Metal-Support Interaction on Pt/ZrO₂ Catalysts for the CO₂ Reforming of CH₄

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Three forms of catalyst modification have been explored to elucidate the reaction mechanism and the role of the support in the CO₂ reforming of CH₄. The results of this study show that partial encapsulation of the metal does not significantly alter the catalytic performance and any differences in performance due to varying pretreatment conditions can be ascribed to variations in the particle size. In addition, promoters can be added to the support to increase the thermal stability, increase CO₂ adsorption capacity, and decrease particle growth. Finally, a Pt/ZrO₂-perovskite physical mixture has exhibited high stability for the reforming reaction in the presence of steam and under elevated pressures.

1. Introduction

As the interest into the reforming of CH₄ with CO₂ has grown, so has the research into finding a catalyst capable of operating at high temperatures and high pressures. In recent years, Pt/ZrO₂ catalysts have been shown to be very stable for the dry reforming reaction when operating at moderate temperatures, 650°C. However, when operating at higher temperatures, 800°C and CH₄:CO₂ ratios greater than 1, the catalyst experienced rapid deactivation due to carbon deposition. Previous studies [1] have provided evidence that on the Pt/ZrO₂ catalyst, the decomposition of CH₄ and the dissociation of CO₂ occur via two independent paths. The first path involves the decomposition of CH₄ on the metal particle, resulting in the formation of H₂. Carbon formed during the decomposition of CH₄ can partially reduce the oxide support near the metal particle or, in the absence of a reducible oxide, form carbon deposits on the metal. The second path is the dissociation of CO₂. The CO₂ adsorbs on the support and when near the metal particle dissociates to form CO and O. The oxygen formed during the dissociation can then reoxidize the support to provide a redox mechanism for continuous cleaning.

The aim of this paper was to study the reaction mechanism and the metal-support interaction on Pt/ZrO₂ catalysts. Specifically, modification of the catalyst by three different mechanisms was explored. First, it was observed that a high temperature reduction causes partial encapsulation of the metal by support species (SMSI-like effect), so the catalyst activity was examined after low and high temperature reduction to observe any effects of encapsulation. Second, promoters were added to the support to improve the reducibility and facilitate oxygen transfer to determine the role of the support in the reduction of carbon...
deposition. Third, a support that is known for high oxygen storage and release capacities was combined with a Pt/ZrO₂ catalyst in a physical mixture to gain an understanding of the role of the oxygen transfer in maintaining high catalytic performance.

2. Experimental

The zirconium hydroxide and lanthanum (5 wt %)-doped ZrO₂ were obtained from Magnesium Elektron Inc. The cerium-doped ZrO₂ was made by aqueous impregnation of cerium nitrate to the zirconium hydroxide. The incipient wetness of the Zr(OH)₄ was 0.2 cm³/g and the weight percent of Ce in the final material 5%. The Ce-doped support was prepared by adding the Ce⁴⁺ to the Zr(OH)₄. Two additional supports were obtained from MEI. The first Pt/Ce-ZrO₂ (Pt/CeZ (MEI)) had a Ce loading of approximately 18%. The second catalyst, which will be referred to as Pt/CoLaZ, contained both Ce and La at a loading of 18% and 5%, respectively. All supports were dried overnight at 110°C, and then calcined at 800°C for 4 h in stagnant air, prior to the impregnation of the metals. The Pt/ZrO₂ (Pt/Z), Pt/La-ZrO₂ (Pt/LaZ), Pt/Co-ZrO₂ (Pt/CoZ), Pt/CeZ (MEI), and Pt/CoLaZ catalysts were prepared by incipient wetness impregnation of a aqueous solution of H₂PtCl₆·6H₂O with a Pt loading of 1.5 wt %. The catalysts were dried overnight at 110°C, calcined in air (30 cm³/min) for 2 h at 400°C, and then reduced in-situ, in H₂ (30 cm³/min) at 500°C for 1 h, prior to reaction.

The LaCoO₃ support was made using a hydroxy acid aided synthesis, which has been described previously [2,3]. Malic acid was used in the synthesis using the appropriate nitrate precursors for the lanthanum and cobalt. After preparation the material was calcined at 800°C in air for 4 h.

3. Results and Discussion

3.1. Reaction Mechanism

Previous work performed by our group using ¹³C-labeled methane pulses has shown that partial reduction of the ZrO₂ support occurs during the decomposition of CH₄. Furthermore, when the catalyst was subsequently exposed to CO₂ pulses, both ¹³CO and ¹⁵CO were observed, indicating that dissociation of the CO₂ occurs, resulting in the removal of carbon from the metal. It was suggested that the oxygen vacancies generated during the decomposition of CH₄ are necessary for the dissociation of CO₂. DRIFTS experiments have been performed to elucidate the role of the vacancies in the dissociation of CO₂. The Pt/Z catalyst was oxidized and subsequently reduced in H₂ at 300°C and then exposed to CO₂ at 300°C. While in the CO₂ atmosphere, no CO was observed on the metal. After flushing in Ar, the catalyst was cooled to room temp and exposed to ethylene. The catalyst was then heated to 300°C in Ar, during which time a band at 2070 cm⁻¹, typical of linear CO adsorbed on reduced Pt, was observed. The appearance of this band suggests that during the decomposition of ethylene, a partial reduction of the support occurred resulting in the formation of CO. After flushing in Ar, the CO signal disappeared. At this point in the experiment, it can be envisioned that the surface of the catalyst is a partially reduced support with the oxygen vacancies located near the perimeter of the metal particle. Subsequent exposure to CO₂ at 300°C resulted in the appearance of the band at 2070 cm⁻¹, indicating that dissociation of the CO₂ vacancy plays an instrumental role.

As previously suggested, oxygen to the support, dissociation to occur after reduction. After the catalyst was flowed in H₂, ¹³CO was observed, indicating the presence of an isotopically labeled supported intermediate mechanism. CH₄ decomposition involves a partial reduction of the support, with CO₂ catalyzed dissociation occurring on the Pt surface, support providing a concentration gradient for the rate of decomposition of the catalyst.

3.2. Encapsulation

It has been previously shown that partial encapsulation of Pt provides increased activity [4]. We have performed high temperature reductant exposure treatments which shows the results of the reductant exposure as well as the H/Pt ratio after each.

![Fig. 1. H/Pt ratio for the catalyst after various reduction/oxidation treatments.](image)

A substantial decrease in the H/Pt ratio at temperature 500°C, coupled with the minimal particle growth on the catalyst after due to sintering could not be observed.
dissociation of the CO₂ had occurred. These results provide strong evidence that the oxygen vacancy plays an instrumental role in the dissociation of CO₂.

As previously suggested, if the oxygen from the dissociation of CO₂ replenished the oxygen to the support, eliminating the presence of the vacancies, one would expect no dissociation to occur after the initial exposure to CO₂. This was, in fact, what was observed. After the catalyst was flushed in Ar, the sample was re-exposed to CO₂ and no CO band was observed, indicating that no dissociation occurred. These experiments, along with the isotopically labeled studies performed previously, provide strong evidence for the two-path mechanism. CH₄ decomposition occurs on the metal resulting in the production of H₂ and a partial reduction of the support. The CO₂ adsorbs at the site of the oxygen vacancy and metal catalyzed dissociation occurs. The resultant oxygen replenishes the oxygen vacancy in the support providing a constant source of oxygen in a redox mechanism. The balance between the rate of decomposition and the rate of dissociation determines the overall stability of the catalyst.

3.2. Encapsulation

It has been previously suggested that a partial reduction of the support may result in partial encapsulation of the metal, and these new interfacial sites may be responsible for increased activity [4]. We have studied this possibility by investigating the effects of low and high temperature reduction on the chemisorption capacity and reforming activity. Figure 1 shows the results of the chemisorption capacity after low and high temperature reduction, as well as the H/Pt ratio after oxidation followed by low reduction.

A substantial decrease in the chemisorption capacity was observed after reduction at temperature 500°C, compared to the sample reduced at 200°C. TEM studies have shown that minimal particle growth occurs after reduction at 500°C, indicating that the loss of metal area due to sintering could not be solely responsible for the loss of chemisorption capacity.
Stronger evidence for a decoration of the metal by the support is demonstrated by the increase in chemisorption capacity after cycles of oxidation and low temperature reduction. Oxidation resulted in a removal of the support from the metal particle, which is demonstrated by the increase in exposed metal area. This reversibility by oxidation is a fingerprint for partial encapsulation and has been previously observed when studying catalysts, which are known to exhibit SMSI [5,6].

The H/Pt ratio after heating to 800°C in He provides a more accurate measurement of the metal area exposed under reaction conditions. The chemisorption capacity for the catalyst reduced at 200°C was significantly less after heating to 800°C. TEM and EXAFS studies have shown that the loss of Pt surface area is due to sintering of the metal. Similar studies have been performed on the catalyst reduced at 500°C. EXAFS studies have shown that the catalyst reduced at 500°C and then heated to 800°C has slightly larger particles than the catalyst reduced at 200°C followed by heating to 800°C. These results suggest that any difference in the chemisorption capacity after heating to 800°C is most likely due to differences in particle size rather than support decoration of the Pt particle.

Activity studies show that high temperature reduction resulted in a slight decrease in the initial activity and did not significantly alter the stability of the catalyst. The most probably explanation for the decreased activity is the decrease in the exposed metal area on the catalyst reduced at high temperatures as demonstrated by EXAFS, chemisorption, and TEM. These studies demonstrate that decoration of the Pt metal by ZrO₂ species is not responsible for the increased activity or stability of the Pt/ZrO₂ catalyst, and the increased performance is more likely due to the ability of the support to facilitate the dissociation of CO₂.

3.3. Promotion of the Support

We have previously shown that the addition of promoters, such as Ce and La, to the support can improve the stability of the catalyst under severely deactivating conditions [7]. Table 1 shows that conversion of CO₂ during an 18 hr reaction at 800°C and a CH₄:CO₂ ratio of 2:1 (GHSV 180,000 h⁻¹) for the Pt/Z, Pt/CoZ and the Pt/LaZ catalysts. The La-promoted and Ce promoted catalysts exhibited higher activity than the unpromoted catalyst, and increasing the loading of Ce improved the catalytic performance. The catalyst containing both Ce and La exhibited similar behavior as the unpromoted sample with only a slight increase in the initial activity.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial CO₂ Conversion</th>
<th>Final CO₂ Conversion</th>
<th>BET Surface Area (m²/gram)</th>
<th>CO₂ Desorption Capacity (mole/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Z</td>
<td>0.3</td>
<td>0.23</td>
<td>35</td>
<td>1x10⁻⁴</td>
</tr>
<tr>
<td>Pt/CoZ</td>
<td>0.39</td>
<td>0.24</td>
<td>39</td>
<td>7x10⁻⁵</td>
</tr>
<tr>
<td>Pt/LaZ</td>
<td>0.42</td>
<td>0.27</td>
<td>55</td>
<td>6x10⁻⁴</td>
</tr>
<tr>
<td>Pt/CoLaZ</td>
<td>0.33</td>
<td>0.24</td>
<td>49</td>
<td>----</td>
</tr>
<tr>
<td>Pt/CoZ (MEI)</td>
<td>0.41</td>
<td>0.31</td>
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</table>

Table 1. Activity, BET surface area, and CO₂ adsorption capacity data for Pt/Z, Pt/CoZ, Pt/LaZ, Pt/CoLaZ, and Pt/CoZ (MEI) catalysts.

Pulse experiments were conducted with the promoted ZrO₂ catalysts, showing increase in the number of active sites in the oxygen storage capacity and subsequent increase in the oxygen storage capacity. XRD studies have shown that the tetragonal phase of the ZrO₂ support has high temperature calcination increases adsorption capacity, which decreases with increasing temperature.

Finally, analysis of the catalysts showed that samples have larger particle size at 500°C reaction at 800°C the unreacted Pt/ZrO₂ promoted samples having larger particle growth increases, which decreases with increasing metal area, but not be previously, decreases the activity.

These results suggest that promoters can improve the catalytic performance of the Pt catalysts. This stabilization results in an increase in the activity of the adsorption sites near the Pt surface. This is not only due to increased residence time in the reaction, but also mainly due to the efficient cleaning of the catalyst. The promotes increase the efficiency of the oxygen storage capacity and catalyst stability.

3.4. Supports with High Temperature Stability

We prepared a La₂Zr₂O₇ perovskite material using XRD, BET, and SEM to determine the structure of the catalyst. No significant differences were found between the fresh catalyst and the catalyst after reaction. It was found that the perovskite materials might be promising for an abundant support material to provide an abundant support for the Pt/ZrO₂ catalyst. The perovskite materials might be promising for an abundant support material to provide an abundant support for the Pt/ZrO₂ catalyst.

Figure 3 shows the performance of the Pt/ZrO₂ catalyst during 10 h of reaction. The results of the Pt/ZrO₂ catalysts showed improvements were observed when the catalyst was exposed to reaction and then exposed to reaction again (Fig. 3) in which the performance
Pulse experiments, which have been reported elsewhere [8], have shown that the promoted ZrO₂ catalysts are more easily reduced in the presence of CH₄, indicating an increase in the number of oxygen vacancies formed with the addition of promoters. This increase in the oxygen vacancies results in an increase in the dissociation of CO₂ and a subsequent increase in the catalyst stability.

XRD studies have shown that the addition of the promoters helps to stabilize the tetragonal phase of the ZrO₂. This stabilization leads to an increase in the surface area after high temperature calcination, as shown in Table 1. In addition, the La-ZrO₂ support had a CO₂ adsorption capacity, which was five times greater than the unpromoted ZrO₂.

Finally, analysis of the EXAFS data for all three catalysts showed that the promoted samples have larger particles than the Pt/Z catalyst after reduction at 500°C. However, after reaction at 800°C the unpromoted catalyst had experienced significant particle growth, while the promoted samples had only minimal sintering. We have shown that as the amount of particle growth increases, so does the loss in activity. Sintering causes not only a loss in exposed metal area, but also reduces the metal-support interfacial area, which, as discussed previously, decreases the stability of the catalyst.

These results suggest that the addition of cerium and lanthanum to the support can improve the catalytic performance through several promotional effects. First, the promoters can increase the thermal stability of the catalyst by stabilizing the tetragonal phase of zirconia. This stabilization results in an increase in the surface area and an increase in the density of CO₂ adsorption sites near the metal particle. Second, the addition of promoters aids in retarding particle growth. This is not only beneficial for increasing the active metal surface exposed for reaction, but also maintains a high particle-support interfacial area which is crucial for efficient cleaning of the metal particle. Finally, it cannot be ruled out that the addition of the promoters increases the oxygen storage capacity of the support. It is possible that increasing the oxygen storage capacity can result in improved cleaning ability and higher catalyst stability.

### 3.4. Supports with High Oxygen Transfer and Storage Capacity

We prepared a LaCoO₃ perovskite support as described above and characterized this material using XRD, BET and O₂ TPD. The results of the XRD confirmed the perovskite structure after calcination at 800°C. BET surface area measurements showed that the LaCoO₃ support had a surface area of approximately 1.5 m²/g, which is significantly lower than the surface area measured for the ZrO₂ (35 m²/g) support. The TPD of O₂ experiments were performed to gain an understanding of the O₂ release capability of the perovskite support. It was found that at temperatures above 700°C, a substantial amount of O₂ was released from the support. This characteristic of the perovskite is strong support for the hypothesis that perovskite materials might be promising catalysts for the reforming reaction, due to the ability to provide an abundant source of oxygen, which would in turn reduce carbon deposition and catalyst deactivation.

Figure 3 shows the CO₂ conversion for a 1:1 physical mixture of LaCoO₃ and Pt/Z catalyst during 10 h of reaction at 800°C and a 2:1 ratio of CH₄:CO₂. For comparison, the results of the Pt/Z catalyst under similar conditions are included. No significant improvements were observed when the perovskite support was mixed with the Pt/Z catalyst and exposed to reaction at 800°C and 2:1 ratio of CH₄:CO₂. However, in a set of experiments (Fig. 3) in which the pressure drop at the reactor outlet was high, some water vapor
accumulated in the reactor. Under these conditions the physical mixture of Pt/Z and LaCoO₃ exhibited high activity and stability.

![Graph showing CO₂ fractional conversion for Pt/Z and Pt/Z-LaCoO₃ physical mixture during reaction at 800°C and a 2:1 ratio of CH₄:CO₂.](image)

Fig. 3. CO₂ fractional conversion for Pt/Z and Pt/Z-LaCoO₃ physical mixture during reaction at 800°C and a 2:1 ratio of CH₄:CO₂. Pt/Z (▲), Pt/Z-LaCoO₃ (○), Pt/Z-LaCoO₃ (presence of steam and elevated pressure) (□).

Similar studies have shown that a Pt/LaCoO₃ catalyst rapidly deactivates at 800°C and a 2:1 feed ratio of CH₄:CO₂ and that the activity can be regained by exposing the catalyst to CO₂. Furthermore, when the Pt/LaCoO₃ catalyst was exposed to reaction with steam and elevated pressure, the catalyst also exhibited high activity with no deactivation observed. Several explanations can be offered for the results observed on the perovskite and physical mixture. One explanation could be that the perovskite quickly loses the ability to provide oxygen to the metal at a rate sufficient enough to prevent carbon deposition. Another possibility is that the rate of oxygen transfer from the bulk to the surface is so fast that the oxygen vacancies necessary for CO₂ dissociation are filled before the dissociation can occur, resulting in an inhibition of the reaction. The results of these studies indicate that although the perovskite support does not appear to be beneficial in excess CH₄ and dry conditions, that this material could be a promising support for this reaction under elevated pressure and in the presence of steam.

1. INTRODUCTION

The CO₂ reforming of CH₄ to produce synthesis gas (CH₄:CO₂) can be used as a feed for Fischer-Tropsch synthesis and as a source of fuels and valuable oxygenates. The CO₂ steam reforming process is extremely high temperature and high pressure, while Ni-supported catalysts are most active at lower temperatures. The catalyst activity depends on the preparation method and pre-treatment conditions. Some catalysts deactivate by coking, while others deactivate by sintering. In this study, we report an investigation of the use of CeO₂ or MgO as support material for Ni catalysts, and the effect on catalytic activity and stability. This behavior was evaluated under various conditions.

REFERENCES