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Infrared spectroscopy study of CO and CO_2 on Ce- and La-promoted Pt/ZrO_2 catalysts

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The adsorption of CO and CO_2 on Pt supported on ZrO_2 and Ce/La-promoted ZrO_2 was studied using DRIFTS. The presence of both La and Ce resulted in a decrease in the adsorption of CO at room temperature after reduction at 350 °C. The reduction in the CO adsorption is ascribed to an increase in the support reducibility when La and Ce are both present. Reduction at 350 °C leads to the formation of oxygen defects in the dual promoted support which have been probed using DRIFTS to monitor CO_2 dissociation. Hydrogen assisted dissociation is demonstrated on the ZrO_2, $CeZrO_2$, and $LaZrO_2$ supports. In the absence of hydrogen, the presence of oxygen vacancies is shown to be necessary for CO_2 dissociation.

KEY WORDS: DRIFTS; carbon monoxide; carbon dioxide; promoted ZrO_2.

1. Introduction

The rare earth oxides and mixed oxides of these rare earth elements have been employed for a variety of reactions including reforming [1–6], water gas shift [7–10], and selective CO oxidation [11–13], because of the unique properties they possess. Ceria, which is a significant component of the three-way automotive catalyst, is known for its high oxygen storage and release capability. The addition of a metal such as Pt or Pd has been shown to increase the reducibility of the support [14] and the ability to extract lattice oxygen from the support near the metal particle has been shown to be instrumental in several reaction mechanisms [15,16]. However, ceria can exhibit low surface area at high temperatures ($<$750 °C) and may not be suitable for reactions which need to operate at elevated temperatures due to equilibrium limitations [17].

Lanthana and the addition of La to catalysts in order to promote a variety of reactions and stabilize support materials are well studied [2,4–6]. Supports containing La have been shown to have the ability to form carbonate species on the surface during high temperature CO_2 reforming reactions which are believed to aid in the prevention of carbon deposition on the active metal site [2]. It has also been suggested that La species may partially decorate Ni particles during the dry reforming reaction inhibiting deactivation [4]. Furthermore, the addition of La to ZrO_2 has been found to aid in the reduction of Pt sintering during high temperature reforming reactions [5,6].

Recent studies performed on mixed oxides of ceria and lanthana have shown that the mixed oxide is more easily reduced in flowing hydrogen than the ceria alone [18]. More recently, the addition of La to CeO_x has been shown to result in a very high surface area material after calcination at 900 °C, with increased oxygen release capabilities [19]. The $Ce(La)O_x$ materials have been suggested to be good supports for both the low temperature water gas shift and selective CO oxidation reaction [8,9]. Similar increases in surface area and oxygen transport ability have been observed on $La_{0.04}Ce_{0.14}Zr_{0.82}O_2$ supports. However, for the high temperature dry reforming reaction, the activity has been found to be lower than the activity of the individually promoted La- or Ce–ZrO_2 catalysts [20]. The decrease in activity is believed to be due to the increased reducibility of the La and Ce containing support, which leads to a strong metal–support interaction and partial encapsulation of the metal particle.

The focus of this paper is to investigate the reducibility of a $Pt/La_{0.04}Ce_{0.14}Zr_{0.82}O_2$ catalyst using CO and CO_2 as probe molecules. The interaction of CO and CO_2 with the metal and the support has been studied using Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS). The results of the adsorption and desorption studies using DRIFTS are presented below with strong evidence for the increased reducibility of the $La_{0.04}Ce_{0.14}Zr_{0.82}O_2$ support.

2. Experimental

2.1. Catalyst preparation

The ZrO_2 support materials studied in this work were received from MEL Chemicals calcined at 700 °C. The supports investigated were ZrO_2, $La_{0.04}Zr_{0.96}O_2$, $Ce_{0.14}Zr_{0.86}O_2$, and $La_{0.04}Ce_{0.14}Zr_{0.82}O_2$. All of the

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supports were calcined at 800 °C in air for 4 h prior to the addition of the metal. The surface areas of the calcined supports as determined by BET surface area analysis are shown in table 1. Pt was added using aqueous incipient wetness impregnation of dihydrogen hexachloroplatinate(IV) salt ($H_2PtCl_6{\cdot}6H_2O$), 99.95% metals basis (Alfa-Aesar). The Pt metal loading (ICPAES, Galbraith Laboratories) is also shown in table 1, along with the nomenclature to be used throughout this paper. After impregnation, all of the catalysts were dried overnight at 120 °C and then calcined at 400 °C for 2 h in air.

2.2. DRIFTS studies

DRIFTS studies were performed using a Bio-Rad FTS-40 IR spectrometer. The samples were mixed with a 1:1 mass ratio of 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 in ultra high purity (UHP) O_2 (20 cc/min) at 350 °C for 1 h followed by reduction in UHP H_2 (20 cc/min) for 1 h at 350 °C. After flushing in He, the samples were exposed to a 1% CO/He (20 cc/min) or 1% CO_2/He (20 cc/min) mixture at temperatures ranging from room temperature to 350 °C. For the hydrogen assisted dissociation studies the catalysts were exposed to a 1% CO_2/He (10 cc/min) and H_2 (10 cc/min) mixture at 350 °C. Background scans were subtracted from all of the data at the respective temperatures. Scans were taken at 4 cm^{-1}. For the experiments in the presence of CO, all of the signals were normalized to the gas phase CO peak.

3. Results and discussion

3.1. Catalyst properties

3.1.1. BET

Table 1 shows the BET surface areas of the supports investigated in this paper after calcination at 800 °C. The results of the surface area studies show that the $La_{0.04}Ce_{0.14}Zr_{0.82}O_2$ support has a surface area near that of the $La_{0.04}Zr_{0.96}O_2$ and $Ce_{0.14}Zr_{0.86}O_2$ supports. All of the promoted supports have surface areas greater than the surface area of the ZrO_2 support after calcination at 800 °C. Previous studies have shown that the addition of small amounts of Ce or La to ZrO_2 results in an increase in the surface area due to a stabilization of the tetragonal phase of ZrO_2 [5]. X-ray diffraction (XRD) studies performed on $La_{0.04}Ce_{0.14}Zr_{0.82}O_2$ support in this work indicate that, similar to the individually promoted supports, the support containing both Ce and La also has a tetragonal structure. From the XRD studies no discernable shifts in the peaks were observed when the promoted supports were compared to the tetragonal ZrO_2 reference spectra.

Table 1

BET surface area analysis and Pt metal loading for the catalysts investigated

Catalyst	BET surface area (m^2/g)	Metal loading (wt%)	Nomenclature
Pt/ZrO_2	25	0.43	PZ
Pt/$Ce_{0.14}Zr_{0.86}O_2$	48	0.42	PCZ
Pt/$La_{0.04}Zr_{0.96}O_2$	50	0.42	PLZ
Pt/$La_{0.04}Ce_{0.14}Zr_{0.82}O_2$	46	0.37	PLCZ

The lack of any peak shifts is likely due to the fact that low levels of Ce and La are used in this study and a solid solution is not formed. Previous studies reported in the literature [17,21,22] for mixtures CeO_2 and ZrO_2 have shown when the CeO_2 content is greater than 25% a solid solution is formed. The resultant XRD spectrum is not purely tetragonal ZrO_2 or cubic CeO_2 but lies somewhere between the two. Concentrations less than 25% result in the stabilization of the tetragonal phase of ZrO_2 [21,22] with no obvious shifts in the peaks. Furthermore, X-ray photoelectron spectroscopy (XPS) studies [17] performed on mixed oxides of CeO_2 and ZrO_2 prepared by co-precipitation have shown surface segregation of Ce oxide on samples that had low weight percents of Ce. It is then likely that since the total amount of Ce and La in this study is much lower than 25% and no evidence of a homogenous solid solution is observed, a higher concentration of Ce and La oxides exist on the surface of the tetragonal zirconia.

3.2. Metal particle size

The presence of La and Ce promoters has been to shown to retard particle growth, especially when exposed to high temperature treatment [5]. Previous work in our laboratory has shown that when the PCZ, PLZ, PLCZ, and PZ catalysts were exposed to reduction at 500 °C and heating to 800 °C, the average particle size for the promoted catalysts was approximately 4.5 nm, while the particle size for the PZ catalyst was approximately 5.2 nm. When the catalysts were reduced at 500 °C without exposure to the high temperature treatment, the particle sizes were near 3 nm and no significant differences in the particle sizes between the promoted and unpromoted supports was observed. Since the catalysts used in this study were only reduced at 350 °C, it is expected that the average particle size would be similar to the catalysts reduced at 500 °C (3 nm) and similar on all of the catalysts studied.

3.3. Room temperature adsorption of CO

DRIFTS studies were performed to investigate the interaction of CO with the Pt and the support. All of the catalysts were oxidized at 350 °C for 1 h in O_2 and the reduced for 1 h in H_2 prior to exposure to CO. Figure 1 shows the spectra for all of the catalysts during exposure to CO at room temperature. All of the spectra have been normalized to the gas phase CO peak. It should be noted that no significant changes in the CO adsorption profiles were observed when the catalysts were flushed in helium at room temperature, indicating that the CO observed is not weakly chemisorbed to the surface.

The peak ascribed to CO linearly adsorbed on a Pt site typically appears between 2069 and 2090 cm^{-1} depending on the type of Pt site. For example, when CO is linearly adsorbed on terrace sites of Pt, the peak appears at slightly higher wave numbers than when CO is adsorbed linearly on Pt step sites [23–25]. The results in figure 1 show that presence of the promoters causes a shift in the primary CO adsorption peak to lower wave numbers (2070 cm^{-1}) compared to the PZ catalyst (2083 cm^{-1}). Shifts in the CO adsorption peak can be due to differences in the amount of CO adsorbed. However, the peak areas for the PZ, PCZ, and PLZ catalysts are very similar which would indicate that no significant differences exist in the amount of CO adsorbed on these catalysts. Furthermore, as discussed above, it is anticipated that the particles size of the Pt on the catalysts are similar which would be consistent with the similar amounts of CO adsorption observed. The shift in the position of the peak could be due to the presence of more defect sites on the promoted supports. Studies have shown that Pt/CeO_2 catalysts with smaller Pt crystallite sizes have a greater adsorption at lower frequencies compared to the same catalysts with higher crystallite sizes [23]. Although the average crystallite sizes in the study are similar, the results suggest that the presence of the promoters leads to the formation Pt particles with more defects sites.

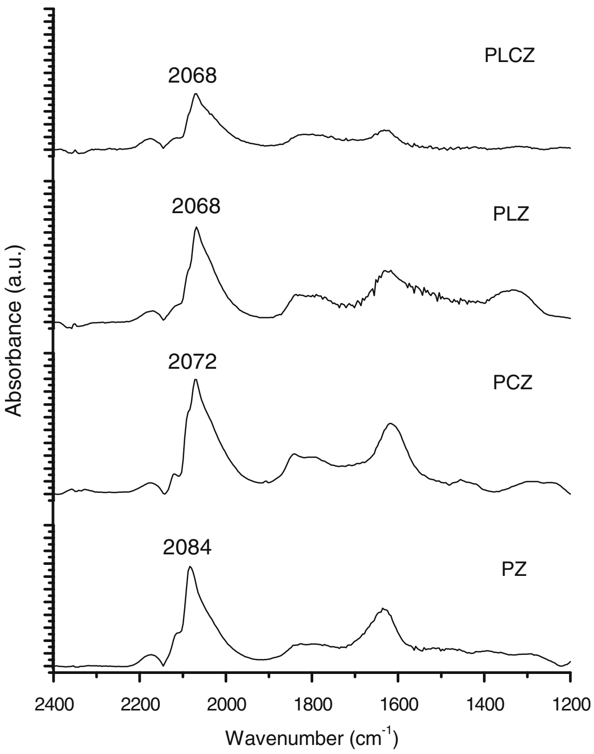

Figure 1. DRIFTS spectra recorded for PZ, PCZ, PLZ, and PLCZ during exposure to 1% CO/He mixture at room temperature.

In contrast to the PZ, PCZ, and PLZ catalysts, the PLCZ catalyst exhibited a significant decrease in the amount of CO adsorbed on the metal and on the support. The elemental analysis studies have indicated that the Pt content on the PLCZ catalyst is lower than the other catalysts studied. However, even when accounting for the difference in the metal loading, the CO adsorption is still significantly decreased in the presence of both La and Ce. These results suggest that less overall metal is exposed for adsorption, or the CO adsorption properties of the Pt had been modified on this catalyst. Since the position of the peak is consistent with the position observed on the individually promoted catalysts, it is unlikely that any significant modification of the Co adsorption properties of the Pt has occurred. Thus, it is likely that less Pt metal is exposed for adsorption.

Figure 1 also shows the appearance of CO adsorption peaks near 1800 cm^{-1}. Although it is difficult to separate bands in the region associated with multiple Pt sites, two peaks near 1840 and 1790 cm^{-1} are observed in the presence of CO at room temperature. These peaks have been previously assigned to bridged and three-fold adsorbed CO on Pt [26]. As was observed for the linearly bound CO, similar amounts of CO bound to bridged and three-fold Pt sites are found on the PZ, PCZ, and PLZ catalysts while the PLCZ catalysts exhibits decreased CO adsorption on multiple Pt sites.

With exposure to CO, peaks in the region generally associated with carbonate and formate species were also observed. For all of the catalysts the largest broad peak was centered at 1632 cm^{-1}. Since the scans are being performed at room temperature, under flowing He, some water vapor may be present in the system which could contribute to a broad peak in this region. Carboxylic acids can also be formed by CO in the presence of residual hydroxyl species; however, these surface species typically appear at slightly higher wave numbers (1670–1695 cm^{-1}) on CeO_2 [23] and it is not likely that they are present in this study.

Figure 1 shows that no significant formation of either carbonate or formate species was observed when the Pt/ZrO_2 catalyst was exposed to CO at room temperature. Others have also reported that while bidentate carbonates on ZrO_2 can be observed when exposed to CO_2, no carbonate or bicarbonate species are observed on ZrO_2 when exposed to CO [27]. In contrast, the La-promoted catalyst showed peaks near 1325 cm^{-1} and a shoulder at 1575 cm^{-1} in the presence of CO. Several studies have reported that formate bands on Pt/CeO_2 appear at 1580 and 1375 cm^{-1} while bidentate carbonate bands appear at slightly lower wave numbers (1560 and 1295 cm^{-1}). Since no significant peaks were observed near 2900 cm^{-1} which would correspond to the C–H stretching in the formate species, we ascribe the peaks observed in this study to bidentate carbonate species. The bidentate species can have a shoulder that appears at 1620 cm^{-1} [27] which could also be contained in the large broad peak.

The PCZ catalyst exhibited a small peak at approximately 1436 cm^{-1} which could be due to the presence of unidentate carbonate formed via the interaction of CO with lattice oxygen and the formation of a vacancy in the support. No significant bidentate carbonate species were observed. The differences in the appearance of the carbonate bands (bidentate and unidentate) for the La- and Ce-promoted catalysts is consistent with the promotional effects of each element. La is known to increase the basicity of the support and favor carbonate formation while Ce is known for promoting support reduction and would facilitate unidentate carbonate formation.

Similar to the peaks corresponding to CO adsorption on the metal, the peaks in the 1650–1200 cm^{-1} region were significantly smaller for the PLCZ catalyst compared to the PZ, PCZ, and PLZ, catalysts. Very small peaks were observed at 1330 and 1435 cm^{-1} suggesting that the dual promoted catalyst has aspects of both of the individually promoted catalysts. These results further support the idea of La rich and Ce rich regions on the surface of the support.

3.4. *Effect of heating in CO*

The effect of heating in CO on the Pt was studied by heating the catalysts from room temperature to 350 °C in the presence of a 1% CO/He mixture. Figure 2a shows the spectrum for the PCZ catalyst in CO at 25 °C and figure 2b contains the spectrum after heating to 350 °C in a 1% CO/He mixture. Although only the spectrum for the PCZ catalyst is shown in figure 2, it should be noted that the other catalysts behaved similarly and any significant differences are outlined below.

For all of the catalysts studied in this work, several changes in the spectrum occurred upon increasing the temperature from 25 to 350 °C. The first change was that the position of the peaks shifted by approximately 40 cm^{-1} to lower wave numbers. Second, the relative intensities of the peaks associated with CO on the Pt changed. Third, the overall intensity of the signal increased with increasing temperature up to 200 °C and then decreased as the temperature further increase to 350 °C. The temperature at which the increase in the intensity stopped corresponded to the temperature at which no significant multi-bound species were observed on the catalyst. Thus, while the peaks associated with the bridged and three-fold adsorbed species were decreasing, the intensity of the peaks associated with linearly adsorbed CO was increasing. All of the changes observed are consistent with a restructuring of the Pt surface in the presence of CO. Previous studies reported in the literature on ZrO_2, CeO_2, and Al_2O_3 supported Pt catalysts are in agreement with the results of this work [23,26].

One interesting difference was observed when the spectra for the promoted catalysts and the unpromoted catalysts in CO at 350 °C were compared. All of the promoted catalysts had a distinct peak that appeared at approximately 1975 cm^{-1} while the unpromoted catalyst showed no significant peak in this region. Although the bridged CO species at room temperature appeared at lower wave numbers (<1900 cm^{-1}), others have reported that bridged CO can be found at >1900 cm^{-1} on terrace sites [28]. However, it is not anticipated that a significant adsorption of multi-bound species would be observed at elevated temperatures. While the assignment of this peak is still unclear, it is apparent that the addition of the promoters, both independently and when present at the same time, modifies the restructuring of the Pt in the presence of CO.

Figure 2c shows the spectrum for the PCZ catalyst during exposure to CO at 25 °C after being heated to

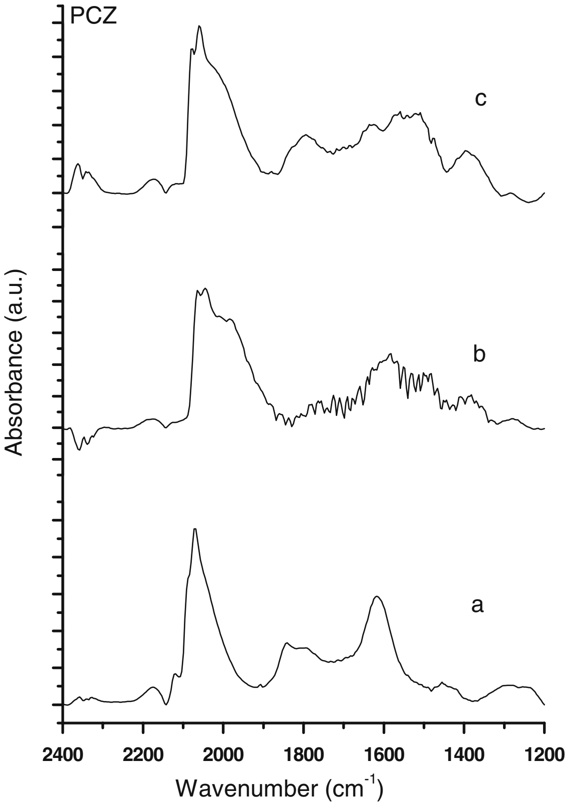

Figure 2. Modification of DRIFTS spectra with exposure to CO at high temperatures for the $Pt/Ce_{0.14}Zr_{0.86}O_2$ catalyst. Spectra during CO exposure at: (a) 25 °C on pretreated catalyst, (b) at 350 °C, and (c) at 25 °C after heating to 350 °C and cooling to room temperature in CO.

350 °C in the presence of CO. Comparison of the spectra in figure 2a and 2c clearly shows that some of the restructuring of the Pt is irreversible. For all of the catalysts, the peaks did not shift back to the original position. It is also interesting to note that the restructuring did not completely eliminate the ability of CO to bind in a multi-bound form as bands between 1850 and 1750 cm^{-1} were observed after cooling to room temperature. This result suggests that even though multi-bound CO species are not present on the surface in significant quantities at 350 °C, the adsorption sites still exist.

The restructuring of the Pt even at low temperatures could be very important for these catalysts since they are potential candidates for the selective CO oxidation and low temperature water gas shift reactions which occur in the temperature range of 80 to 350 °C. The studies reported in this work show that it is imperative to use *in situ* techniques to study the structure of the Pt when the reaction involves CO, because any characterization of the Pt surface pre- and post- reaction is different than the actual surface under reactions conditions.

3.5. *CO desorption*

The effect of the promoters on the CO desorption from the metal was investigated. The catalysts were each exposed to a 1% CO/He mixture at room temperature and then flushed in He until no changes in the spectrum were observed. The catalysts were then heated to 350 °C in He in 50 °C increments while monitoring the CO remaining on the surface. Although no quantitative information was obtained from this desorption study, qualitative information regarding the effect of the promoter on the adsorption of CO and the relative stability of each species on the surface was obtained.

Figure 3 shows the spectra for the PZ catalyst when heating from 25 to 200 °C in He. No significant differences in the spectrum are observed upon heating to 50 °C. However, even as low as 100 °C, the intensity of the peak at 2084 cm^{-1} ascribed to CO linearly adsorbed on the Pt has decreased and shifted to slightly lower wave numbers. Also apparent is a shift in the position of the multi-bound species from near 1800 cm^{-1} to a very small band at 1750 cm^{-1}. At 100 °C the band near 1632 cm^{-1} also decreases which is due to the removal of residual water. When the temperature reaches 150 °C a significant decrease in the intensity of the linear CO is observed as well as a further shift in the position to 2072 cm^{-1}. Further increasing the temperature to 200 °C resulted in complete disappearance of all CO bands.

Figure 4 shows the spectra for the PLZ catalyst during the CO desorption experiments. The PLZ, PCZ, and PLCZ spectra look similar for all of the temperatures studied and so the spectrum for only one of the catalysts is shown. Similar to the PZ catalyst, the peak corresponding to the linearly adsorbed CO exhibits a decrease in intensity and a slight shift to lower wave numbers as the temperature increases. Unlike the unpromoted catalyst, both the decrease and the shift occur at 50 and by 150 °C, a majority of the band for the CO on the metal has disappeared. Also, in contrast to the unpromoted sample, the bands corresponding to CO on the support remain, even at 200 °C. It is interesting to note that the band in the region of 1450 cm^{-1} become larger as the temperature is increased. These bands typically correspond to unidentate and bidentate carbonate which would be formed by the reduction of the support with CO. Although this may be surprising for the La_2O_3 which is not typically considered to be a reducible oxide, other studies have shown that surface reduction of similar supports such as ZrO_2 can occur [29]. This reduction is not a bulk reduction of the oxide but a generation of a partially reduced surface.

The results of the CO desorption studies suggest that the presence of the promoters does have a small effect on the adsorption of CO on Pt. When Ce and La were present, either individually or as dual promoters, the temperature at which CO desorption occurred decreased compared to the unpromoted catalyst suggesting that the promoters decrease the activation energy for desorption of CO. For all of the catalysts investigated, the multi-bound CO was removed at lower temperatures

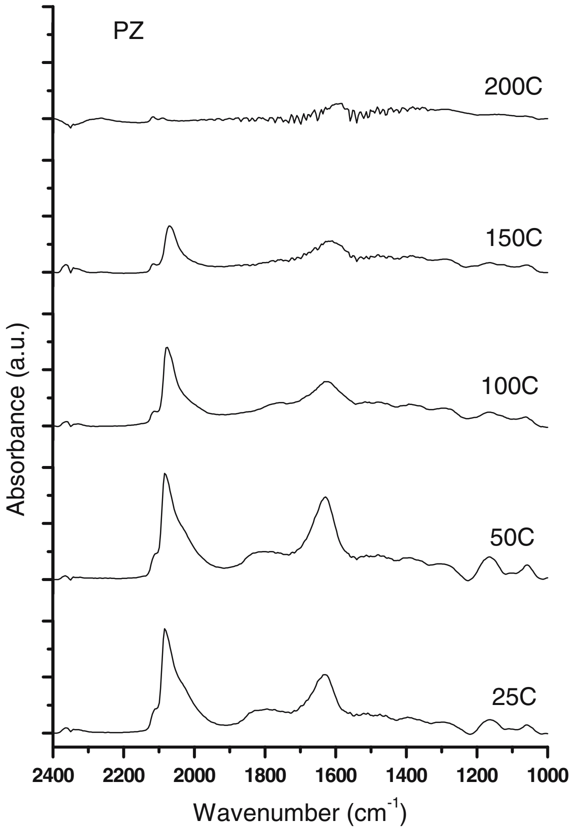

Figure 3. Evolution of DRIFTS spectra for Pt/ZrO_2 while heating in Ar after exposure to a 1% CO/He mixture at room temperature.

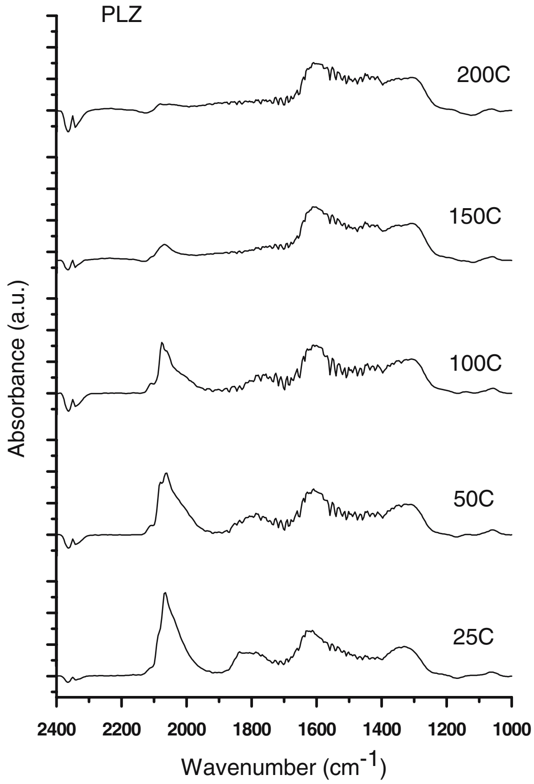

Figure 4. Evolution of DRIFTS spectra for Pt/$La_{0.04}Zr_{0.96}O_2$ while heating in Ar after exposure to a 1% CO/He mixture at room temperature.

compared to the linear CO, however the promoted catalysts appeared to have more multi-bound CO at 100 °C then the unpromoted catalyst. In addition, the multi-bound CO bands at 100 °C were shifted to lower wave numbers compared to the spectra at 25 °C. This shift is consistent with CO adsorption studied over Pt/Al_2O_3 [26], which reported that the heat of adsorption (and corresponding activation energy for desorption) of the bridged species was less than that of the three-fold species. Finally, unlike the unpromoted catalyst, the decrease in the bands associated with CO on the metal was accompanied by an increase in the bands ascribed to CO interaction with the support, indicating that the promoters facilitate CO spillover from the metal to the support.

3.6. FTIR of CO_2

FTIR studies of CO_2 adsorption were performed at 350 °C to probe the adsorption and dissociation characteristics of CO_2 on the catalysts. Each catalyst was oxidized at 350 °C for 1 h in O_2 and then reduced in H_2 at 350 °C for 1 h prior to the experiment. The catalysts were flushed in He until no changes in the background spectrum were observed. After a stable background spectrum was obtained, each catalyst was exposed to a 1% CO_2/He mixture (20 cc/min) at 350 °C. The background spectrum taken in He at 350 °C was used to obtain the absorbance spectra for each experiment.

Figure 5 shows the region of the spectra associated with CO adsorbed on Pt for the various catalysts during exposure to 15 cc/min of 1% CO_2/He at 350 °C. No CO adsorption on the Pt was observed during the exposure to CO_2 for the PZ, PCZ, or PLZ catalysts. CO adsorption on the Pt would be expected if dissociation of the CO_2 were occurring under these conditions. Thus, the results suggest that CO_2 dissociation does not occur on the pre-oxidized and pre-reduced ZrO_2, $La_{0.04}Zr_{0.96}O_2$ or $Ce_{0.14}Zr_{0.86}O_2$ supported Pt catalysts at 350 °C.

The spectrum for the PLCZ catalyst under the same conditions is also shown in figure 5. In contrast to the individually promoted and unpromoted supports, the catalyst containing both Ce and La showed peaks at 2068 and 1988 cm^{-1}. These peaks are consistent with the linear CO observed on the PLCZ catalyst during the CO exposure studies discussed previously. Thus, the catalyst containing both Ce and La demonstrates the ability to dissociate CO_2 after reduction at 350 °C.

Following exposure to CO_2, all of the catalysts were flushed in He for 30 min and then exposed to the 1% CO_2/He mixture for a second time. The results obtained for the second exposure were the similar to what was observed during the first exposure. That is, the PZ, PCZ, and PLZ catalysts did not show any CO adsorbed on Pt, while the PLCZ catalyst exhibited a peak at 2055 cm^{-1}.

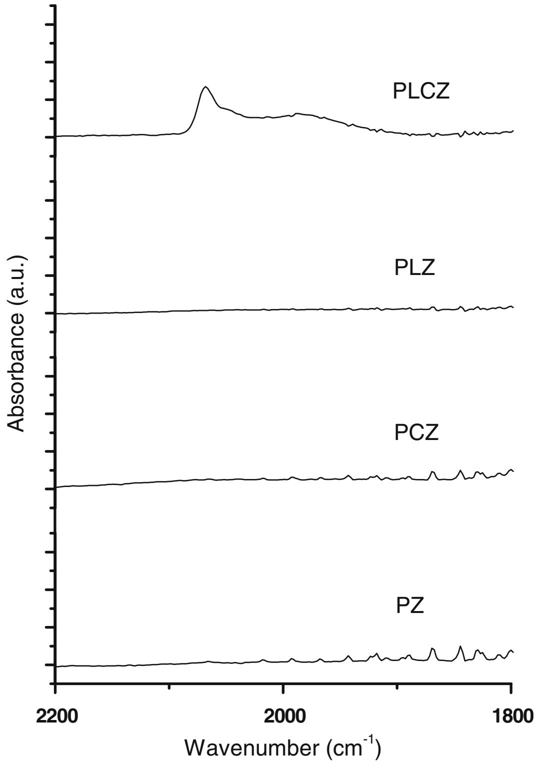

Figure 5. DRIFTS spectra recorded for PZ, PCZ, PLZ, and PLCZ during exposure to 1% CO_2/He mixture at 350 °C.

The shift in the position of the CO peak was also observed for the PLCZ catalyst during the CO exposure studies where the initial linear CO peak at room temperature appeared at 2068 cm^{-1}, and the CO peak at 350 °C was at 2057 cm^{-1}. The shift in peak position can be ascribed to the reconstruction of the Pt in the presence of CO at 350 °C, which has been demonstrated previously during the CO adsorption studies.

In addition to the surface reconstruction, it is also possible that the decrease in the peak position is due to a decrease in the total amount of CO adsorbed on the metal during the second exposure period. Previous studies have suggested that the dissociation of CO_2 on Ce-promoted ZrO_2 is facilitated by oxygen vacancies that are present in the surface of the support lattice [5]. When these vacancies are present near the perimeter of a metal particle, CO_2 dissociation occurs resulting in the formation of adsorbed CO species on the metal surface and replenishment of lattice oxygen on the surface of the support. In the absence of a reducing environment, the oxygen formed during the dissociation of CO_2 would reduce the number of vacancies near the perimeter of the particle and could result in a decrease in dissociation capacity during subsequent exposures.

Following the second exposure to CO_2 the catalysts were again flushed in He for 30 minutes. To further probe CO_2 dissociation on the various catalysts, the samples were exposed to a mixture of 1% CO_2/He and H_2 at 350 °C. Figure 6 shows that immediately following exposure to the mixture of CO_2 and H_2, large amounts of linearly adsorbed CO on the Pt particles were observed for all of the catalysts. The largest peak observed on the PZ catalyst was centered at 2075 cm^{-1}, while all of the promoted catalysts had peaks appearing at slightly lower wave numbers (~2065 cm^{-1}). The promoted catalyst also had a large peak near 1980 cm^{-1}. It should be noted that the amount of CO observed on the PLCZ catalysts during exposure to CO_2 and H_2 was greater than in the presence of CO_2 alone. Again, the size and the position of all of the peaks observed during exposure to CO_2 and H_2 are consistent with the CO peaks observed for each of the catalysts at 350 °C during exposure to CO.

The appearance of the CO bound to the Pt during exposure to CO_2 and H_2 suggests that hydrogen assisted CO_2 dissociation is occurring on the PZ, PCZ, and PLZ catalysts. The fact that more CO is observed on the PLCZ catalyst during exposure to CO_2 and H_2 than was observed during exposure to CO_2 alone also suggests that some hydrogen assisted CO_2 dissociation also occurs on this catalyst. However, it is important to note that CO_2 dissociation occurred on the PLCZ in the absence of hydrogen, suggesting that the simultaneous presence of the Ce and La does impact the catalyst ability to dissociate CO_2.

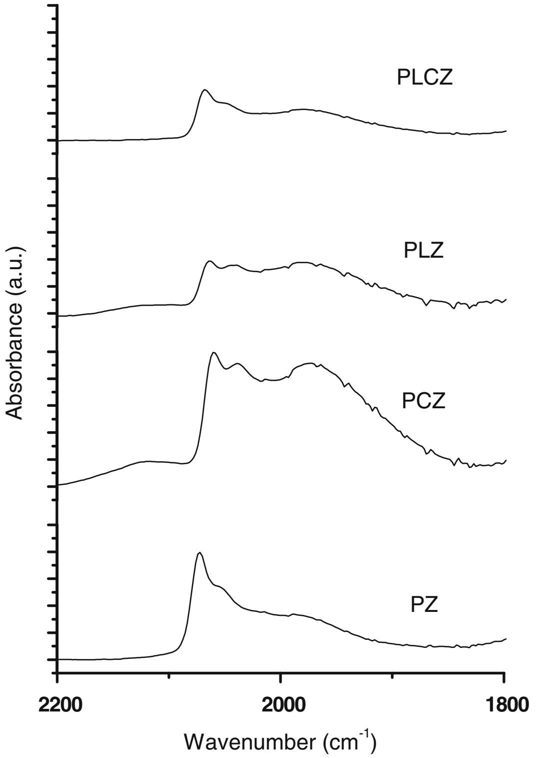

Figure 6. DRIFTS spectra recorded for PZ, PCZ, PLZ, and PLCZ during exposure to 1% CO_2/He mixture and H_2 at 350 °C.

It has been previously suggested that reducibility of a support can play a role in the activation of co-reactants for reactions such CO oxidation [12], low temperature water gas shift [8–10], and the carbon dioxide reforming of methane [5,17]. It has been proposed that the surface reduction of a support, and the resultant generation of oxygen vacancies in the support lattice, can aid in the dissociation of CO_2, H_2O, and O_2 [5,17,30,31]. We have previously reported that small amounts of surface reduction can occur near the metal particle on 1.5 wt% PZ, PCZ, and PLZ catalysts [5] and that CO_2 dissociates independently after the surface reduction was imposed. However, the catalysts used in that study were reduced at 500 °C in hydrogen and the support reduction studies were performed at 800 °C. The catalysts used in this study have purposefully been reduced at low temperatures (350 °C) to minimize any support reduction and subsequent formation of oxygen vacancies. The results of this work, which demonstrate that the dissociation of CO_2 does not occur on the PZ, PCZ, and PLZ at 350 °C in the absence of hydrogen, provide strong support for the role of the oxygen vacancies in facilitating the dissociation of CO_2 on supported Pt catalysts.

In contrast to the PZ, PCZ, and PLZ catalysts, the PLCZ catalyst did show CO_2 dissociation at 350 °C in the absence of hydrogen. Temperature programmed reduction (TPR) studies have been performed on the PLCZ catalyst after the same low temperature oxidation and reduction pre-treatments in this study. The experiment showed that the major reduction peak was centered at 197 °C and that the H_2/Pt ratio for the hydrogen consumption corresponding to this peak was approximately 2.6. The temperature of reduction is higher than the reduction temperature observed on the PZ catalyst (175 °C) and the H_2/Pt ratio is also higher than for the PZ catalyst (1.1). As discussed before, the ZrO_2 support is not expected to be a highly reducible support material, with only slight surface reduction being observed near the metal particle at high temperatures. This idea is confirmed by the near unity H_2/Pt ratio observed on the PZ catalyst. However, the PLCZ catalyst shows significantly more hydrogen consumed than what would be expected for the reduction of the metal. We ascribed the increase in hydrogen consumption to an increase in the low temperature reducibility of the surface of the support near the metal particle. The increased reducibility leads to an increase in the number of oxygen vacancies formed during reduction at 350 °C, and these vacancies facilitate the dissociation of CO_2 in the absence of hydrogen. The increased reducibility at low temperatures could be beneficial for reactions at low temperatures such as the low temperature water gas shift or selective CO oxidation reaction, in which the support reduction plays a part in the reaction mechanism.

3.7. *Effect on reactivity*

All of the characterizations performed on the Pt/$La_{0.04}Ce_{0.14}Zr_{0.82}O_2$ catalyst suggest that the simultaneous reduction of the metal and support can occur during reduction at 350 °C. The results of the TPR studies suggest that even at temperatures as low as 195 °C support reduction can occur. The reduction is ascribed to the simultaneous presence of Ce and La in the support because the formation of vacancies is not observed under the same conditions for the individually promoted catalysts.

For many reactions including methane reforming, water gas shift, and selective CO oxidation, the reducibility of a support is an important factor in determining the overall activity and stability of the catalyst. A support which shows an increased ability to form oxygen defects without losing stability is a potentially good support material for the above mentioned reactions. Many studies have shown that strong metal–support interactions can occur on supports such as TiO_2, La_2O_3, $LaCoO_3$, and even ZrO_2 under some conditions [32–36]. Some results have suggested that the metal–support interaction can be beneficial for performance, because new more reactive, partially reduced supports sites are created. However, if the degree of support reduction is too great, significant loss of exposed metal area due to the encapsulation can result in apparent decreased activity.

In order to compare the effect of the reducibility on the catalytic performance during high temperature and low temperature reactions, a 0.37 wt% Pt/$La_{0.04}Ce_{0.14}Zr_{0.82}O_2$ and a 0.42 wt% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst were tested for the high temperature CO_2 reforming and the low temperature water gas shift reactions. For the high temperature reforming reaction the activity was recorded after 9 h of the dry reforming of methane at 800 °C and a 1:1 CH_4:CO_2 feed ratio. Prior to the reaction, the catalysts were reduced *in situ* in H_2 for 1 h at 500 °C and then heated to 800 °C in He. Although the stability of the catalysts was identical, the activity of the PLCZ catalyst was significantly lower than the PCZ catalyst. The rate of reaction after 9 h was 5×10^{-2} mol CH_4 reacted/g of Pt/s for the PCZ catalyst and approximately 3×10^{-2} mol CH_4 reacted/g of Pt/s for the PLCZ catalyst. As previously discussed, the BET surface areas of the supports and the metal particle sizes were similar for the two catalysts. Based on the similarity in the characterization between the materials, the lower activity observed on the Pt/$La_{0.04}Ce_{0.14}Zr_{0.82}O_2$ catalyst is ascribed to significant reduction of the support after reduction at 500 °C leading to a loss of Pt metal exposed for the reaction. Thus, in the case of reforming where high temperature reduction and reaction is necessary, the increased reducibility of the $La_{0.04}Ce_{0.14}Zr_{0.82}O_2$ support hinders the catalytic performance.

The same rate comparison was made for the two catalysts after 9 h of the low temperature water gas shift reaction at 230 °C. The catalysts were reduced *in situ* at 230 °C in H_2 prior to reaction and the reaction was performed with a 2:1 ratio of H_2O:CO and 10% CO in the dry feed. In contrast to the high temperature reforming reaction, the activity of the PLCZ catalyst was observed to be slightly greater than the activity of the PCZ catalyst for the low temperature water gas shift reaction, with the final rates being 4×10^{-3} mol CO reacted/g of Pt/s and 3×10^{-3} mol CO reacted/g of Pt/s, respectively. The results of the TPR studies have demonstrated that reduction of the PLCZ support can occur at temperatures as low as 195 °C and it is expected that formation of surface oxygen defects on the PLCZ catalyst would be significant during reaction. Thus, the increased reducibility of the catalyst containing both Ce and La and the ability to formation oxygen defects for the activation of water would result in the increased activity observed. It is likely that the lower reaction and reduction temperature aids in the formation of vacancies but is not significant enough to result in encapsulation of the metal particle under reaction conditions resulting in improved performance.

4. Conclusions

DRIFTS has been used to study CO and CO_2 adsorption on Pt supported on Ce and La modified ZrO_2 catalysts. Reduction at 350 °C is sufficient to cause significant oxygen defect formation in the surface of the support material when both Ce and La are present. The increased ability to form oxygen vacancies is attributed to the presence of a higher concentration of La and Ce on the surface of the ZrO_2 which is more easily reduced.

Hydrogen assisted CO_2 dissociation was demonstrated on all of the catalysts at 350 °C. In the absence of hydrogen, only the Pt/$La_{0.04}Ce_{0.14}Zr_{0.82}O_2$ catalyst was capable of dissociating CO_2 at 350 °C which is attributed to the formation of oxygen defects in the support after reduction at 350 °C. The increased reducibility of the $La_{0.04}Ce_{0.14}Zr_{0.82}O_2$ support can be advantageous for reactions in which the oxygen storage and release capacity is important in the reaction mechanism. However, high temperature reduction and reaction can lead to encapsulation of the metal and a detrimental loss of active metal exposed for reaction.

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