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Segregation of Pt and Re during CO_2 reforming of CH_4

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Pt–Re supported on $Ce_{0.52}$ $Zr_{0.48}$ O_2 was studied for the carbon dioxide reforming of methane at 800 °C. Diffuse reflectance fourier transform infrared spectroscopy and temperature programmed reduction studies suggest that Pt and Re segregation occurs during the reaction. The segregation results in an increase in the Pt sites available for CH_4 decomposition and results in the bimetallic catalyst exhibiting an increase in the conversion of methane with time on stream. After 20 h of reaction, the CH_4 conversion observed for the bimetallic catalyst was the same as the CH_4 conversion observed for the monometallic catalyst.

KEY WORDS: CH_4 reforming; Pt–Re; bimetallic; syngas production; segregation.

1. Introduction

Steam reforming of methane has been traditionally used to produce synthesis gas with high H_2:CO product ratios [1,2]. However, research over the past years has shown the carbon dioxide (dry) reforming of methane to be a promising alternative. The primary benefit of dry reforming is derived from its low H_2:CO ratio, which is preferred for hydroformylation, carbonylation, Fischer-Tropsch synthesis [3], and production of oxygenated compounds. Also, the combination of dry reforming with steam reforming and partial oxidation allows for a tunable reaction to achieve a target syngas ratio [4,5].

Commercialization of dry reforming has been limited due to equilibrium considerations and its highly endothermic nature, which require temperatures near 800 °C for acceptable conversions [6,7]. At such temperatures, the catalyst deactivates due to carbon deposition. Supports with low acidity and high oxygen mobility have been studied as a means of reducing carbon deposition [8–11]. For example, the promotion of ZrO_2 with Ce has been shown to increase the stability of the catalyst [8] for the dry reforming reaction. The enhanced performance has been ascribed to several factors including the ability of the promoters to retard Pt particle growth and the increased oxygen storage and release capability of the support. Both of these promotional effects increase the long term activity. The higher dispersion increases the metal sites available for CH_4 decomposition and the promoters provide oxygen to the metal-support interface which facilitates the removal of carbon from the surface of the metal particle [8].

In the naphtha reforming literature, promoters such as Re have been used to prevent carbon deposition [12]. Increasing the Pt–Re interaction has been shown to reduce coke deposition [13], improve Pt dispersion [14], increase surface area, and significantly enhance the catalysts' selectivity and stability [12]. However, the exact interaction between Re and Pt (and Re and the support) is still not well understood. The most widely accepted explanation for the enhanced properties of bimetallic catalysts is the formation of an alloy [15–22], in which Re and Pt, both reduced to the metallic state, interact strongly, Some studies have indicated that Re stabilizes Pt dispersion by anchoring Pt to the support [23–25] while other studies have stated that there is no Pt–Re alloy or significant metal interaction [26–34]. For example, Bertolacini and Pellet found that a physical mixture of monometallic Re catalysts and Pt catalysts to be equivalent to the bimetallic catalyst [35]. However, others have shown that Re oxides can migrate over the surfaces of the support [21,22] and have speculated that Re oxide migrates to the site of the Pt particle.

Although a lot of work has been published on the Pt–Re interaction and the catalysts for naphtha reforming, very little work has focused on the use of Re or other metallic promoters for the dry reforming reaction, Richardson and coworkers have reported that a 0.5 wt% Pt–Re/γ-Al_20_3 catalyst with a 1:4 ratio of Pt:Re was stable for more than 250 h for dry reforming, steam reforming, and mixed reforming at temperatures between 700 °C and 850 °C [36,37]. They have also studied Pt–Re systems on dense ceramic foam supports and demonstrated good stability at temperatures above 700 °C [38]. However, no detailed studies have been reported on the use of Re as a promoter for Pt supported on reducible oxides such as CeO_2 or $Ce_xZr_{1\text{-}x}O_2$.

We have previously shown that the addition of Sn as a metallic promoter to a Pt/ZrO_2 catalyst resulted in a

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significant decrease in the activity of the catalyst for the dry reforming reaction [9]. Post reaction characterization of the catalyst indicated that the Sn was oxidized under reaction conditions and formed a Sn oxide ring around a metallic Pt core [9]. The formation of the ring disrupted the interaction between the Pt and the support, decreasing the ability of the support to facilitate carbon removal through oxygen exchange.

Based on the positive results indicating that Re can be used to reduce carbon deposition for the dry reforming reaction over Pt/Al_2O_3 catalysts, we have investigated the addition of Re to Pt supported on a highly reducible mixed oxide. Specifically, this paper investigates the activity, stability and Pt–Re interaction during the dry reforming reaction over a $Pt–Re/Ce_{0.52}Zr_{0.48}O_2$ catalyst containing 0.1 wt% Pt and 0.4 wt% Re to determine if, unlike the Pt-Sn bimetallic catalyst, the Pt–Re catalyst is stable under the dry reforming conditions.

2. Experimental

2.1. Catalyst preparation

The $Ce_{0.52}$ $Zr_{0.48}O_2$ support material studied in this work was received from MEL Chemicals calcined at 700 °C. The support was further calcined at 800 °C (the temperature of reaction) for 4 h prior to the addition of the metal. The catalysts were prepared using aqueous incipient wetness co-impregnation of dihydrogen hexachloroplatinate (IV) salt ($H_2PtCl_6{\cdot}6H_20$), 99.95% metals basis (Alfa-Aesar), and rhenium (V) chloride, ($ReCl_5$), 99.9% metals basis (Alfa-Aesar). The Pt metal loading was 0.1 wt% and the Re loading was 0.4 wt%. After impregnation, all catalysts were dried overnight at 120 °C and then calcined at 400 °C for 2 h in air. The $Pt/Ce_{0.52}Zr_{0.48}O_2$ and $Pt–Re/Ce_{0.52}$ $Zr_{0.48}O_2$ catalysts will be referred to as PCZ and PRCZ, respectively. For the TPR studies, a 0.4 wt% $Re/Ce_{0.52}Zr_{0.48}O_2$ catalyst was prepared and will be referred to as RCZ.

2.2. Catalytic activity

Dry reforming reactions were performed in a fixed bed quartz flow reactor (10.5 mm ID) at atmospheric pressure and 800 °C. A 100 mg catalyst sample was diluted with 300 mg of silicon carbide prior to loading into the reactor. The catalysts were reduced in hydrogen at 400 °C for 1 h, and then heated to 800 °C in argon. The reforming reaction was carried out using a stoichiometric CH_4:CO_2 ratio at 100 cc/min. The reactor effluent was analyzed using an SRI GC equipped with a TCD and a Supelco Carboxen 1010 Plot capillary column (30 m, 0.53 mm ID).

2.3. Catalyst characterization

CO was used as a probe molecule to qualitatively investigate number of exposed Pt atoms before and after reaction. The adsorption of CO was studied using diffuse reflectance fourier transform infrared spectroscopy (DRIFTS) on a Bio-Rad IR spectrometer. 100 mg of catalyst was mixed in a 1:1 mass ratio of catalyst to KBr. The mixture of catalyst and KBr was dried overnight at 120 °C before use. The samples were ground to a fine powder and then placed in a Harrick Scientific DRIFTS high temperature cell, capable of reaching 800 °C. The samples were oxidized at 400 °C for 1 h followed by reduction in hydrogen for 1 h at 400 °C. After flushing in He the samples were cooled to room temperature and then background scans were taken in He. Each final spectrum was the average of 256 scans at a resolution of 4 cm^{-1}. CO adsorption was performed by exposing the catalyst to a 1 CO/He flow (15 cc/min) at room temperature. Background scans were subtracted from all of the data at the respective temperature. For the experiments in the presence of CO, all signals were normalized to the gas phase CO peak.

Temperature programmed reduction with hydrogen was performed using a Micromeretics 2010 adsorption apparatus equipped with a thermal conductivity detector. Each experiment was performed on 100 mg of catalyst. Flow rates for all of the gases used for the pretreatment and reduction was 15 cc/min. For the reduction studies, the catalyst was exposed to 5 H_2 in Ar and, after a steady baseline signal was achieved at room temperature, the temperature was increased to 800 °C at 8 °C/min. Pulses of hydrogen were used to quantify the hydrogen consumption.

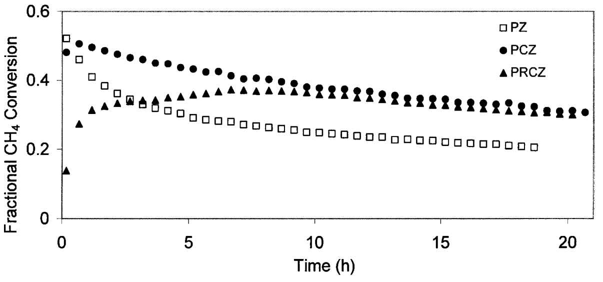

Figure 1. CH_4 conversion for the $Pt/Ce_{0.48}Zr_{0.52}O_2$ (PCZ), $Pt–Re/Ce_{0.48}Zr_{0.52}O_2$ (PRCZ), and Pt/ZrO_2 (PZ) catalysts during dry reforming of CH_4 at 800°C with a 1:1 ratio of CH_4:CO_2.

3. Results and discussion

Figure 1 shows the conversion of CH_4 during the dry reforming reaction at 800 °C and a stoichiometric feed of CH_4 and CO_2 for the PCZ and PRCZ catalysts. The initial conversion for the PCZ catalyst was near 50% and decreased during the 20 h of reaction to 30%. The rate of deactivation was higher during the first 5 h of reaction but gradually decreased such that only a 1% decrease in activity was observed during the last 5 h of reaction. For comparison, a 0.1 wt% Pt/ZrO_2 (PZ) catalyst under the same conditions, exhibited very similar initial conversion (51%) but showed significant deactivation within the first 5 h of reaction, Again the rate of deactivation slowed, with the final conversion after 17 h of reaction near 20%. The deactivation observed on the PZ and PCZ catalyst has been previously ascribed to coke formation that occurs during the reaction [8,39]. XPS and TPO studies previously reported in the literature have shown that the addition of Ce does not result in a change in the type of carbon deposited during the reaction [39]. However, it has been speculated that the ZrO_2 support, especially when promoted with Ce, can facilitate carbon removal from the Pt located at the perimeter of the Pt particle, in close proximity to the support [8,10]. The long term activity is then ascribed to the Pt that is not covered by coke and represents a balance between the rate of CH_4 decomposition and the rate of CO_2 dissociation.

Figure 1 also shows that profile for the $Ce_{0.52}$ $Zr_{0.48}$ O_2 catalyst containing both Pt and Re (PRCZ). The initial conversion of the bimetallic catalyst (13%) is lower than the initial conversion for the monometallic catalysts, which is most likely due to the presence of Re reducing the number of Pt atoms available for reaction. In contrast to the monometallic catalyst, the PRCZ catalyst exhibited a significant increase in conversion during the first 5 h of reaction. The maximum conversion was observed after 7 h of reaction (37%), and then the conversion gradually decreased with time on stream, It should be noted that the conversion of the bimetallic catalyst was the same as the monometallic catalyst after 10 h of reaction, and the two catalysts exhibited the same performance for the remainder of the experiment.

The induction period observed for the PRCZ catalyst implies that some modification of the catalyst is occurring under reaction conditions that results in enhanced activity, Similar to the increased conversion, the H_2/CO ratio also increased during the induction period, which would indicate that the decomposition of methane was increased more than the dissociation of CO_2. Previous work in the literature has shown that Pt and Re supported on Al_2O_3 can form alloys if the catalyst is dried in air at temperatures less than 500 °C and reduced at between 400 °C and 500 °C [40]. Since the catalysts in this study were calcined at 400 °C for 2 h and then reduced at 400 °C, it is expected that some degree of alloy formation has occurred during the pretreatment.

The increased activity observed during the first 7 h of reaction could be due to segregation of the Pt and Re under reaction conditions. Segregation of the Pt and Re has been previously reported due to the lower surface free energy of Pt compared to the Re [41]. It has been suggested that the Pt preferentially segregates to the step edges such that the surface sites with lowest coordination are filled first [41]. Others have suggested that Pt–Re catalysts contain very small bimetallic clusters that are Re enriched on the surface [42]. In order to probe the possibility of Pt–Re segregation, temperature programmed reduction (TPR) studies were performed on the catalysts before and after reaction. Figure 2a shows the hydrogen consumption for the 0.1 wt% PCZ catalyst, Only one peak is observed centered at 208 °C. The amount of hydrogen consumed is greater than the amount of Pt on the catalyst, indicating that some surface reduction of the support is occurring due to hydrogen spillover.

Figure 2b shows the TPR profile for a 0.4 wt% Re/$Ce_{0.52}$ $Zr_{0.48}$ O_2 (RCZ) catalyst prepared as a reference sample. The temperature of reduction for the Re catalyst is shifted to significantly higher temperatures (433 °C) compared to the Pt catalyst. Also, the amount of hydrogen consumed is less than the amount consumed for the Pt catalyst even though the loading of Re is four times greater. TPR studies of 0.3 wt% Re supported on Al_2O_3 have shown that Re reduction occurs between 500 °C and 600 °C, and that only 55% of the Re is reduced from the Re^{+7} state to metallic Re [43]. The temperature of reduction for the catalyst in this study is shifted to lower temperatures compared to the one reported in the literature. The shift on temperature is ascribed to the higher loading of metal on the catalyst used in this study, which has been previously observed for Au catalysts as well [44].

The third profile (c) shown in figure 2 is the hydrogen consumption for the bimetallic PRCZ catalyst. The temperature of reduction for this catalyst is approximately 65 °C higher than for the PCZ catalyst but still significantly lower than the Re catalyst. The temperature of reduction agrees with the temperature (300 °C) previously reported for a Pt–Re/Al_2O_3 with 0.3 wt% Pt and 0.3 wt% Re [43]. Although the amount of hydrogen consumed during the reduction of the bimetallic catalyst is less than the sum of the hydrogen consumption for the individual Pt and Re catalysts, it is still greater than the amount required for complete reduction of the Pt and Re. The decrease in the reduction temperature and the appearance of only one reduction peak clearly shows that the Pt and Re are in contact and that the Pt catalyzes the reduction of Re. The decrease in the hydrogen consumption could indicate a decrease in the reduction of the support due to decreased interaction between the Pt and the support caused by the presence of Re.

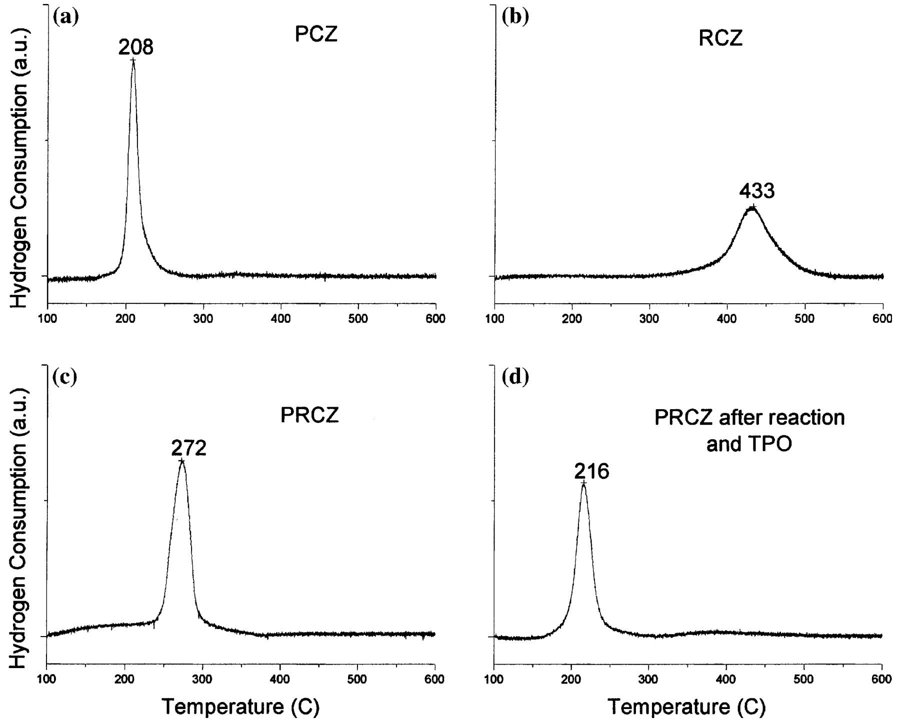

Figure 2. Hydrogen consumption during temperature programmed reduction of Pt/$Ce_{0.48}Zr_{0.52}O_2$ (a), Re/$Ce_{0.48}Zr_{0.52}O_2$ (b), Pt–Re/$Ce_{0.48}Zr_{0.52}O_2$ (c) and Pt Re/$Ce_{0.48}Zr_{0.52}O_2$ after reaction and TPO (d).

The final graph (d) in figure 2 shows the hydrogen consumption for the PRCZ catalyst after reaction. Prior to the TPR, the catalyst was subjected to a temperature programmed oxidation (TPO) treatment to remove any carbon species that were deposited during the reaction. The TPO consisted of heating the catalyst to 700 °C in a 5% O_2/He (30 cc/min) flow while raising the temperature at 8 °C/min. As a reference, fresh samples of PCZ and PRCZ catalysts were exposed to the same TPO treatment and the effect on the reduction temperature was observed. For both reference catalysts, the TPO treatment without reaction resulted in a 60–70 °C increase in the temperature of reduction. In contrast, the PRCZ catalyst which was exposed to the TPO after reaction, exhibited a lower temperature of reduction (216 °C) compared to the fresh bimetallic catalyst (272 °C). In fact, the temperature of reduction was much closer to the temperature observed for the fresh PCZ catalyst. In addition to the shift to lower temperatures for the large reduction peak, a small amount of hydrogen consumption was observed between 350 °C and 450 °C on the bimetallic catalyst after reaction. Comparing the spectra of the bimetallic catalyst after reaction to the reference samples indicates that the shift in the reduction peak to lower temperatures after reaction is not caused by the TPO treatment, as the TPO treatment on a fresh catalyst causes an increase in the temperature of reduction. Thus, it is suggested that the lowering of the reduction temperature is a result of changes that occur during reaction, The appearance of two reduction peaks and the positions of the peaks and are consistent with the proposed segregation of the Pt and Re during the dry reforming reaction.

Further probing of the segregation was performed using DRIFTS studies of CO adsorption. CO can be used as a probe molecule for exposed Pt atoms by monitoring for the linearly adsorbed CO bands between 2080 and 2060 cm^{-1} [45,46]. Previous reports of CO adsorption on Re/Al_2O_3 have shown that bands in the range of 2116, 2035, 2002, 1961 and 1933 cm^{-1} are characteristic of Re. The band at 2035 cm^{-1} was ascribed to metallic Re while the other bands were ascribed to $Re_2(CO)_{10}$ [45]. When a Pt–Re/Al_2O_3 catalyst was exposed to CO, a dominant band appeared at 2075 cm^{-1} due to Pt–CO, with additional bands at 2112, 2007, 1963 and 1933 cm^{-1} [45]

The catalysts used in this study were reduced at 400 °C *in situ.* Figure 3a shows that the absorbance spectra for the PCZ catalyst after exposure to CO and flushing in He at room temperature. Two peaks are observed, one at 2080 cm^{-1} and the other at 2064 cm^{-1}. The two peaks differ slightly in position from what has been reported for Pt/Al_2O_3, but slight shifts in the peak position are likely due to the different support and the lower metal loading. Based on previous reports in the literature [47,48,49], the peak at the higher wavenumber is ascribed to CO adsorbed on terrace sites, while the lower wavenumber peak is associated with CO adsorbed on step sites.

As shown in figure 3b, exposing the PRCZ catalyst to CO resulted in significant changes to the spectra. The peaks that were present on the PCZ catalyst (2080 and 2062 cm^{-1}) are also present on the PRCZ catalyst. In addition to the Pt peaks, new peaks appeared at 2105, 2070, 2034, 2012 and 1983 cm^{-1} which are characteristic of the presence of Re [45]. The bands at 2034, 2012 and 1983 cm^{-1} are very broad and thus the reported values are only estimates of the peak positions. The amount of adsorption observed on the bimetallic catalyst is much lower than on the PCZ catalyst. Although an exact quantitative analysis of the amount of CO adsorbed can not be performed because of the possible differences in the samples, greater than 50 reduction in the adsorption on Pt was observed. Since the metal loading was equivalent on the two catalysts, this implies that a significant decrease in the number of Pt atoms available for CO adsorption occurred with the addition of Re. Since the loading of Re is four times that of the Pt, it is possible that in the fresh catalyst the surface of the bimetallic particles may be rich in Re. This surface enrichment of Re would also explain the low activity observed at the beginning of the dry reforming reaction.

CO adsorption was also performed on the PRCZ catalyst after reaction. Again, the sample underwent a TPO to remove carbon deposits and then a reduction at 400 °C prior to exposure to CO. Figure 3c shows the absorbance spectrum after exposure to CO at room temperature and flushing in He. The lower wavenumber bands (2034, 2010 and 1983 cm^{-1}) that were present on the unreacted PRCZ catalyst were still present after reaction. In addition, peaks at 2069 and 2083 cm^{-1} were observed. The most notable change in the spectrum for the PRCZ after reaction was the increase in the intensity of the CO adsorption peaks. Compared to the PRCZ catalyst before reaction, the intensity was more than 4 times greater, with the largest peak at 2069 cm^{-1}.

The increase in absorbance spectrum intensity of the bimetallic catalyst after reaction is ascribed to the segregation of the Pt and Re. As previously discussed, Pt has been shown to segregate to the step edges of a Pt–Re cluster [41]. The migration of Pt to the surface of the cluster would result in an increase in the CO adsorption observed, especially in the region between 2080 and 2060 cm^{-1}, In addition to the CO that adsorbs on the Pt, CO would also adsorb on the Re, resulting in an overall increase in the CO adsorption observed.

4. Conclusions

Based on the TPR and DRIFTS studies performed on the Pt–Re/$Ce_{0.48}$ $Zr_{0.52}O_2$ catalyst before and after reaction, we ascribe the induction period observed

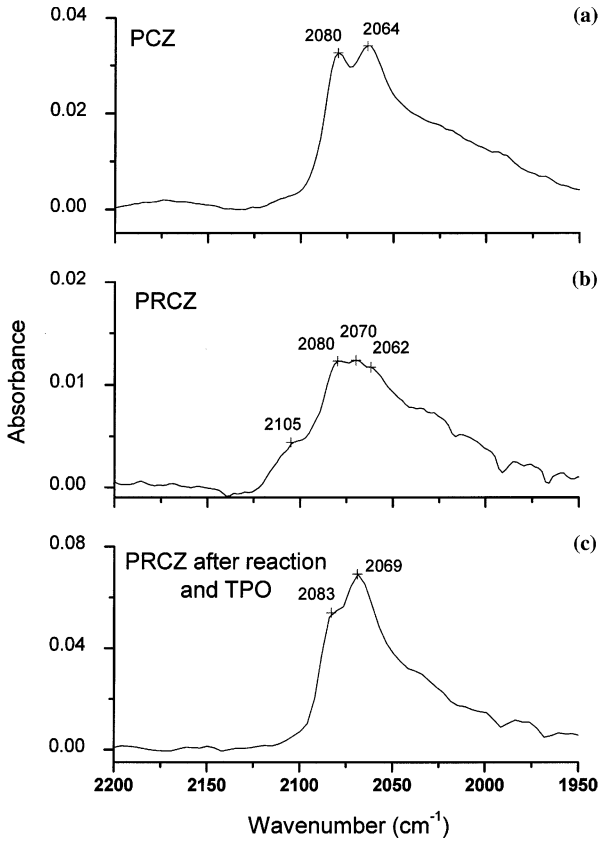

Figure 3. Comparative absorbance spectra for Pt/$Ce_{0.48}Zr_{0.52}O_2$ (a), Pt–Re/$Ce_{0.48}Zr_{0.52}O_2$ (b) and Pt–Re/$Ce_{0.48}Zr_{0.52}O_2$ after reaction and TPO (c) after exposure to CO at room temperature and flushing in He.

during the dry reforming reaction to the segregation of Pt and Re under reaction conditions. Unlike the Pt–Sn catalysts, the Pt–Re catalyst exhibited an increase in activity suggesting a different segregation model. We ascribe the increase in the CH_4 conversion at the start of the reaction to the surface segregation of Pt which would result in an increase in the number of sites exposed for CH_4 decomposition.

In the Pt–Sn system previously studied, the Sn blocked the interaction between the Pt and the support, which has been shown to be important in the mechanism of CO_2 dissociation and the long term activity of the catalyst. However, unlike Sn, which is considered inert for the dry reforming reaction, Re has the ability to adsorb CO_2 and participate in the reaction much like the reducible supports. The similar long term behavior of the Pt–Re/$Ce_{0.48}Zr_{0.52}O_2$ and Pt/$Ce_{0.48}Zr_{0.52}O_2$ catalysts is ascribed to the presence of highly disperse Pt on the bimetallic catalyst after the segregation, and the ability of Re to participate in the dissociation of CO_2 similar to the $Ce_{0.48}Zr_{0.52}O_2$ support. In contrast to supports such as Al_2O_3, Ce-promoted ZrO_2 has the ability to facilitate the dissociation of CO_2 and retard Pt sintering, and thus no significant benefit of promotion with Re is observed.

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