Catalytic Performance of Ce$_{0.6}$Y$_{0.4}$O$_2$-Supported Platinum Catalyst for Low-Temperature Water–Gas Shift Reaction

Sang Moon Lee, Geo Jong Kim, Seung Hyun Lee, In Hyuck Hwang, Sung Chang Hong,* and Sung Su Kim*©

Department of Environmental Energy Engineering, Kyonggi University, 94-6 San, Iui-dong, Youngtong-ku, Suwon-si, Gyeonggi-do 443-760, Republic of Korea

ABSTRACT: In this study, Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ catalyst was prepared using a citric sol–gel method and was used as a catalyst for a water–gas shift (WGS) reaction. Compared to 1 wt % Pt/CeO$_2$ and Pt/Y$_2$O$_3$ catalysts, the Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ catalyst showed a much higher WGS catalytic activity. At 250 ºC, the conversion of carbon monoxide was 86.35% at a weight hourly space velocity of 30,000 cm$^3$ g$_{cat}^{-1}$ h$^{-1}$. The physicochemical properties of the catalysts were investigated via X-ray diffraction, transmission electron microscopy, chemisorption, H$_2$ and CO temperature-programmed reduction, and in situ diffuse reflection infrared Fourier transform spectroscopy. These results confirmed that the catalytic activity did not depend on the dispersion and particle size of platinum. The high reducibility of the Ce$_{0.6}$Y$_{0.4}$O$_2$ support plays a crucial role in improving the activity of the Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ catalyst, and this improvement can also be explained by the reduction in CO adsorption strength.

INTRODUCTION

A water–gas shift (WGS) reaction is important for high-purity hydrogen production, and this WGS reaction can increase the H$_2$ concentration as well as increase the CO concentration in feed streams for fuel cell applications. The WGS reaction is moderately exothermic, reversible, and equilibrium limited. It occurs in two steps to overcome the thermodynamic restrictions of the WGS reaction at higher temperatures. A high-temperature shift reactor is used to rapidly convert CO, and a low-temperature shift reactor is used to shift the equilibrium toward H$_2$ production. However, commercially available WGS catalysts are not appropriate as compact reformers for low-temperature fuel cells. Furthermore, the WGS catalysts have problems related to: (1) volume, weight, and cost (30–50% of the fuel processor), (2) transient response to changes in feed composition and temperature, (3) pyrophoricity, (4) deactivation in the presence of excess steam, (5) and the long time, that is, a lengthy precondition step is necessary for catalyst activation. Many attempts have been made to develop novel catalysts for a single-step WGS reactor to solve the disadvantages of using commercial WGS catalysts. Noble metal (e.g., Pt, Pd, and Au)-based catalysts have been reported as promising single-stage WGS catalysts due to their high catalytic activity at low temperatures as well as tolerance in chemical poisoning. Among noble catalysts, highly active and stable Pt-based catalysts have been extensively studied for compact fuel cell applications. Reducible Pt-based catalysts have been found to show a higher activity compared to that of Rh, Ru, or Pd, and various metal oxide supports have also been investigated to increase the catalytic activity with low-temperature WGS reactions. Panagiotopoulou et al. reported that the WGS catalytic activity of Pt-based catalysts depends strongly on the support’s physicochemical properties, and this activity significantly depends on reducible support rather than irreducible support. Pt/CeO$_2$ catalysts have been extensively investigated for use as a water–gas shift catalysts. However, the activity and stability of the Pt/CeO$_2$ catalyst at low temperatures still need to improve. Many studies have examined ceria-based mixed oxides supporting Pt catalysts, including Pd/CeO$_2$–TiO$_2$, Pt/Ce$_2$Zr$_{1−x}$O$_2$, Pt/Si–Ce, and Pt/Ce$_{0.6}$La$_x$O$_{2−δ}$ to increase the reducibility of the catalyst. Pt supported on Ce-rich Pt/Ce$_{0.8}$Zr$_0.2$O$_2$ samples is more active than that on Pt/CeO$_2$ and Jeong et al. reported that the Pt/Ce$_{0.6}$Zr$_0.4$O$_2$ catalyst exhibits a high Pt dispersion and supports reducibility and oxygen storage capacity.

In this study, we used the Ce(NO$_3$)$_3$·6H$_2$O and Y(NO$_3$)$_3$ precursors to obtain the oxygen vacancy for nonstoichiometric Ce$_{0.6}$Y$_{0.4}$O$_2$ excluding zirconium. We synthesized platinum catalyst supported on cerium–yttria (1 wt % Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$) by the citrate sol–gel method for a low-temperature WGS reaction, and the physicochemical characteristics and redox properties of the catalysts were investigated via temperature-programmed reduction (TPR), X-ray diffraction (XRD), transmission electron microscopy (TEM), and diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) analyses.

RESULTS AND DISCUSSION

Catalytic Activity and Physicochemical Characteristics. Figure 1 shows the CO conversions of Pt/CeO$_2$, Pt/Y$_2$O$_3$, and Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ catalysts as a function of reaction temperature at a weight hourly space velocity (WHSV) of 30...
Considerable differences in catalytic activity at 250 °C were observed depending on the support. The Pt/Ce0.6Y0.4O2 catalyst is significantly more active than Pt/Y2O3 and Pt/CeO2. For Pt/Ce0.6Y0.4O2, the CO conversion was about 86.35% at 250 °C, and complete conversion (100%) of CO was achieved at 300–400 °C, reaching equilibrium values.

The Pt/CeO2 catalyst showed higher CO conversion than the Pt/Y2O3 catalyst at 250 °C. We compared the low-temperature water–gas shift activity over our Pt/Ce0.6Y0.4O2 catalyst with previously reported Pt-based catalysts, and these results are summarized in Table 1. Of course, a direct comparison cannot be performed accurately due to the difference in experiment conditions, such as space velocity, pressure, inlet gas concentration, Pt dispersion, and loadings. Most importantly, the Pt/Ce0.6Y0.4O2 catalyst prepared by the sol–gel method has been first reported in this study, and it has a superior catalytic activity at 250 °C. We only confirmed that the long-term stability of Pt/Ce0.6Y0.4O2 catalyst was well maintained for 24 h at the temperature at 250 °C (not shown). However, in this study, in case of catalysts of Pt/CeO2 and Pt/Y2O3, as the initial conversion was very low at 250 °C, catalytic stability was not compared.

Table 1. Comparison of Water–Gas Shift Reaction Activity of Pt/Ce0.6Y0.4O2 and Pt-Based Catalysts Reported in the Recent Literature

| Catalyst                  | Pt loading (wt %) | temp. (°C) | S/C ratio | WHSV (cm³ gcat⁻¹ h⁻¹) | TOF (s⁻¹) | ref |
|---------------------------|-------------------|------------|-----------|-----------------------|-----------|-----|
| Pt/HAP-10.5               | 0.77              | 300        | 2         | 150 000               | 0.550     | 18  |
| Pt/FAP                    | 0.78              | 300        | 2         | 150 000               | 0.600     | 18  |
| Pt/CeO2                   | 0.74              | 300        | 2         | 150 000               | 0.730     | 18  |
| Pt–4Na–TiO₂               | 1                 | 300        | 2         | 40 000                | 3.820     | 19  |
| Pt/Ce₆₋₈Y₄₋₄O₂            | 0.5               | 250        | 8.7       | N/A                   | 0.215     | 20  |
| Pt/Al₂O₃                  | 1                 | 250        | 1.33      | 24 000                | 0.012     | 21  |
| Pt/Al₂O₃                  | 1                 | 250        | 1.33      | 24 000                | 0.085     | 21  |
| Pt/ZrO₂                   | 1                 | 250        | 1.33      | 24 000                | 0.047     | 21  |
| Pt/Ce₆₋₈Zr₄₋₄O₂           | 1                 | 250        | 1.33      | 24 000                | 0.250     | 21  |
| Pt/Ce₆₋₈Zr₄₋₄O₂           | 1                 | 250        | 1.33      | 24 000                | 0.216     | 21  |
| Pt/Al₂O₃                  | 3.9               | 240        | 1.91      | 125 000               | 0.007     | 22  |
| Pt/Mo₂C                   | 3.9               | 240        | 1.91      | 125 000               | 1.900     | 22  |
| 4Pt–Mo₂C/Al₂O₃            | 3.8               | 240        | 1.91      | 125 000               | 0.810     | 22  |
| Pt/Al₂O₃                  | 0.82              | 250        | 3.22      | 4524–22 620           | 0.009     | 23  |
| Pt/Al₂O₃–Na               | 0.82              | 250        | 3.22      | 4524–22 620           | 0.880     | 23  |
| Pt/Al₂O₃–Li               | 0.82              | 250        | 3.22      | 4524–22 620           | 0.260     | 23  |
| Pt/Al₂O₃–K                | 0.82              | 250        | 3.22      | 4524–22 620           | 0.260     | 23  |
| Pt/Ce₆₋₈Y₄₋₄O₂            | 1                 | 250        | 3         | 30 000                | 0.548     | this work |

Gas hourly space velocity (h⁻¹).

Figure 2 shows the XRD patterns of Pt/CeO2, Pt/Y2O3, and Pt/Ce0.6Y0.4O2 catalysts. For the Pt/CeO2 catalyst, the XRD pattern of CeO2 consists of six main peaks at 28.57, 33.00, 47.60, 56.39, 59.13, and 69.51 °C corresponding to (111), (200), (220), (311), (222), and (400) planes, respectively. The cubic ceria phase with a fluorite structure was observed in XRD analysis (JCPDS card no. 34-394).24 For the Pt/Y2O3 catalyst,
The XRD pattern of Y$_2$O$_3$ consists of five main peaks at 20.5, 29.2, 33.9, 48.6, and 57.7° corresponding to (211), (222), (400), (440), and (622) planes, respectively. The pattern exhibits well-defined diffraction high-crystallinity peaks, and all peaks were attributed to the cubic structure of Y$_2$O$_3$ (JCPDS card no. 86-1326, space group $Ia\overline{3}$). The diffraction peaks of Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ catalysts showed a difference in the intensity, and the full width at half maximum of the peaks was changed. Ce$_{0.6}$Y$_{0.4}$O$_2$ mixed support existed in amorphous phase as distortions of the CeO$_2$ and Y$_2$O$_3$ lattices regardless of the Ce-Y synthesis. This indicates that the substitution of cerium ions (0.092 nm) by similar Y ions (0.090 nm) in the Ce$_{0.6}$Y$_{0.4}$O$_2$ mixed oxide support could occur, and the interaction of Ce and Y could destroy the long-range order structure of CeO$_2$ or Y$_2$O$_3$ by using a Ce and Y precursor in the citric acid sol–gel process.

The physicochemical characteristics and turnover frequency (TOF) at 250 °C of the Pt-based catalysts are shown in Table 2. The specific surface area of the Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ catalyst (63.68 m$^2$ g$^{-1}$) is much higher than that of Pt/CeO$_2$ and Pt/Y$_2$O$_3$. The Pt dispersion results showed that platinum is well dispersed for the Pt/CeO$_2$ catalyst (34.27% by CO, 92.52% by H$_2$), whereas Pt dispersions of the Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ (18.89% by CO, 36.39% by H$_2$) and Pt/Y$_2$O$_3$ (13.30% by CO, 32.97% by H$_2$) catalysts are lower than that of the Pt/CeO$_2$ catalyst. The calculated TOFs at 250 °C for all catalysts are also presented in Table 2. The TOFs are more than 3 times higher for the Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ catalyst than for Pt/CeO$_2$. A TEM analysis was conducted to observe the particle size of Pt, and the results are shown in Figure 3. Interestingly, the Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ catalyst had the smallest Pt size of approximately 2.3−3.4 nm, and the particle sizes of Pt/CeO$_2$ and Pt/Y$_2$O$_3$ were about 4.1−7.5 and 4.8−14.7 nm, respectively. According to the above XRD and specific surface area results, the crystalline peak of the synthesized Ce$_{0.6}$Y$_{0.4}$O$_2$ support was quite broad and has relatively very large specific surface area and pore volume. The fact that Pt dispersion is small when Pt is impregnated in Ce$_{0.6}$Y$_{0.4}$O$_2$ support means that the quantity of CO gas to be adsorbed is little, and it could be presumed that Pt exists even in pore bulk of Ce$_{0.6}$Y$_{0.4}$O$_2$ support. This is probably the reason why Pt is well incorporated into the bulk amorphous phase of the Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ catalyst. These results for the physicochemical characteristics indicate that the catalytic activity does not depend on the metal dispersion or metallic surface area for Pt/CeO$_2$, Pt/Y$_2$O$_3$, and Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ catalysts. The results

| Catalyst | Surface Area (m$^2$ g$^{-1}$) | Total Pore Volume (cm$^3$ g$^{-1}$) | Metal Dispersion (a) (%) | Metal Dispersion (b) (%) | Metallic Surface Area (m$^2$ g$^{-1}$) | TOF (s$^{-1}$) |
|----------|-----------------------------|-----------------------------------|-------------------------|-------------------------|---------------------------------|--------------|
| Pt/CeO$_2$ | 3.1973                     | 0.0015                           | 34.27                   | 92.52                   | 84.6388                         | 0.1579       |
| Pt/Y$_2$O$_3$ | 4.5842                     | 0.0019                           | 13.30                   | 32.97                   | 32.8389                         | 0.1290       |
| Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ | 63.6840                    | 0.0290                           | 15.89                   | 36.39                   | 39.2344                         | 0.5479       |

(a) Determined by the CO chemisorption data. (b) Determined by the H$_2$ chemisorption data.

Figure 3. TEM images of (a) Pt/CeO$_2$, (b) Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$, and (c) Pt/Y$_2$O$_3$ catalysts and Pt particle size distributions of (d) Pt/CeO$_2$, (e) Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$, and (f) Pt/Y$_2$O$_3$ catalysts.
metal-based catalysts such as Pt/CeO$_2$, Pt/TiO$_2$, Ru/TiO$_2$, and loadings and dispersion or crystallite size for various noble properties of Pt/CeO$_2$, Pt/Y$_2$O$_3$, and Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ catalysts terms of TOF is meaningless. The factors that a occurs on the support or interface site, the compared activity in properties rather than by Pt dispersion. If CO adsorption occurs on the support or interface site, the compared activity in terms of TOF is meaningless. The factors that affect the redox properties of Pt/CeO$_2$, Pt/Y$_2$O$_3$, and Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ catalysts need to be examined. These results are in good agreement with earlier work by Panagiotopoulou et al.,$^6$ who reported that the turnover frequency (TOF) does not depend on the metal loadings and dispersion or crystallite size for various noble metal-based catalysts such as Pt/CeO$_2$, Pt/TiO$_2$, Ru/TiO$_2$, and Pt/Al$_2$O$_3$. 

**Redox Properties.** H$_2$ TPR experiments were performed to investigate the reducibility of the catalyst used in this study. Figure 4a shows the H$_2$ TPR profiles of the pure CeO$_2$, TiO$_2$, and Ce$_{0.6}$Y$_{0.4}$O$_2$ supports. For the CeO$_2$ support, the TPR peak of CeO$_2$ shows two reduction bands. The first low-temperature band (max. 450 °C) was caused by the reduction of the surface ceria.$^{27-30}$ This reduction pathway has been founded in terms of the removal of surface capping oxygen ions attached to surface Ce$^{4+}$ species.$^{29}$ The high-temperature reduction band (max. 790 °C) in the reference material is attributed to the reduction of bulk CeO$_2$ to Ce$_2$O$_3$.$^{30}$ For the Y$_2$O$_3$ support, the reduction of the Y$_2$O$_3$ support alone is difficult, with no TPR peak observed at all temperature ranges. Compared to the TPR of individual CeO$_2$ and Y$_2$O$_3$ supports, the reduction curves in the Ce$_{0.6}$Y$_{0.4}$O$_2$ support increase. This result indicates an increase in the reducibility by introducing a yttria element into the ceria matrix, and this is in good agreement with other detailed studies.$^{16}$ Lee et al.$^{31}$ reported that when the Ce ion was doped into the TiO$_2$ support, reduction peaks of the Ce/TiO$_2$ catalyst emerged at 410, 480, and 515 °C. The first peak (410 °C) was attributed to a reduction of the surface oxygen as stoichiometric ceria (Ce$^{4+}$−O−Ce$^{4+}$),$^{32}$ and the second peak (480 °C) was attributed to a reduction of the nonstoichiometric ceria (Ce$^{3+}$−O−Ce$^{4+}$).$^{33}$ Unlike other catalysts, the reduction peaks of the Ce/TiO$_2$ catalyst slightly overlapped at 515 °C, and this may be due to a slight reduction of Ti$^{4+}$ to Ti$^{3+}$ in the bulk TiO$_2$ after the ceria oxide on the surface has been reduced by hydrogen. Compared to the reduction properties of pure CeO$_2$ and TiO$_2$ and Ce/TiO$_2$ catalysts, the reduction temperature of the Ce/TiO$_2$ catalyst decreased, which is likely due to interactions between Ce and TiO$_2$. The interactions between ceria and the TiO$_2$ phase are weaker. As a result, the reduction of Ce$^{4+}$−O−Ce$^{4+}$ or Ce$^{4+}$−O−Ti$^{4+}$ species of Ce/TiO$_2$ occurs at a lower temperature than that in other catalysts. This result means that reduction was increased by Ce ion impregnated into the TiO$_2$ support with a lower calcination temperature. In this study, according to the literature described above, reduction peaks for the Ce$_{0.6}$Y$_{0.4}$O$_2$ support emerged at 324, 390, and 488 °C. The first reduction peak at 324 °C was attributed to a reduction of the surface oxygen of the nonstoichiometric ceria and yttria (Ce−O−Y), the second peak at 390 °C was attributed to a reduction of the stoichiometric ceria (Ce$^{4+}$−O−Ce$^{4+}$), and the last peak at 488 °C was attributed to a reduction of the nonstoichiometric ceria (Ce$^{3+}$−O−Ce$^{4+}$). The reduction profiles of platinum catalysts supported on CeO$_2$, Y$_2$O$_3$, and Ce−Y are presented in Figure 4b. The Ce−Y synthesis of the supports after platinum impregnation leads to the formation of platinum oxides with a different stoichiometry depending on the type of support,$^{31-36}$ and Pt-based catalysts have a lower temperature peak and two broad peaks at 50−200 and 300−600 °C. Reduction peaks of Pt/CeO$_2$ and Pt/Y$_2$O$_3$ have very low intensity compared to that on cerium-modified Y$_2$O$_3$ support. Lower temperature reduction peaks were attributed to a reduction in the surface PtO$_x$ species.$^6$ Reduction peaks at medium temperatures (300− 600 °C) were attributed to a reduction peak of the interaction with Pt and Ce$_{0.6}$Y$_{0.4}$O$_2$ support or Ce$_{0.6}$Y$_{0.4}$O$_2$ supports. All these observations in the TPR results confirm that Pt/Ce$_{0.6}$Y$_{0.4}$O$_2$ which has high WGS activity, showed a lower TPR peak (PtO$_x$) at lower temperature as well as high oxygen mobility of Ce$_{0.6}$Y$_{0.4}$O$_2$ species. This increase in the O$^{2-}$ ion concentration (related to oxygen vacancies) with the synthesis of Ce$_{0.6}$Y$_{0.4}$O$_2$ supports reflects high oxygen mobilities of PtO$_x$ and Ce$_{0.6}$Y$_{0.4}$O$_2$ species and thus easily participates in the WGS reaction.

CO TPR results provide relative amounts of reducible all sites (support or active metal or interface) by CO adsorption on the catalyst surface, and we can determine the continuous CO reduction reaction pathway with reaction temperature. Thus, CO TPR experiments were also performed, and the
results are shown in Figure 5, in which the responses of CO₂ and H₂ produced are plotted as functions of temperature. In this study, a reduction CO peak of Pt/Ce₀.₆Y₀.₄ has a very large consumption peak compared to that on the Pt/CeO₂ and Pt/Y₂O₃ catalysts.

For the Pt/Ce₀.₆Y₀.₄ catalyst, the reduction profile of CO consists of a low-temperature peak at 100–180 °C, a medium-temperature broad peak evolving from 200 to 400 °C, and a high-temperature peak, which appears at temperatures around 550–800 °C. The CO₂ peak was observed and the H₂ peak was not observed in Figure 6b,c. Thus, the first peak at 100–180 °C was attributed to a reduction in the PtOₓ species as follows

$$\text{CO}_{\text{ads}} + \text{PtO} \rightarrow \text{Pt} + \text{CO}_2$$  \hspace{1cm} (1)

The CO₂ profile at medium temperature (200–400 °C) is always accompanied by the formation of H₂; this result indicates that CO₂ and H₂ are formed at the same time. Because the only hydrogen source is the –OH group on the support, the simultaneous formation of CO₂ and H₂ can be attributed to the WGS reaction as follows

$$\text{CO}_{\text{ads}} + 2\text{OH}^-(\text{support}) \rightarrow \text{CO}_2 + \text{H}_2 + \text{O}_2^-(\text{support})$$  \hspace{1cm} (2)

Panagiotopoulou et al. showed that the reaction occurs at the metal–support interface between the CO adsorbed on the metallic Pt site and –OH groups on the support. Finally, the CO₂ profile at a high temperature (550 °C) was observed with the CO reduction profile, and it can be attributed to the CO consumption reaction as follows

$$\text{CO}_{\text{ads}} + \text{Ce₀.₆Y₀.₄O₂(support)} \rightarrow \text{CO}_2 + \text{Ce₀.₆Y₀.₄O₂−δ(support)}$$  \hspace{1cm} (3)

However, the high temperature (550 °C) was not within the WGS reaction temperature region. Thus, the reduction in Pt/Ce₀.₆Y₀.₄O₂ at medium temperatures (180–500 °C) is important within this temperature region. Zhu et al. reported that the main reaction pathways suggested for the WGS reaction over the reducible Pt catalyst is an associative pathway with an interaction of CO on Pt metal with hydroxyl groups on the support, leading to the formation of formate species, which then decomposes to CO₂ and H₂.

Bruij et al. reported that the strong Pt metal and CeO₂ support interaction significantly enhances the ability of the admetal of dissociating the O–H bonds in water due to large electronic change. A redox pathway, CO adsorbed on Pt is oxidized by oxygen ion from the support to form CO₂ and the oxygen vacancy site is refilled by H₂O with releasing H₂ as a redox pathway. On the basis of our study, the Ce₀.₆Y₀.₄O₂-supported Pt catalyst improved catalyst reducibility, favoring the creation of OH groups as active sites related to oxygen defects in the support for the WGS reaction.

**DRIFT Study.** Figure 6 shows the DRIFT results from the Pt/Y₂O₃, Pt/CeO₂, and Pt/Ce₀.₆Y₀.₄O₂ catalysts. The adsorbed CO species were examined by injecting CO gas in the temperature range from 25 to 300 °C. For the Pt/Y₂O₃ catalyst (Figure 6a), two bands were maintained in the temperature range from 25 to 100 °C; these bands were attributed to CO adsorbed on Ptδ₊ sites (2085 cm⁻¹) and CO adsorbed on PtO (2112 cm⁻¹). The broad bands observed at 2175 cm⁻¹ are due to CO gas, which are present in all spectra. The bands observed at 2085 cm⁻¹ were attributed to vibrational frequencies higher than those expected from the CO adsorbed on reduced Pt metal sites and, consistent with previous results, can be attributed to CO adsorbed on partially oxidized platinum (Ptδ−CO). The linearly adsorbed CO peak on the metallic Pt sites was observed at 2068 cm⁻¹, which is more thermally stable, and this peak disappeared at temperatures higher than 200 °C. All CO bands disappeared upon an increase in temperature to above 300 °C. The DRIFT spectra of the Pt/CeO₂ catalyst are shown in Figure 6b. The relative intensities of the bands attributed to CO adsorbed on Ptδ⁻ sites

![Figure 5. CO TPR profiles of Pt/CeO₂, Pt/Y₂O₃, and Pt/Ce₀.₆Y₀.₄O₂ catalysts: (a) CO profile, (b) CO₂ profile, and (c) H₂ profile.](image-url)
lower than that required for the Pt/Y2O3 and Pt/CeO2 catalysts. DRIFT results of Pt/Y2O3, Pt/CeO2, and Pt/Ce0.6Y0.4O2 could reduce the rate of reaction at low temperature. From the strong adsorption of CO could block the active sites and it the catalyst surface at low temperature. It is believed that the indicated that the weakly adsorbed CO is easily desorbed from indicates the relative adsorption strength of CO; this result results in a significant enhancement of the activation of the adsorbed CO species and a very weak PtO—CO bond. The DRIFT spectra of the highly active Pt/Ce0.6Y0.4O2 catalysts are shown in Figure 6c. The spectrum for the Pt/Ce0.6Y0.4O2 catalyst is characterized by two bands in the CO adsorption strength.

Figure 6. DRIFT spectra of (a) Pt/Y2O3, (b) Pt/CeO2, and (c) Pt/Ce0.6Y0.4O2 catalysts. (d) 25 °C CO adsorption for 15 min; (e) 50 °C N2 desorption for 15 min; (f) 100 °C N2 desorption for 15 min; (g) 150 °C N2 desorption for 15 min; (h) 200 °C N2 desorption for 15 min; (i) 250 °C N2 desorption for 15 min; (j) 300 °C N2 desorption for 15 min; and (k) 350 °C N2 desorption for 15 min.

(2085 cm⁻¹) and PtO (2112 cm⁻¹) are higher than those of the Pt/Y2O3 catalyst. The band attributed to CO adsorbed on Pt⁶⁺ sites (2085 cm⁻¹) was maintained in the spectra up to 100 °C and the band disappeared over 150 °C. The CO adsorbed on the PtO (2112 cm⁻¹) band was maintained in the temperature range from 25 to 300 °C. The CO adsorbed on PtO bands disappeared upon an increase in temperature to above 300 °C, which is thermally more stable and exhibits a strong PtO—CO bond. The DRIFT spectra of the highly active Pt/Ce0.6Y0.4O2 catalysts are shown in Figure 6c. The spectrum for the Pt/Ce0.6Y0.4O2 catalyst is characterized by two bands in the CO adsorbed on PtO (2112 cm⁻¹), and the bands observed at 2175 cm⁻¹ are due to gas-phase CO. The bands attributed to the CO adsorbed on Pt⁶⁺ sites (2085 cm⁻¹) were not observed. The most interesting observation is that the temperature required to eliminate CO adsorbed on the PtO peak (100 °C) is much lower than that required for the Pt/Y2O3 and Pt/CeO2 catalysts (250–300 °C). This clearly shows that Pt/Ce0.6Y0.4O2 catalyst results in a significant enhancement of the adsorption of the adsorbed CO species and a very weak PtO—CO bond. It indicates the relative adsorption strength of CO; this result indicated that the weakly adsorbed CO is easily desorbed from the catalyst surface at low temperature. It is believed that the strong adsorption of CO could block the active sites and it could reduce the rate of reaction at low temperature. From the DRIFT results of Pt/Y2O3, Pt/CeO2, and Pt/Ce0.6Y0.4O2 catalysts, the disappearance of the peak may reasonably suggest that the adsorbed CO can react with oxygen from the Ce0.6Y0.4O2 support for the Pt/Ce0.6Y0.4O2 catalyst. In contrast, adsorption of CO is still strong, which makes it difficult to transport oxygen from Y2O3 or CeO2 to CO chemisorbed on Pt sites for Pt/Y2O3 and Pt/CeO2 catalysts.

■ CONCLUSIONS

The catalytic performances and properties were investigated for Ce0.6Y0.4O2-supported platinum catalysts prepared by the citric sol–gel method for low-temperature water–gas shift reaction. The WGS catalytic activity of the Pt/Ce0.6Y0.4O2 catalyst was greatly enhanced compared to that of the Pt/Y2O3 and Pt/CeO2 catalysts. The catalytic activity does not depend on the metal dispersion or metallic surface area, whereas the increase in activity is directly correlated with an enhancement in the reducibility of the support. The Ce0.6Y0.4O2-supported Pt catalyst improved the catalyst reducibility, favoring the creation of OH groups as active sites related to oxygen vacancy in the support for a WGS reaction. Furthermore, a high reducibility of the Ce0.6Y0.4O2 support plays an important role in increasing the activity, and the Pt/Ce0.6Y0.4O2 catalyst can reduce the CO adsorption strength.

■ EXPERIMENTAL SECTION

Catalyst Preparation. CeO2 and Y2O3-supported Pt catalysts were prepared using wet impregnation with commercial CeO2 (<5 μm, 99.9%) and Y2O3 (99.99%) supplied by Aldrich Chemical Co. The CeO2 and Y2O3 supports were prepared by impregnation with PtCl4 (>99.9%, Sigma-Aldrich Chemical Co.) aqueous solution at the required concentration to obtain 1 wt % Pt. The calculated amount of PtCl4 (>99.9%, Sigma-Aldrich Chemical Co.) was dissolved in distilled water at 80 °C. Next, the calculated amount of CeO2 or Y2O3 support was slowly added to the solution while stirring. The mixed solution was agitated as a slurry for over 1 h, followed by evaporation at 70 °C using a rotary vacuum evaporator (Eyela Co. N-N series). After evaporation, the slurry was dried at 110 °C for 24 h. To remove the residual chlorine, the catalyst was reduced in a tubular furnace at 300 °C using 30% H2 for 1 h and finally calcined at 400 °C in air for 4 h. Then, the obtained samples were ground and sieved through a 40–50 mesh. To combine the Ce and Y precursors, the Ce0.6Y0.4O2·δ support was prepared by citrate sol–gel method, as previously described in the literature. In particular, a calculated amount of Ce(NO3)3·6H2O (>99.99%, Sigma-Aldrich Chemical Co.) and Y(NO3)3·6H2O (>99.8%, Sigma-Aldrich Chemical Co.) precursor was dissolved in distilled water to form a 0.1 M solution of the total metal ions. The solution pH was kept at 2.0 through the dropwise addition of 5 M nitric acid solution.
Then, citric acid was added about 1.5 times the total molar amount of metal ions in solution. The mixed solution was heated up to 70 °C while stirring to assist in the polymerization and condensation reactions. Finally, a gel-like yellowish material was obtained. After drying at 110 °C for 24 h, the solid powder became spongy. Then, the sample was calcined at 400 °C in an air atmosphere to eliminate all organic residues from the synthesis procedure. The 1 wt % Pt/CeO2 catalyst was prepared in accordance with the same procedure given above for 1 wt % Pt/CeO2 and 1 wt % Pt/Y2O3 catalysts. Finally, the Pt/CeO2 catalyst can be obtained.

Catalytic Activity Test. Water–gas shift activity tests were performed with a H2O to CO ratio of 3 and a weight hourly space velocity (WHSV) of 30 000 cm3 gcat−1 h−1. The gases fed to the reactor consisted of 5% CO and 15% H2O/N2 using mass flow controllers (MKS, Mass Flow Controller). Water was pumped into a vaporizer superheated at 450 °C using a micro liquid pump (Jasco, MINICHEMI PUMP). The water–gas shift apparatus consisted of a fixed-bed reaction system composed of a quartz tube (inner diameter: 8 mm, height: 650 mm) and a catalytic bed fixed using quartz wool. The gas composition was detected using an Agilent 6890N gas chromatograph equipped with a thermal conductivity detector and two packed columns (6 Å molecular sieves and Porapak-Q). A pressure indicator (Alicat, PC-100PSIG-D) was used to measure the pressure drop in the catalyst bed.

The turnover frequency (TOF) is defined as moles of converted CO per mole of exposed Pt atoms on the surface per second. The exposed Pt atoms on the surface were calculated from the dispersion obtained from CO chemisorption.

Characterizations. X-ray diffraction (XRD) analysis was performed using an X-ray diffractometer (PANalytical X’Pert PRO MRD) with Cu Kα radiation.

Temperature-programmed reduction (TPR) with H2 was measured using 10% H2/Ar at a total flow rate of 50 cm3 min−1 and 0.3 g of catalyst. Prior to the H2 TPR experiment, the catalyst was pretreated at 400 °C at a flow rate of 10% O2/Ar for 0.5 h and subsequently cooled to room temperature. The hydrogen consumption was monitored by increasing the temperature to 800 °C (10 °C min−1) using Autochem 2920 (Micrometrics).

The temperature-programmed reduction (TPR) of CO was measured using 5% CO/Ar and 0.3 g of the catalyst at a total flow rate of 50 cm3 min−1. Before the CO TPR measurement, the catalyst was pretreated at 400 °C at a flow rate of 10% O2/Ar for 0.5 h and subsequently cooled to room temperature. During the CO TPR experiments, H2 (2) and CO2 (44) products were continuously monitored by increasing the temperature to 800 °C (10 °C min−1) using a quadrupole mass spectrometer (QMS 200M).

Field emission-transmission electron microscope (TEM) images were obtained with a JEM-2100 F (JEOL) microscope (200 keV voltage). All catalyst powders were prepared by suspending an ultrasonicated catalyst powder in ethanol and placing the suspension on a Cu grid.

The dispersion and crystallite size of the catalysts were characterized via CO or H2 chemisorption at 50 °C using Autochem 2920 (Micrometrics). The catalyst samples were activated with 10% H2 at 400 °C for 0.5 h and then cooled to 50 °C and saturated with CO or H2 pulses.

The surface area and total pore volume of the catalysts were analyzed using ASAP 2010 C (Micromeritics Co.), and the values were calculated using the Brunauer–Emmett–Teller equation. Each sample was analyzed after degassing in a vacuum at 110 °C for 3–5 h.

In situ IR spectra were collected using a 660 plus Fourier transform infrared (FT-IR) spectrometer (JASCO) equipped with a CaF2 window and an mercury cadmium telluride detector, by recording 30 scans at a resolution of 4 cm−1. All catalysts were preheated in Ar at 400 °C for 1 h. Then, a mixture of 5% CO/Ar gas was fed into the sample. After steady state was reached, the FT-IR spectra were recorded at 25–350 °C.

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: schong@kyonggi.ac.kr (S.C.H.).
E-mail: sskim@kyonggi.ac.kr (S.S.K.).

**ORCID**

Sung Su Kim: 0000-0002-4195-0980

**Notes**

The authors declare no competing financial interest.

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