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Metal-Support Interaction on Pt/ZrO_2 Catalysts for the CO_2 Reforming of CH_4

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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 CO_2 reforming of CH_4. 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 CO_2 adsorption capacity, and decrease particle growth. Finally, a Pt/ZrO_2-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 to the reforming of CH_4 with CO_2 has grown, so has the research into finding a catalyst capable of operating at high temperatures and high pressures. In recent years, Pt/ZrO_2 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 CH_4:CO_2 ratios greater than 1, the catalyst experienced rapid deactivation due to carbon deposition. Previous studies [1] have provided evidence that on the Pt/ZrO_2 catalyst, the decomposition of CH_4 and the dissociation of CO_2 occur via two independent paths. The first path involves the decomposition of CH_4 on the metal particle, resulting in the formation of H_2. Carbon formed during the decomposition of CH_4 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 CO_2. The CO_2 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/ZrO_2 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/ZrO_2 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 ZrO_2 were obtained from Magnesium Elektron Inc. The cerium-doped ZrO_2 was made by aqueous impregnation of cerium nitrate to the zirconium hydroxide. The incipient wetness of the $Zr(OH)_4$ was 0.2 cm^3/g and the weight percent of Ce in the final material 5%. The Ce-doped support was prepared by adding the Ce^{4+} to the $Zr(OH)_4$. Two additional supports were obtained from MEI. The first Pt/Ce-ZrO_2 (Pt/CeZ (MEI)) had a Ce loading of approximately 18%. The second catalyst, which will be referred to as Pt/CeLaZ, 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/ZrO_2 (Pt/Z), Pt/La-ZrO_2 (Pt/LaZ), Pt/Ce-ZrO_2 (Pt/CeZ), Pt/CeZ (MEI), and Pt/CeLaZ catalysts were prepared by incipient wetness impregnation of an aqueous solution of $H_2PtCl_6.6H_2O$ with a Pt loading of 1.5 wt %. The catalysts were dried overnight at 110°C, calcined in air (30cm^3/min) for 2 h at 400°C, and then reduced *in-situ*, in H_2 (30 cm^3/min) at 500°C for 1 h, prior to reaction.

The $LaCoO_3$ 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 ^{13}C-labeled methane pulses has shown that partial reduction of the ZrO_2 support occurs during the decomposition of CH_4. Furthermore, when the catalyst was subsequently exposed to CO_2 pulses, both ^{13}CO and ^{12}CO were observed, indicating that dissociation of the CO_2 occurs, resulting in the removal of carbon from the metal. It was suggested that the oxygen vacancies generated during the decomposition of CH_4 are necessary for the dissociation of CO_2. DRIFTS experiments have been performed to elucidate the role of the vacancies in the dissociation of CO_2. The Pt/Z catalyst was oxidized and subsequently reduced in H_2 at 300°C and then exposed to CO_2 at 300°C. While in the CO_2 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 CO_2 at 300°C resulted in the appearance of the band at 2070 cm^{-1}, indicating that dissociation of the CO_2 had occurred. These results provide strong evidence that the oxygen vacancy plays an instrumental role in the dissociation of CO_2.

As previously suggested, if the oxygen from the dissociation of CO_2 replenished the oxygen to the support, eliminating the presence of the vacancies, one would expect no dissociation to occur after the initial exposure to CO_2. This was, in fact, what was observed. After the catalyst was flushed in Ar, the sample was re-exposed to CO_2 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. CH_4 decomposition occurs on the metal resulting in the production of H_2 and a partial reduction of the support. The CO_2 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.

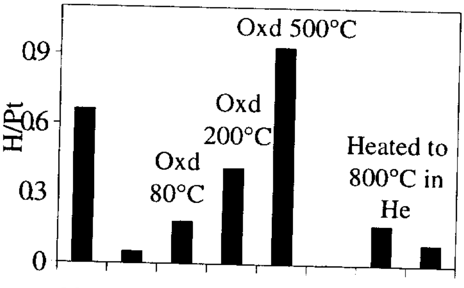

Fig. 1. H/Pt ratio for the Pt/ZrO_2 catalyst after various reduction/oxidation treatments.

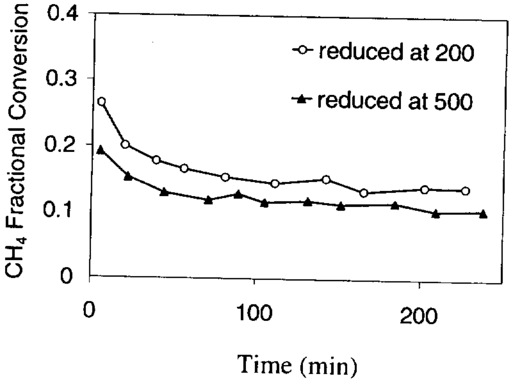

Fig. 2. CH_4 fractional conversion after reduction at 500°C and reduction at 200°C. Reaction at 800°C and a 2:1 ratio of CH_4:CO_2.

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 ZrO_x species is not responsible for the increased activity or stability of the Pt/ZrO_2 catalyst, and the increased performance is more likely due to the ability of the support to facilitate the dissociation of CO_2.

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 CO_2 during an 18 hr reaction at 800°C and a CH_4:CO_2 ratio of 2:1 (GHSV 180,000 h^{-1}) for the Pt/Z, Pt/CeZ 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.

Catalyst	Initial CO_2 Conversion	Final CO_2 Conversion	BET Surface Area m^2/gram	CO_2 Desorption Capacity moles/gram
Pt/Z	0.3	0.23	35	1×10^{-4}
Pt/CeZ	0.39	0.24	39	7×10^{-5}
Pt/LaZ	0.42	0.27	55	6×10^{-4}
Pt/CeLaZ	0.33	0.24	49	----
Pt/CeZ (MEI)	0.41	0.31	----	----

Table 1. Activity, BET surface area, and CO_2 adsorption capacity data for Pt/Z, Pt/CeZ, Pt/LaZ, Pt/CeLaZ, and Pt/CeZ (MEI) catalysts.

Pulse experiments, which have been reported elsewhere [8], have shown that the promoted ZrO_2 catalysts are more easily reduced in the presence of CH_4, 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 CO_2 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 ZrO_2. This stabilization leads to an increase in the surface area after high temperature calcination, as shown in table 1. In addition, the La-ZrO_2 support had a CO_2 adsorption capacity, which was five times greater than the unpromoted ZrO_2.

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 expose 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 the density of CO_2 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 $LaCoO_3$ perovskite support as described above and characterized this material using XRD, BET and O_2 TPD. The results of the XRD confirmed the perovskite structure after calcination at 800°C. BET surface area measurements showed that the $LaCoO_3$ support had a surface area of approximately 1.5 m^2/g, which is significantly lower than the surface area measured for the ZrO_2 (35 m^2/g) support. The TPD of O_2 experiments were performed to gain an understanding of the O_2 release capability of the perovskite support. It was found that at temperatures above 700°C, a substantial amount of O_2 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 CO_2 conversion for a 1:1 physical mixture of $LaCoO_3$ and Pt/Z catalyst during 10 h of reaction at 800°C and a 2:1 ratio of CH_4:CO_2. 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 CH_4:CO_2. 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 $LaCoO_3$ exhibited high activity and stability.

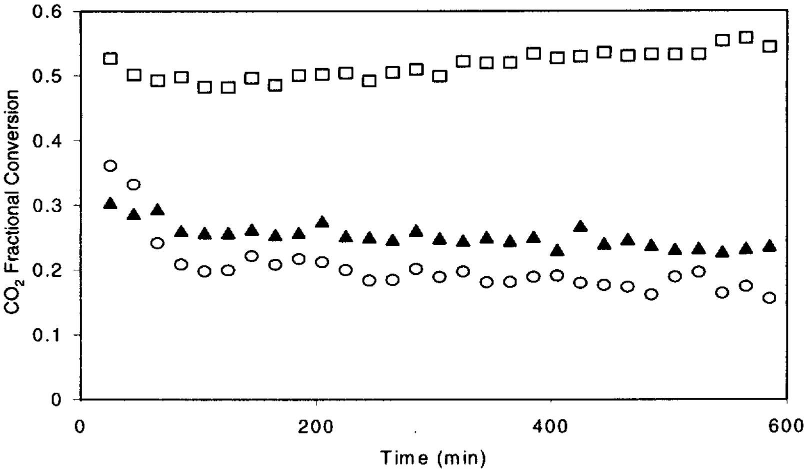

Fig. 3. CO_2 fractional conversion for Pt/Z and Pt/Z-$LaCoO_3$ physical mixture during reaction at 800°C and a 2:1 ratio of CH_4:CO_2. Pt/Z (▲), Pt/Z-$LaCoO_3$ (○), Pt/Z-$LaCoO_3$ (presence of steam and elevated pressure) (□).

Similar studies have shown that a Pt/$LaCoO_3$ catalyst rapidly deactivates at 800°C and a 2:1 feed ratio of CH_4:CO_2 and that the activity can be regained by exposing the catalyst to CO_2. Furthermore, when the Pt/$LaCoO_3$ 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 looses 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 CO_2 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 CH_4 and dry conditions, that this material could be a promising support for this reaction under elevated pressure and in the presence of steam.

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