this is the amount of Ru metal accessible to H\textsubscript{2} during TPR, it can be assumed that this approximates the amount of Ru taking part in the reaction during DRM. The summary for the amount of carbon formed normalized with respect to the weight of Ru exposed during the reaction is shown in Table A.5.

Table A.5. Summary of carbon formation analyzed by TPO for 0.5\% Ru/Al\textsubscript{2}O\textsubscript{3} and LSRuZ spent at reactant feed ratio of CH\textsubscript{4}:CO\textsubscript{2}=1:1, 1:2, and 2:1 at the space velocity of 18000 mL g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1} at 785 °C \textsuperscript{b}.

<table>
<thead>
<tr>
<th>Inlet feed ratio (CH\textsubscript{4}:CO\textsubscript{2})</th>
<th>0.5% Ru/Al\textsubscript{2}O\textsubscript{3} (g\textsubscript{carbon}/g\textsubscript{Ru})</th>
<th>LSRuZ (g\textsubscript{carbon}/g\textsubscript{Ru})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>0.374</td>
<td>0.25</td>
</tr>
<tr>
<td>1:2</td>
<td>0.054</td>
<td>0.041</td>
</tr>
<tr>
<td>2:1</td>
<td>0.406</td>
<td>0.393</td>
</tr>
</tbody>
</table>

\textsuperscript{b} TPO was conducted from 40 °C to 950 °C at 5 °C/min under flowing 5\%O\textsubscript{2}/He at 30 mL/min.

For CH\textsubscript{4}:CO\textsubscript{2} of 1:1 and 1:2, the amount of carbon formed is greater for 0.5\% Ru/Al\textsubscript{2}O\textsubscript{3} as compared to LSRuZ. For CH\textsubscript{4}:CO\textsubscript{2} = 2:1, there is no experimentally significant difference in carbon formation over the two catalysts. The catalysts operating under a CH\textsubscript{4}:CO\textsubscript{2} = 2:1 feed ratio are under carbon favoring regime [see Figure A.8], and thus the carbon formed is significant for this ratio as compared to the other ratios. In this regime, both catalysts form almost equivalent amount of carbon. The fact that there is no significant decrease in X\textsubscript{CH\textsubscript{4}} with time for either catalyst [Figure A.7 (a)] may be explained by the reaction conditions (e.g., temperature) being sufficiently severe that the deactivated portion of the catalyst beds does not affect the observed X\textsubscript{CH\textsubscript{4}}. Figure A.9 (a-c) shows the TPO plots for the two catalysts after 200 minutes of reaction at CH\textsubscript{4}:CO\textsubscript{2} feed ratios of 1:1, 1:2 and 2:1 at 785°C.
Figure A.9. TPO profiles for catalyst treated with reactant feed ratios of a) 1:1, b) 1:2, and c) 2:1 at pressure of 1 atm, space velocity of 18,000 mL g$_{\text{cat}}$ h$^{-1}$, and bed temperature of 785°C.
CH$_4$:CO$_2$ = 1:1. TPO results for the catalysts treated with an equimolar gas flow rate (CH$_4$:CO$_2$ = 1:1) are shown in Figure A.9 (a). LSRuZ showed a single peak at 660°C which can be attributed to the deposition of carbon on the oxide surface of the catalyst as observed earlier by Haynes, et al [14]. For the 0.5% Ru/Al$_2$O$_3$ catalyst, a large peak was observed at 640°C with a shoulder at 760°C. Qualitatively, the carbon associated with the 660°C and 640°C peaks would appear to be the same species of carbon, likely attributable to the carbon deposited near the Ru-Al$_2$O$_3$ interface on the 0.5% Ru/Al$_2$O$_3$ [14]. The quantity of the carbon formed per gram of Ru was higher in the case of the 0.5% Ru/Al$_2$O$_3$ catalyst at all the three investigated reactant ratios. This may be due to the fact that partial substitution of Sr for La creates structural defects in the crystal lattice thus promoting higher oxygen ion mobility, limiting carbon formation [11, 14, 23].
CH$_4$:CO$_2$ = 1:2. For the catalysts treated with a reactant feed ratio of CH$_4$:CO$_2$ = 1:2, results showed three peaks on LSRuZ and four peaks on 0.5% Ru/Al$_2$O$_3$ catalyst [Figure A.9 (b)]. For LSRuZ, the presence of a peak at a lower temperature of 180°C indicated the presence of a relatively reactive carbon species, which is probably polymeric in nature and deposited on or near the active Ru sites [24]. Apart from this peak, two small peaks were observed on LSRuZ at 580°C and at 640°C. The proximity of these peaks indicates that two kinds of carbon species were present on the surface which had similar reactivity. These peaks at relatively higher temperatures could be due to the carbon deposited on the oxide surface, as observed earlier in Figure A.9 (a) and previously reported by Haynes, et al [14].

On the 0.5%Ru/Al$_2$O$_3$ catalyst, the peak at 200°C suggests the presence of polymeric carbon species (as observed in LSRuZ) which is located on or very near the active metal. The other two peaks at 440°C and 510°C can be attributed to the carbon present at the metal-support interface [14, 23, 24]. The peak observed at 840°C could indicate the presence of carbon deposited on the alumina support. The amount of carbon deposited on 0.5% Ru/Al$_2$O$_3$ (0.054 g$_{\text{carbon}}$/g$_{\text{Ru}}$) was more than that deposited on pyrochlore (0.041 g$_{\text{carbon}}$/g$_{\text{Ru}}$). Of particular importance in these results is that the amount of carbon deposited (per g$_{\text{Ru}}$) on both catalysts was less than that observed when the inlet reactant feed ratio of 1:1. This is due to the fact that with excess CO$_2$ in the feed, the formation of carbon is thermodynamically limited (Figure A.8) [25].

CH$_4$:CO$_2$ = 2:1: For CH$_4$:CO$_2$ = 2:1, TPO in Figure A.9 (c), shows that carbon formation was observed over both catalysts, but the quantity of carbon was again higher for the 0.5% Ru/Al$_2$O$_3$ catalyst viz., 0.406 g$_{\text{carbon}}$/g$_{\text{Ru}}$ compared to the LSRuZ, which showed 0.393 g$_{\text{carbon}}$/g$_{\text{Ru}}$. Also, the amount of carbon formed per g$_{\text{Ru}}$ for both catalysts was greater than that observed for the other reactant feed ratios i.e. 1:1 and 1:2, confirming the expected effect of higher
concentrations of CH\textsubscript{4} in the feed (see Figure A.8). The TPO profiles in Figure A.9 (c) shows that the species of carbon deposited on both catalysts had nearly the same reactivity. Peak at 640 °C for LSRuZ is attributed to the presence of carbon present on the oxide surface and peak at 610 °C for Ru/Al\textsubscript{2}O\textsubscript{3} is attributed to the carbon present on metal-support interface as mentioned earlier for TPO profile for ratio 1:1. These TPO peak positions indicate that similar carbon species were deposited on or near the surface metal atoms for both catalysts as observed in an earlier study [14]. Peaks present on both catalysts at higher temperatures, 770°C for LSRuZ and 790°C for Ru/Al\textsubscript{2}O\textsubscript{3} may also indicate the presence of graphitic carbon which is highly resistant towards oxidation [11].

A.3.7.2. Characterization of the Spent Catalysts by XRD

Figure A.10 shows the XRD pattern for the LSRuZ pyrochlore catalyst after experiments at 635°C, 735°C, and 835°C for 410 min.

![XRD pattern for LSRuZ pyrochlore catalyst](image)

Figure A.10. Comparison of the XRD patterns for fresh and catalysts spent at different temperatures.
To compare the results, the diffraction pattern of the fresh catalyst is also included in the same figure. The diffraction pattern of the catalyst spent after reaction at all temperatures is identical to diffraction pattern of the fresh catalyst, confirming that the catalyst retained its pyrochlore structure even after exposure to reducing conditions at such high reaction temperatures. The presence of a perovskite phase was not detected for the spent catalysts, meaning that high temperatures did not result in segregation of Sr from the bulk of pyrochlores to form a detectable separate perovskite phase.

A.4. Conclusion

The pre- and post-reaction XRD results show that the pyrochlore maintained its crystalline structure after the exposure to CH₄/CO₂ reforming conditions at temperatures up to 835°C. The XPS results show that the 92% of the surface Ru species for the fresh calcined pyrochlore are in the Ru⁴⁺ state with minor amount of Ru⁰, whereas for Ru/Al₂O₃ the major portion of the surface was comprised of RuO₂, RuO₃ and RuO₄ species. XPS and TPR results show that there was little Ru at the pyrochlore surface which means that a substantial part of the metal was substituted into the pyrochlore structure unlike the 0.5% Ru/Al₂O₃ catalyst, as expected. Study of the catalyst activity under varying temperatures (635°C, 735°C, and 835°C) shows that the H₂/CO ratios are significantly lower than the equilibrium values while the X_CO₂ for both catalysts at 635°C and 735°C is higher than the thermodynamic equilibrium value at these temperatures. This may be due to the relative rate of RWGS being greater than the competing reactions which consume CO₂ i.e., DRM and the reverse Boudouard reaction.
The $X_{\text{CO}_2}$ is near equilibrium at 835°C for both the catalysts. At 635°C, $X_{\text{CH}_4}$ for 0.5% Ru/Al$_2$O$_3$ showed a significant decrease with time suggesting occurrence of methane decomposition resulting in C(s) deposition to a larger extent compared to LSRuZ. At 735°C and 835°C, the $X_{\text{CH}_4}$ for both the catalysts was similar and reached equilibrium unlike $X_{\text{CH}_4}$ at 635°C. For feed ratio CH$_4$:CO$_2$ = 1:1, $X_{\text{CH}_4}$ for 0.5% Ru/Al$_2$O$_3$ was greater than LSRuZ, primarily due to CH$_4$ decomposition occurring to a larger extent over 0.5% Ru/Al$_2$O$_3$ than LSRuZ. This was confirmed by the TPO of the two catalysts for this feed ratio.

Both the catalysts had similar $X_{\text{CO}_2}$ and reached equilibrium for ratio 1:1 at 785°C. When the feed ratio was 1:2, $X_{\text{CO}_2}$ for Ru/Al$_2$O$_3$ showed a statistically significant increase with respect to time suggesting a greater rate of the RWGS reaction over Ru/Al$_2$O$_3$ compared to LSRuZ. The $X_{\text{CH}_4}$ for both catalysts was near equilibrium for feed ratio 1:2 at 785°C. When the feed ratio was 2:1, the $X_{\text{CH}_4}$ for 0.5% Ru/Al$_2$O$_3$ was greater than the LSRuZ due to methane decomposition resulting in C(s) formation which is confirmed in the TPO results. For 2:1 ratio, the $X_{\text{CO}_2}$ value was near equilibrium for both the catalysts. The experimental H$_2$/CO ratio values were significantly lower than the equilibrium value at all feed ratios for both the catalysts. Lower H$_2$/CO ratio in the product gas means there was more CO formed and less C(s) which suggests that both the catalysts were kinetically inhibiting C(s) formation at conditions that thermodynamically favors C(s) deposition. The TPO profiles of the catalysts show that carbon formed over 0.5% Ru/Al$_2$O$_3$ was more than that formed over LSRuZ at all the feed ratios, showing that LSRuZ kinetically inhibits C(s) formation compared to 0.5% Ru/Al$_2$O$_3$. 

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A.5. References


Appendix B: Academic Activity

B.1. Journal Publications


B.2. National Conference Presentations (Presenter Underlined)


2. D. Pakhare, V. Schwartz, V. Abdelsayed, D. Haynes, D. Shekhawat, J. Spivey, “Kinetic and transient studies of dry (CO$_2$) reforming of CH$_4$ over Rh substituted lanthanum
zirconate (La$_2$Zr$_2$O$_7$) pyrochlores”, 247$^{\text{th}}$ American Chemical Society (ACS) National Meeting, Dallas, TX, March 16 – 20, 2014.


B.3. **International Conference Presentations** (Presenter Underlined)


B.4. **Awards and Honors**


2. Koke’s Travel Award for the 23$^{rd}$ North American Catalysis Society (NACS) meeting, June 2013, Louisville, KY.

3. Travel grant from 10$^{th}$ Natural Gas Conversion Symposium committee, March 2013, Doha, Qatar.

4. Coates Travel Award for 10$^{th}$ Natural Gas Conversion Symposium, March 2013, Doha, Qatar.

5. Best poster award from 175 posters at the 10$^{th}$ Natural Gas Conversion Symposium, March 2013, Doha, Qatar.
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Title: Role of metal substitution in lanthanum zirconate pyrochlores (La2Zr2O7) for dry (CO2) reforming of methane (DRM)

Author: Devendra Pakhare

Publication: Applied Petrochemical Research

Publisher: Springer

Date: Jan 1, 2012

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Title: Characterization and activity study of the Rh-substituted pyrochlores for CO2 (dry) reforming of CH4

Author: Devendra Pakhare

Publication: Applied Petrochemical Research

Publisher: Springer

Date: Jan 1, 2013

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C.5. Permission to Use Appendix A

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Title: CO2 Reforming of CH4 over Ru-Substituted Pyrochlore Catalysts: Effects of Temperature and Reactant Feed Ratio

Author: Sarthak Gaur, Devendra Pakhare, Hongyi Wu, Daniel J. Haynes, and James J. Spivey

Publication: Energy & Fuels

Publisher: American Chemical Society

Date: Apr 1, 2012

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Appendix D: Proof of Principal Authorship

D.1. Proof for Chapter 2

A review of dry (CO₂) reforming of methane over noble metal catalysts

Devendra Pahare and James Spivey*

Dry CO₂ reforming of methane (DRM) is a well-studied reaction that is of both scientific and industrial importance. This reaction produces syngas that can be used to produce a wide range of products, such as hydrogen and ammonia, by means of Fischer-Tropsch synthesis. DRM is intrinsically accompanied by deactivation due to carbon deposition. DRM is also a highly exothermic reaction and requires operating temperatures of 800–1000 °C to attain high equilibrium conversion of CH₄ and CO₂ to H₂ and CO and to minimize the thermodynamic driving force for carbon deposition. The most widely used catalysts for DRM are based on Ni. However, many of these catalysts undergo severe deactivation due to carbon deposition. Noble metal catalysts have been studied and are typically found to be much more resistant to carbon deposition than Ni catalysts, but are generally uneconomical. Noble metals can also be used to promote the Ni catalysts in order to increase their resistance to deactivation. In order to design catalysts that minimize deactivation, it is necessary to understand the elementary steps involved in the activation and conversion of CH₄ and CO₂. This review will cover DRM literature for catalysts based on Rh, Ru, Pt, and Pd metals. This includes the effect of these noble metals on the kinetics, mechanism, and deactivation of these catalysts.

1. Introduction

1.1. Rationale for studying DRM

Fossil fuels are our major source of energy and have a great impact on human welfare. With the depletion of these fossil fuels due to continuously increasing energy demand, there is a need to investigate ways to utilize the available resources like natural gas reserves to produce fuels and chemicals that are

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James Spivey received BS and MS degrees in Chemical Engineering from NC State University and a PhD in the same field from Louisiana State University (LSU). He is currently the James Stiven Professor of Chemical Engineering at LSU, where his research interests focus on the use of heterogeneous catalysts for the conversion of syngas and low molecular weight hydrocarbons to high energy and higher value chemicals.
D.2. Proof for Chapter 3
DOI 10.1007/s12303-012-0014-6

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Role of metal substitution in lanthanum zirconate pyrochlores
(La$_2$Zr$_2$O$_7$) for dry (CO$_2$) reforming of methane (DRM)

Devendra Pakhare · Daniel Haynes ·
Dushyant Shelkawat · James Spivey

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Abstract Dry (CO$_2$) reforming of methane (DRM) produces syngas with H$_2$/CO ratio of ≤1. In this work, we report the use of pyrochlores (A$_2$B$_2$O$_7$) as catalysts for this reaction. Here, we examine lanthanum zirconate pyrochlores, LZ, with lanthanum and zirconium occupying the A and B sites, respectively. Three catalysts are tested: LZ and two pyrochlores in which the B-site has been isomorphically substituted with (a) Ru (2 wt%) (designated LRuZ) and (b) Pt (3.78 wt%) (designated LPtZ). These levels of substitution by weight correspond to identical atomic levels of substitution at the B-site. The effect of isomorphic substitution of Ru and Pt on the structure and activity of the pyrochlores in DRM is studied in this work. ICP-OES, XRD, H$_2$ and CH$_4$ TPR were used to characterize the structure of the catalysts. XRD results confirmed the formation of the La$_2$Zr$_2$O$_7$ phase in the bulk of the pyrochlores. H$_2$ TPR showed higher reduction temperatures for LPtZ compared to LRuZ, suggesting a less reducible, stable Pt in the pyrochlores structure compared to Ru. Quantitative analysis showed that LRuZ consumed 0.534 mg H$_2$/gcat, whereas LPtZ consumed only 0.161 mg H$_2$/gcat, corresponding to much greater extent of reduction for LRuZ compared to LPtZ. CO formation during CH$_4$ TPR showed that both materials have reactive lattice oxygen which helps in reducing carbon formation during DRM.

Temperature programmed oxidation studies of the catalyst immediately after CH$_4$ TPR showed greater carbon formation over LPtZ (1.67 g$_{C}/g_{cat}$) compared to LRuZ (1.17 g$_{C}/g_{cat}$) suggesting that Pt activates CH$_4$ to a greater extent compared to Ru. Temperature programmed DRM surface reaction showed that the light off temperature for LRuZ was about 45 °C lower than that of LPtZ. These are novel results and constitute the first report of which we are aware for Pt and Ru substituted pyrochlores for DRM.

Keywords Dry reforming · Lanthanum zirconate · Pyrochlores · Lattice oxygen · Isomorphic substitution · Penyvskite

Introduction

Dry reforming of methane (DRM) produces commercially important syngas that can be used for chemical processes like Fischer–Tropsch or synthesis of various chemicals [5, 6]. One of the problems associated with DRM is catalyst deactivation due to carbon deposition [3, 5, 8]. In addition to carbon deposition, DRM is highly endothermic reaction (ΔH$_{298K}$ = 59.1 kJ mol$^{-1}$) and requires temperatures approaching 900–1,000 °C to reach high equilibrium syngas yields. These temperatures lead to sintering of conventional supported metal catalysts. Thus, there is a need to develop catalysts that will reduce carbon formation due to sintering and carbon deposition [2, 11, 20, 23]. Pyrochlores are ternary metal oxides based on the fluorite structure with general formula of A$_2$B$_2$O$_7$ [25]. Large cations like rare earth elements occupy the A-site, whereas the B-site is occupied by a transition metal with a smaller atomic radius [16]. The pyrochlore structure allows limited isomorphic substitution of catalytically active metals like Ru, Rh, Pt at the B-site

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D.3. Proof for Chapter 4

Effect of reaction temperature on activity of Pt- and Ru-substituted lanthanum zirconate pyrochlores (La$_{2}$Zr$_{2}$O$_{7}$) for dry (CO$_{2}$) reforming of methane (DRM)

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ABSTRACT

Dry (CO$_{2}$) reforming of methane (DRM) is a highly endothermic reaction ($\Delta H^\text{f} = +391$ kcal/mol) producing syngas (H$_{2}$ and CO) with the H$_{2}$/CO ratio of ~1. DRM requires reaction temperatures above ~800 $^\circ$C for complete equilibrium conversion to CO and H$_{2}$, and is inevitably accompanied by carbon deposition. Here we examine lanthanum zirconate (La$_{2}$Zr$_{2}$O$_{7}$) pyrochlores, with the larger trivalent cation La and a smaller tetravalent cation Zr occupying A and B sites, respectively. Three catalysts are tested: La$_{2}$Zr$_{2}$O$_{7}$ [12] and two pyrochlores in which the B-site has been isomorphically partially substituted with (a) Ru [2.00 wt%] [RuZ] and (b) Pt (3.78 wt%) [PtZ]. The levels of substitution by weight correspond to identical atomic levels of substitution at the B-site. Here, activation energies are determined as a function of Ru or Pt substitution on the B-site. The results show that activation energies based on both CH$_{4}$ and CO$_{2}$ reaction rates are much lower for RuZ than PtZ. Conversion of CH$_{4}$ (X$_{CH_{4}}$) and CO$_{2}$ (X$_{CO_{2}}$) was greater for RuZ compared to PtZ at 525°C, 575°C, and 625°C throughout an on-stream time of 600 min. After each 600-min run, temperature programmed oxidation (TPO) showed that total carbon formation decreased with increasing reaction temperature, although the stability of the deposited carbon increased with increasing reaction temperature.

1. Introduction

Dry reforming of methane (DRM) produces synthesis gas with H$_{2}$/CO ratio of ~1 [1], which can be used for processes like Fischer-Tropsch synthesis of various chemicals [2–6]. Both CH$_{4}$ and CO$_{2}$ are potentially valuable feedstocks for synthesizing commercially important higher-value products [7]. However, one of the major problems associated with DRM is catalyst deactivation due to carbon deposition [2,4,8]. In addition to carbon deposition, DRM is highly endothermic reaction and requires temperatures above ~800 $^\circ$C to achieve high equilibrium syngas yields. These temperatures lead to deactivation due to sintering of conventional supported metal catalysts [9–12].

Pyrochlores are thermally stable ternary metal oxides with general formula of A$_{2}$B$_{2}$O$_{7}$ [13,14]. Large cations like rare earth elements usually occupy the A-site and transition metals occupy the B-site [15]. Isomorphic substitution of catalytically active metals like Ru or Pt in the B-site produces thermally stable and active catalysts that are resistant to carbon formation due to increased oxygen conductivity within the lattice [15]. Perhaps the most widely studied catalysts for the DRM reaction are based on Ni due to its low cost and availability; however, many Ni-based catalysts undergo severe deactivation due to carbon deposition [8,16–19]. Metals like Pt and Ru can be used to inhibit carbon formation [7].

Despite the well-known thermal stability of pyrochlores [13,15], we are aware of only one study of these materials for DRM other than our group, i.e., by Asgharli et al. [20]. In that paper, Asgharli et al. studied Eu$_{2}$Ir$_{2}$O$_{7}$ pyrochlores with Eu occupying the A-site and the catalytically active metal Ir occupying the B-site. Above 342°C, these materials completely decomposed to Eu$_{2}$O$_{3}$ and Ir metal.

Here, we report the DRM reaction over two substituted pyrochlores in which Ru or Pt is substituted at the B site at equal atomic levels. These materials have been characterized and reported in our earlier work [21]. Here, we determine the activation energies for the reaction rates based on both CH$_{4}$ and CO$_{2}$ over these materials. The DRM reaction was carried out at 525°C, 575°C, and 625°C for 600 min and the conversion of CH$_{4}$ and CO$_{2}$ formation of H$_{2}$ and CO was monitored as a function of time. The reaction was followed by temperature programmed oxidation to characterize the carbon formed over the catalyst.
Characterization and activity study of the Rh-substituted pyrochlores for CO₂ (dry) reforming of CH₄

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Abstract Isomorphic substitution of Rh at varying levels on the B site of lanthanum zirconate pyrochlore (La₂Zr₂O₇, designated LZ) resulted in the formation of thermally stable catalysts suitable for fuel reforming reactions operating at 900 °C. Three specific catalysts are reported here: (a) unsubstituted lanthanum zirconate (LZ), (b) LZ with 2 wt% substituted Rh (L2RhZ), and (c) LZ with 5 wt% substituted Rh (L5RhZ). These catalysts were characterized by XRD, XPS, and H₂-TPR. XRD of the fresh, calcined catalysts showed the formation of the pyrochlore phase (La₂Zr₂O₇) in all three materials. In L5RhZ, the relatively high level of Rh substitution led to the formation of LaRhO₃ perovskite phase which was not observed in the L2RhZ and LZ pyrochlores. TPR results show that the L5RhZ consumed 1.57 mg H₂/gcat, which is much greater than the 0.508 H₂/gcat and 0.155 mg H₂/gcat for L2RhZ and LZ, respectively, suggesting that the reducibility of the pyrochlore structure increases with increasing Rh-substitution. DRM was studied on these three catalysts at three different temperatures of 550, 575, and 600 °C. The results showed that CH₄ and CO₂ conversion was significantly greater for L5RhZ compared to L2RhZ and no activity was observed for LZ, suggesting that the surface Rh sites are required for the DRM reaction. Temperature programmed surface reaction showed that L5RhZ had light-off temperature 80 °C lower than L2RhZ. The spent catalysts after runs at each temperature were characterized by temperature programmed oxidation (TPO) followed by temperature programmed reduction and XRD. The TPO results showed that the amount of carbon formed over L5RhZ is almost half of that formed on L2RhZ.

Keywords Dry reforming · Lanthanum zirconate · Pyrochlores · Lattice oxygen · Isomorphic substitution · Perovskite · Reverse water gas shift

Introduction

Pyrochlores are a class of ternary metal oxides based on the fluorite structure with a cubic unit cell with a general formula of A₂B₂O₇. An important property of these materials is that catalytically active noble metals can be substituted isomorphically on the B site to form a crystalline catalyst. These materials consist of vacancies at the A and O sites, which facilitate oxygen ion migration within the structure [1]. The A site is usually a large cation (typically rare earth elements) and the B site cations have a smaller radius (usually transition metal) [2]. For the pyrochlore structure to be stable it is necessary that the ionic radius ratio of A and B site cations be between 1.46 and 1.78 [1]. The ratio of the ionic radii for La₂Zr₂O₇ is 1.61 [3]. If the ratio of the ionic radii is greater than 1.78, a perovskite phase can be formed. Below a ratio of 1.46 a fluorite structure is formed [4]. Catalytically active metals like Ru, Rh, Pt can be
CO₂ Reforming of CH₄ over Ru-Substituted Pyrochlore Catalysts: Effects of Temperature and Reactant Feed Ratio

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Abstract: Dry reforming of methane (DRM) was performed on a 1% Ru-substituted lanthanum strontium carbonate pyrochlore, La₄₋₁ₓSrₓRu₂O₇₋₁ₓO₂₋₁ₓ (LSRu₂O₇₋₁ₓ), and results were compared to a commercially available 0.5% Ru/Al₂O₃ catalyst at different bed temperatures and reactant feed ratios. X-ray diffraction of the fresh LSRu₂O₇₋₁ₓ confirmed the formation of the La₄₋₁ₓSrₓRu₂O₇₋₁ₓ pyrochlore face-centered cubic lattice using a modified Pechini synthesis procedure. Results from X-ray photoelectron spectroscopy (XPS) on the fresh calcined pyrochlore showed the presence of RuO₂, which was also present along with both RuO₂ and RuO₃ in the 0.5% Ru/Al₂O₃ catalyst. Temperature-programmed reduction (TPR) showed that Ru was reducible in both catalysts, but the primary TPR peak for Ru reduction was 140 °C higher for the LSRu₂O₇₋₁ₓ pyrochlore than that for 0.5% Ru/Al₂O₃ consistent with the incorporation of Ru within the pyrochlore. The effect of the CH₄/CO₂ feed ratio on the activity was studied by varying the feed ratio at 1:1, 2:1, and 1:2 at a constant temperature of 775 °C. At 633 °C, 0.5% Ru/Al₂O₃ showed higher apparent CO₂ conversion (XCO₂) and a lower H₂/CO ratio in the product gas than the LSRu₂O₇₋₁ₓ pyrochlore, suggesting that the extent of the reverse water-gas shift (RWGS) reaction was greater on 0.5% Ru/Al₂O₃. At 833 °C, equilibrium conversion of CH₄ and CO₂ were reached on both catalysts and remained constant with time over 7 h. There were no significant differences in XCO₂ and XH₂ between the two catalysts with time on stream at 735 and 833 °C. The effect of the CH₄/CO₂ inlet feed ratio on products was also studied at a constant space velocity for both catalysts. Results showed that, for CH₄/CO₂ = 1:2, XCO₂ for 0.5% Ru/Al₂O₃ was 70% and a H₂/CO ratio of about 0.60 compared to 62% and 0.63 for the pyrochlore. The higher XCO₂ and lower H₂/CO ratio for 0.5% Ru/Al₂O₃ suggest that the RWGS reaction on this catalyst is kinetically faster than on LSRu₂O₇₋₁ₓ. For CH₄/CO₂ = 2:1, XCO₂ of 0.5% Ru/Al₂O₃ was 62% and that for pyrochlore was 58%. This small but statistically significant difference indicates slightly higher CH₄ decomposition over 0.5% Ru/Al₂O₃ than pyrochlore at this feed ratio. Temperature-programmed oxidation (TPO) of the post-run catalysts showed that the LSRu₂O₇₋₁ₓ catalyst formed less oxidizable carbon per gram of reducible Ru (C₆H₁₂O₆) compared to 0.5% Ru/Al₂O₃ likely because of the greater oxygen mobility in the pyrochlore.

1. Introduction

Dry reforming of CH₄ (DRM) has received considerable attention in recent years and as a means of using carbon-free energy sources, such as solar or wind, to capture and store or transport this clean energy in the form of CO and H₂. A major limitation of DRM is catalyst deactivation, which has generally been attributed to either sintering of the active metal or carbon formation on active sites of the catalyst. Deactivation because of carbon formation on metallic sites is generally thought to be caused by either CH₄ decomposition and/or the Boudouard reaction (CO disproportionation). Dependence on the reaction conditions and the reactant composition, carbon build-up can be thermodynamically favorable and must be kinetically limited. Decomposition of CH₄ is favored at high temperatures, whereas the Boudouard reaction is favored at low temperatures. To thermodynamically limit carbon formation, DRM at a CH₄/CO₂ ratio of less than 1 has to be operated at T > 800 °C. Carbon deposition also depends upon the active metal. In general, the noble metals (Rh, Ru, Pt, Pd, and Ir) have been shown to be more resistant toward deactivation by carbon than non-noble metals, such as Ni. At the same time, the limited availability and higher cost of these noble metals prohibit their commercial application. Ni has been the preferred catalyst for dry reforming because of its lower cost and appreciable activity. However, Ni-based catalysts are prone to rapid deactivation because of carbon formation. It has been proposed that metal oxide supports having strong Lewis basicity help to reduce deactivation because of carbon formation. Pyrochlores have the empirical formula A₂B₂O₇, where “A” is a rare-earth element and “B” is a transition element. These pyrochlores have a defect fluorite structure and possess ordered cations (A and B), oxygen anions (O), and vacancies (O<sup>−</sup>), with the A, B, O, and O<sup>−</sup> sites occupying the 16d, 16e, 4f, and 8b sites, respectively. Substitution of metals at the A and B sites in certain pyrochlore formulations yields a refractory material that...
LSRuZ, which showed 0.365 gcarbon/gRu. Also, the amount of carbon formed per unit surface area for both catalysts was greater than that observed for the other reactant feed ratios, i.e., 1:1 and 1:2, confirming the expected effect of higher concentrations of CH₂ in the feed (see Figure 8). The TPO profiles in Figure 9c show that the species of carbon deposited on both catalysts had nearly the same reactivity. The peak at 640 °C for LSRuZ is attributed to the presence of carbon present on the oxide surface, and the peak at 610 °C for Ru/Al₂O₃ is attributed to the carbon present on the metal-support interface, as mentioned earlier for the TPO profile for the ratio of 1:1. These TPO peak positions indicate that similar carbon species were deposited on or near the surface metal atoms for both catalysts, as observed in an earlier study. Peaks present on both catalysts at higher temperatures, 770 °C for LSRuZ and 790 °C for Ru/Al₂O₃, may also indicate the presence of graphitic carbon, which is highly resistant toward oxidation.

3.7.2 XRD Studies of the Spent Catalysts. Figure 10 shows the XRD pattern for the LSRuZ pyrochlore catalyst after experiments at 635, 735, and 835 °C for 410 min. To compare the results, the diffraction pattern of the fresh catalyst is also included in the same figure. The diffraction pattern of the catalyst after the reaction at all temperatures is identical to the diffraction pattern of the fresh catalyst, confirming that the catalyst retained its pyrochlore structure even after exposure to reducing conditions at such high reaction temperatures. The presence of a perovskite phase was not detected for the spent catalysts, meaning that high temperatures did not result in segregation of Sr from the bulk of pyrochlores to form a detectable separate perovskite phase.

4. CONCLUSION
The pre- and post-reaction XRD results show that pyrochlore maintained its crystalline structure after exposure to CH₄/CO₂ reforming conditions at temperatures up to 835 °C. The XPS results show that 92% of the surface Ru species for the fresh calcined pyrochlore are in the RuO³⁺ state, with a minor amount of Ru²⁺, whereas for Ru/Al₂O₃, the major portion of the surface was comprised of RuO₂, RuO₂, and RuO₄ species. XPS and TPR results show that there was little Ru at the pyrochlore surface, which means that a substantial part of the metal was substituted into the pyrochlore structure, unlike the 0.8% Ru/Al₂O₃ catalyst, as expected. The study of the catalyst activity under varying temperatures (635, 735, and 835 °C) shows that the H₂/CO₂ ratio is significantly lower than the equilibrium values, while XCO₂ for both catalysts at 635 and 735 °C is higher than the thermodynamic equilibrium value at these temperatures. This may be due to the relative rate of RWGS being greater than the competing reactions that consume CO₂, i.e., DRM and the reverse Boudouard reaction.

XCO₂ is near equilibrium at 835 °C for both of the catalysts. At 635 °C, XCH₄ for 0.5% Ru/Al₂O₃ showed a statistically significant decrease with time, suggesting the occurrence of methane decomposition resulting in C(0) deposition to a larger extent compared to LSRuZ. At 735 and 835 °C, XCH₄ for both of the catalysts was similar and reached equilibrium, unlike XCH₄ at 635 °C. For the feed ratio CH₄/CO₂ = 1:1, XCH₄ for 0.5% Ru/Al₂O₃ was greater than that for LSRuZ, probably because of CH₄ decomposition occurring to a larger extent over 0.5% Ru/Al₂O₃ than LSRuZ. This was confirmed by the TPO of the two catalysts for this feed ratio.

Both of the catalysts had similar XCO₂ and reached equilibrium for the feed ratio of 1:1 at 785 °C. When the feed ratio was 1:2, XCO₂ for Ru/Al₂O₃ showed a statistically significant increase with respect to time, suggesting a greater rate of the RWGS reaction over Ru/Al₂O₃ compared to LSRuZ. XCO₂ for both catalysts was near equilibrium for the feed ratio of 1:2 at 785 °C. When the feed ratio was 2:1, XCH₄ for 0.5% Ru/Al₂O₃ was greater than that for LSRuZ because of methane decomposition resulting in C(0) formation, which is confirmed in the TPO results. For the 2:1 ratio, the XCO₂ value was near equilibrium for both of the catalysts. The experimental H₂/CO ratio values were significantly lower than the equilibrium value at all feed ratios for both of the catalysts. A lower H₂/CO ratio in the product gas means that there was more CO formed and less C(0), which suggests that some of the catalysts were kinetically inhibiting C(0) formation at conditions that thermodynamically favor C(0) deposition. The TPO profiles of the catalysts show that carbon formed over 0.5% Ru/Al₂O₃ was more than that formed over LSRuZ at all of the feed ratios, showing that the extent to which LSRuZ kinetically inhibits C(0) formation is greater than 0.5% Ru/Al₂O₃.

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**REFERENCES**

Vita

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