Aqueous phase reforming of ethylene glycol on Pt/\(\text{CeO}_2–\text{ZrO}_2\): effects of cerium to zirconium molar ratio†

Seongho Jeon,†a Hyungwon Ham,†a Young-Woong Suhb and Jong Wook Bae†a

The aqueous-phase reforming (APR) reaction of ethylene glycol was investigated on platinum-supported \(\text{CeO}_2–\text{ZrO}_2\) mixed oxides with different molar ratios of \(\text{Ce}/(\text{Ce} + \text{Zr})\). The main role of the molar ratio of \(\text{Ce}/(\text{Ce} + \text{Zr})\) on the \(\text{CeO}_2–\text{ZrO}_2\) mixed oxides was found to be to alter the dispersion of active platinum crystallites and concomitantly change the hydrogen productivity and stability. The different amounts of surface oxygen species on the defect sites of \(\text{CeO}_2–\text{ZrO}_2\) altered the dispersion of platinum crystallites and changed the metal-support interactions between the nano-scale platinum crystallites and the oxygen vacancy defect sites on the \(\text{CeO}_2–\text{ZrO}_2\) surface. A larger dispersion of platinum crystallites and a larger surface area were observed for the Pt/\(\text{CeO}_2–\text{ZrO}_2\) having a \(\text{Ce}/(\text{Ce} + \text{Zr})\) molar ratio of 4 : 6, and the catalyst showed a higher conversion of ethylene glycol to hydrogen by forming thermally stable platinum crystallites through their strong interactions with the defect sites of the \(\text{CeO}_2–\text{ZrO}_2\) surface.

1 Introduction

Biomass-derived alternative energy sources have been greatly investigated since fossil energy resources such as coal, petroleum and natural (or shale) gas have been depleted and their usage has produced severe environmental pollution. Therefore, clean hydrogen energy from the chemical treatment of biomass through the aqueous phase reforming (APR) reaction has been recognized as one of the alternative renewable energy sources to replace the conventional energy sources from natural gas or petroleum reforming processes.†–5 The APR reaction of biomass-derived chemicals is known to be a reforming reaction operating at lower temperatures than that of the hydrocarbon reforming reaction, showing high production rates of pure hydrogen due to the higher activity of a simultaneous water-gas shift (WGS) reaction. In general, for the chemical transformation of biomass containing C–C and C–O bonds, many kinds of supported metal catalysts can produce various gaseous products through C–C cleavage to form CO and \(\text{H}_2\) and C–O cleavage to form hydrocarbons under mild reaction conditions.†–5 Supported metals such as Pt, Ru, Rh, Ir, and Ni on various supporting materials have been known to be efficient catalytic systems for selective C–C cleavage, and the supported Co and Fe metals are also known to be active catalysts for the WGS reaction.†–8 Among them, the supported Pt and Pd metals are well known as active components for the APR reaction due to their high activities for C–C cleavage as well as the WGS reaction.† The main APR reaction of ethylene glycol (EG) can be attributed to the following four representative reactions.†–7

\[
\begin{align*}
\text{C}_2\text{H}_4\text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 2\text{CO}_2 + 5\text{H}_2 \quad \text{(C–C cleavage)} \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \quad \text{(water-gas shift)} \\
\text{C}_2\text{H}_6\text{O}_2 & \rightarrow \text{C}_2\text{H}_6\cdot\text{O}_2 + (x/2)\text{H}_2 \quad \text{(dehydrogenation)} \\
\text{CO} + 3\text{H}_2 & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \text{(methanation)}
\end{align*}
\]

Supported platinum catalysts generally show a higher catalytic activity for the APR reaction of EG by adsorption on the reduced metallic platinum surface, which can decompose C–C and C–O bonds effectively through the above APR reactions of \(1\)–\(3\), which can also change the product distributions depending on the extents of C–C and C–O cleavage.† The C–C cleavage reaction is known to mainly produce high purity hydrogen through a concomitant WGS reaction of CO to form the final product of CO\(_2\). However, the selective C–O cleavage reaction can produce light alkane products through the methanation reaction of \(4\). Therefore, the catalysts having a higher activity for the selective C–O cleavage reaction with a dominant C–C cleavage activity can increase the conversion of EG to high purity hydrogen by easily forming active intermediates through a subsequent WGS reaction.†
To obtain higher hydrogen productivity in the APR reaction, platinum crystallites need to be uniformly distributed on the porous support by forming proper interactions between the active metal and supporting materials. Among them, ceria (CeO₂) is well known to be in the form of Ce₂O₃ and CeO₂ oxides with a higher oxygen storage capacity, and CeO₂ can be partially reduced by removing O²⁻ ions from the surface with the concomitant formation of anion vacancy defect sites through the redox reactions between Ce⁴⁺ and Ce³⁺ species. The generated oxygen vacancy defect sites can strongly interact with the deposited metal crystallites. In addition, significantly different physicochemical properties of CeO₂–ZrO₂ mixed oxides can be obtained after incorporation of zirconium into cerium oxide structures. Generally, zirconia (ZrO₂) has three different main phases, namely monoclinic, tetragonal and cubic structures, and the facile structural changes between them, simply by changing the concentration of zirconium ions, have been known to largely alter the surface properties of CeO₂–ZrO₂ mixed oxides. Therefore, CeO₂–ZrO₂ mixed oxides have been greatly applied as supporting materials of heterogeneous catalysts due to their high surface area, high thermal stability, oxygen storage character, oxygen mobility, facile control of active metal dispersion by forming a strong metal–support interaction, and so on. The defect sites of CeO₂–ZrO₂ were attributed to the low-coordinate vacant sites, which can be assigned as two different vacant sites, namely cation vacancy or anion vacancy (or oxygen vacancy). These vacant sites can alter the dispersion of active metals and result in different catalytic activities by modifying the properties of the supported metal.

In the present study, the effects of the vacant sites or surface oxygen concentrations of CeO₂–ZrO₂ mixed oxides having different molar ratios of Ce/(Ce + Zr) were investigated to elucidate the different dispersions of active platinum crystallites and the catalytic activity for the APR reaction of EG. As far as we know, many investigations concerning platinum containing catalysts for the APR reaction have been carried out to now; however, the roles of the surface properties of CeO₂–ZrO₂ metal oxides, such as the oxygen vacancy defect sites, in the metal dispersions and activities have not been thoroughly investigated. In addition, since the sol–gel method has been known to be a facile synthesis method for highly porous metal oxides through homogenization and crystalline stabilization, the dispersion of platinum crystallites on the well-controlled porous CeO₂–ZrO₂ surfaces can clearly verify the effects of the surface vacant sites of the CeO₂–ZrO₂, with different dispersions of platinum crystallites, and the metal-support interactions on the catalytic activity.

2 Results and discussion

2.1 Catalytic activity of the Pt/CeO₂–ZrO₂ catalysts

The catalytic activities in terms of carbon conversion, H₂ production rate, and selectivity are summarized in Table 1. The catalytic activity for the APR reaction of EG was found to be maximized on Pt/CeO₂–ZrO₂(4), showing 43.3% conversion of EG to gaseous products and a hydrogen production rate of 30.0 mL g⁻¹ cat⁻¹ min⁻¹ with an insignificant variation in gaseous product distributions. The EG conversions and H₂ production rates were found to be in the ranges of 15.8–43.3% and 11.6–30.0 mL g⁻¹ cat⁻¹ min⁻¹, respectively, the lowest value being shown by Pt/CeO₂. Interestingly, the selectivity for CO (observed in the 0 to 3.4% range) was inversely proportional to the CO₂ selectivity (observed in the 20.8 to 25.3% range), showing a lower CO selectivity on Pt/CeO₂–ZrO₂(4), which suggests a higher WGS activity on the most active Pt/CeO₂–ZrO₂(4) catalyst. In addition, the EG conversions to hydrocarbons on the Pt/CeO₂–ZrO₂ were observed to be below 0.8%, except for Pt/ZrO₂ with a conversion of 2.1%. As reported in previous work, the APR of polyols for hydrogen production is a structure-sensitive reaction, with a linear increase in intrinsic activity with the increase in average platinum cluster size, and acid sites on the catalyst surface are favorable for the hydrocarbon formation instead of hydrogen. Therefore, the observed higher conversion of EG and lower selectivity for CO on Pt/CeO₂–ZrO₂(4) seems to be mainly attributed to the formation of small platinum crystallites. The catalytic activity with time on stream is also shown in Fig. 1. At the beginning of the APR reaction, even though lower conversions of EG were observed on all the Pt/CeO₂–ZrO₂ catalysts, a higher conversion of EG at steady-state was observed on Pt/CeO₂–ZrO₂(4) and a lower conversion on Pt/CeO₂, which suggest that significant surface changes, especially the aggregation of platinum crystallites, seem to be responsible for the different steady-state activities.

In addition, the selectivity for hydrocarbons, which were found to be mainly CH₄ and C₂H₆, decreased with the increase in CeO₂ concentration in the CeO₂–ZrO₂ mixed oxides, from 2.1% on Pt/CeO₂ to 0.5% on Pt/ZrO₂. This difference seems to be possibly attributed to the presence of small amounts of active oxygen species on the ZrO₂-rich mixed metal oxides in the reforming reaction of the adsorbed hydrocarbon intermediates. Based on previous studies, a higher capacity of active oxygen storage on the CeO₂ surface can also greatly enhance the catalytic activity for the reforming reaction of hydrocarbon intermediates derived from EG into syngas. This assumption can be also supported by the observation of similar catalytic activity above 5 wt% Pt on CeO₂–ZrO₂(4), as shown in ESI Table S1. The insignificant increase in activity at higher platinum loading on CeO₂–ZrO₂(4) of above 5 wt% can be attributed to the possible aggregation of platinum crystallites, which can concomitantly alter the surface properties of the CeO₂–ZrO₂ by selectively adsorbing on the active oxygen vacancy sites, suppressing the dispersion of platinum crystallites and simultaneously reducing the hydrocarbon formation. The variations in APR activities and selectivities with 0, 3, 5, and 9 wt% Pt impregnated in CeO₂–ZrO₂(4) are also summarized in ESI Table S1. Interestingly, significant catalyst deactivation after 10 h on stream was observed for the 3 wt% Pt/CeO₂–ZrO₂(4) and no activity was observed on the bare CeO₂–ZrO₂(4) support as shown in ESI Fig. S1 due to the possible severe coke deposition on the active platinum sites, which can be attributed to the suppressed WGS reaction by hindrance of the complete removal of the coke intermediates from the decomposed EG reactant. Therefore, the observed higher APR activity on Pt/CeO₂–ZrO₂(4) can be possibly attributed to a higher dispersion of platinum.
Table 1 Catalytic activity on the Pt/CeO2–ZrO2 catalysts

<table>
<thead>
<tr>
<th>Notation</th>
<th>EG conversion to gas (%)</th>
<th>H2 production rate (mL gcat⁻¹ min⁻¹)</th>
<th>Selectivity (%)</th>
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<tr>
<td>Pt/ZrO2</td>
<td>25.1</td>
<td>17.1</td>
<td>73.9</td>
</tr>
<tr>
<td>Pt/CeO2–ZrO2(3)</td>
<td>35.0</td>
<td>23.1</td>
<td>73.3</td>
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<tr>
<td>Pt/CeO2–ZrO2(4)</td>
<td>43.3</td>
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<td>74.3</td>
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<td>Pt/CeO2–ZrO2(5)</td>
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<td>73.2</td>
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<td>Pt/CeO2</td>
<td>15.8</td>
<td>11.6</td>
<td>75.3</td>
</tr>
</tbody>
</table>

a HCs represents the formed hydrocarbons, which are mainly C1–C4 linear paraffins.

Crystallites due to an abundant presence of oxygen vacancy sites on the CeO2–ZrO2(4) surface. These positive characteristics of CeO2–ZrO2(4) can also alter the platinum dispersion due to strong adsorbance on the oxygen vacancy sites of the CeO2–ZrO2 support, which possibly resulted in a higher APR activity as explained in the following section.

2.2 Physicochemical properties of the Pt/CeO2–ZrO2 catalysts

The surface structures and defect sites of the fresh Pt/CeO2–ZrO2 were mainly characterized through XRD, Raman, XPS, and FT-IR analyses. The powder XRD patterns of the fresh Pt/CeO2–ZrO2 are displayed in Fig. 2(A). The characteristic diffraction peaks of cubic CeO2, tetragonal ZrO2 and monoclinic ZrO2 phases were clearly observed with an insignificant intensity of platinum due to the low concentration, consistent with previous investigations. A slight shift to higher diffraction peak positions occurred at around 2θ = 33, 47 and 56° with the increase in ZrO2 concentration in the CeO2–ZrO2 mixed oxides and has been suggested to be due to the significant structural changes in the CeO2–ZrO2, which can be significantly altered with variations in Ce/Zr molar ratio through the incorporation of zirconium species into the matrix of CeO2, forming the mixed metal oxide structures of Ce2Zr2O8 and Ce2Zr2O7 phases with a higher oxygen storage/release capacity. In general, the thermodynamically stable phases of CeO2–ZrO2 mixed oxides have been known to be a monoclinic zirconium-rich phase and a cerium-rich cubic phase showing different diffraction peak positions, and the ZrO2 phases have been known to be the most stable ones, which are assigned to monoclinic, tetragonal, and cubic phases. From the XRD results, the lattice parameters of CeO2–ZrO2 decreased with the increase in zirconium concentration, which can be attributed to the smaller atomic size of zirconium than that of the cerium species. However, the crystallite sizes (i.e. grain sizes of the CeO2–ZrO2 support), calculated from the most intense first peak on the fresh Pt/CeO2–ZrO2, which is assigned to the cubic-CeO2 or tetragonal-ZrO2 at the two theta value around 2θ = 29°, were found to be minimized on CeO2–ZrO2(4) with a value of 6.2 nm as summarized in ESI Table S2. However, the pure CeO2 and ZrO2 showed much bigger crystallite sizes of around 13.0–14.4 nm. The observed smaller crystallite size of metal oxides on CeO2–ZrO2(4) can be attributed to the possible incorporation of the small-size zirconium species in the matrix of CeO2, and the extent was also maximized in the CeO2–ZrO2(4) metal oxide. Furthermore, these different phases and crystallite sizes of the CeO2–ZrO2 metal oxides with different oxygen vacancy sites can greatly alter the dispersion of platinum crystallites, which resulted in a maximum activity on Pt/CeO2–ZrO2(4) as summarized in Table 1.

In addition, the oxygen vacancy defect sites on the CeO2–ZrO2 metal oxides, which were correlated with the F-center with a significant variation according to the ratio of Ce/Zr, seem to alter the platinum dispersion during the calcination and reduction steps. The variation in platinum crystallite sizes can be greatly affected by the type of oxide supports, and these platinum crystallites have been well reported to be sintered easily and to different extents depending on the reduction and calcination conditions, as confirmed by previous studies using EXAFS, EELS and in situ XPS analyses. The defect sites on the metal oxide surfaces, which can be correlated with the F-center, can change the crystallite sizes of the supported metal on the metal oxide support through electron transfer between the support and active metal. When the F-center concentration increases, the crystallite size of the metal generally decreases through the generation of large numbers of defect sites on the CeO2–ZrO2 support. The Ce3+ ions on the CeO2–ZrO2 can counteract the zirconia fluorite phase by increasing the lattice strain energy, and can generate new defect sites by forming a less-ordered amorphous structure of the CeO2–ZrO2 metal.

Fig. 1 Catalytic activity of the Pt/CeO2–ZrO2 catalysts with time on stream (h).
oxide. Therefore, these defect sites can greatly change the platinum dispersion with a concomitant change in the surface area of the CeO$_2$–ZrO$_2$ support. To measure the defect sites on the CeO$_2$–ZrO$_2$ metal oxides, Raman analysis was carried out on the fresh Pt/CeO$_2$–ZrO$_2$ and the patterns of the Raman shifts are displayed in ESI Fig. S2.† The Pt/CeO$_2$, having a unique cubic phase, showed an intense peak at around 463 cm$^{-1}$, and the peak was broadened with the increase in ZrO$_2$ concentration in the CeO$_2$–ZrO$_2$. This peak broadness indicates the increase in the lattice strain of the cubic phase, and the simultaneous enhancement in the F-center concentration through decreasing crystallinity of the metal oxides and significant formation of oxygen vacancy defect sites. Therefore, the mixed metal oxides of CeO$_2$–ZrO$_2$ seem to have a larger lattice strain and F-center concentration than the ZrO$_2$ or CeO$_2$ mono-metal oxide supports. However, the ZrO$_2$ having three phases, namely tetragonal, monoclinic and cubic phases, showed somewhat complicated Raman shifts as shown in ESI Fig. S2.† These defects sites on CeO$_2$–ZrO$_2$ seem to be related with the surface acidity as well by generating Brønsted acid sites during the catalyst preparation step, which can also greatly alter the dehydration (C–O cleavage) activity towards glycerol. On Pt/ZrO$_2$, the well-defined tetragonal phases of ZrO$_2$ were observed at the Raman shifts of 146, 261, 327, 472 and 636 cm$^{-1}$ and the monoclinic phases of ZrO$_2$ at 174, 186 and 376 cm$^{-1}$. In addition, these acid sites on the Pt/CeO$_2$–ZrO$_2$ can originate from the surface hydroxyl groups, which may strongly interact with the active platinum crystallites by easily activating water molecules to produce OH species for the enhanced WGS reaction and C–O bond cleavage reactions. The ratio of the two peaks at ~460 cm$^{-1}$ (denoted as $I_{146}/I_{460}$) and at ~600 cm$^{-1}$ (denoted as $I_{600}$) can also represent the relative oxygen vacancy sites, which are assigned to the CeO$_2$ vibrations as the triply degenerate TO mode, and the defect-induced mode associated with oxygen vacancy sites due to the presence of Ce$_3^+$ ions.† A higher $I_{600}/I_{146}$ value of 1.27 for Pt/CeO$_2$–ZrO$_2(4)$, as shown in ESI Fig. S3† and Table 2, suggests the presence of larger oxygen vacancy sites, compared with the values of 1.15, 0.74, and 0.03 for Pt/CeO$_2$–ZrO$_2(3)$, Pt/CeO$_2$–ZrO$_2(6)$ and Pt/CeO$_2$, respectively. Furthermore, the ratios of Ce$_3^+/(Ce^{4+} + Ce^{3+})$ from XPS analysis, as shown in ESI Fig. S3† and Table 2, also strongly support the Raman results, and the somewhat higher ratio of 0.22 on Pt/CeO$_2$–ZrO$_2(4)$ compared with the other catalysts in the range of 0.16–0.21 can be attributed to the presence of the larger number of Ce$_3^+$ ions in the CeO$_2$–ZrO$_2$ structures. Therefore, these defect sites generated from the mixed metal oxides of CeO$_2$–ZrO$_2$ can greatly alter the platinum dispersion and the metal–support interaction through an electron-transfer mechanism between the platinum crystallites and the oxygen vacancy defect sites and acid sites of the CeO$_2$–ZrO$_2$ support.

As shown in Table 2, the surface areas of the CeO$_2$–ZrO$_2$ prepared using the sol–gel method were found to be in the range of 29.2–74.0 m$^2$ g$^{-1}$, with the largest surface area shown for CeO$_2$–ZrO$_2(6)$ and the smallest area for ZrO$_2$. The different surface areas of the CeO$_2$–ZrO$_2$ supports can be related with the different F-center concentrations and the lattice strain energies, generating different numbers of oxygen vacancy sites on the surface of CeO$_2$–ZrO$_2$. The slightly decreased surface areas of the Pt/CeO$_2$–ZrO$_2$ were found to be 15.9–63.7 m$^2$ g$^{-1}$, with the largest area shown for Pt/CeO$_2$–ZrO$_2(4)$ and the smallest area for Pt/ZrO$_2$ due to the different dispersions of the deposited platinum crystallites on the outer surface of the CeO$_2$–ZrO$_2$ supports with different metal–support interactions. Interestingly, the Pt/CeO$_2$–ZrO$_2$ catalysts, having large numbers of defect sites correlated with the F-center concentration, showed a larger surface area compared with Pt/CeO$_2$ and Pt/ZrO$_2$. The pore volumes of the Pt/CeO$_2$–ZrO$_2$ also showed the same trend as the surface area variation, with values of 0.05–0.27 cm$^3$ g$^{-1}$. However, the average pore diameters uniformly decreased with the increase in CeO$_2$ concentration in the CeO$_2$–ZrO$_2$ mixed oxides, from 22.9 nm in Pt/ZrO$_2$ to 11.5 nm in Pt/CeO$_2$. The different surface areas and pore volumes seem to be mainly attributed to the different lattice strain energies and oxygen vacancy sites during the preparation steps of the CeO$_2$–ZrO$_2$ mixed oxides through the sol–gel method. These physicochemical properties can greatly alter the catalytic activity by generating different surface areas of the impregnated metallic platinum crystallites and different mass-transport rates of the reactants and products during the APR reaction.
To verify the dispersion of the active platinum metal crystallites on the CeO$_2$–ZrO$_2$ supports, CO chemisorption analysis was carried out on the Pt/CeO$_2$–ZrO$_2$ and the results are summarized in Table 2. The dispersions of platinum crystallites were maximized on Pt/CeO$_2$, and with a value of 16.9%, the surface areas of the metallic platinum crystallites were found to be around 5.3–6.7 nm, showing the smallest size for Pt/CeO$_2$–ZrO$_2(4)$ with an average crystallite size of 3.3 nm, with the crystallites highly dispersed on the crystalline CeO$_2$–ZrO$_2$ surface. On the CeO$_2$–ZrO$_2$ mixed oxide supports, much smaller platinum crystallites were observed compared with the mono-metal oxides of CeO$_2$ and ZrO$_2$. The crystallite sizes of metallic platinum showed an inverse volcano-curve pattern, which can be directly correlated with the APR activity of EG conversion to gas products. The smallest metallic crystallite size of platinum and its largest surface area seem to be strongly related with the numbers of surface oxygen vacancies on the CeO$_2$–ZrO$_2$ mixed oxide supports, which can be also strongly interact with the surface platinum crystallites.\(^{24,25}\) These results suggest that a higher dispersion of platinum crystallites can be obtained on CeO$_2$–ZrO$_2(4)$, having a larger number of defect sites and oxygen vacancy sites and these effects may change the metal–support interaction as well, simultaneously changing the catalytic stability.

2.3 Effect of metal–support interaction on the activity of the Pt/CeO$_2$–ZrO$_2$ catalysts

The reduction behaviors of the CeO$_2$–ZrO$_2$ supports and the Pt/CeO$_2$–ZrO$_2$ catalysts were further investigated through H$_2$-TPR experiments to verify the metal-support interaction and reducibility. The TPR patterns are displayed in Fig. 3. As shown in Fig. 3(A), the reduction peaks of the CeO$_2$–ZrO$_2$ supports revealed one distinctive peak at around 550–650 °C, except for the CeO$_2$ support, which suggests partial reducibility of the CeO$_2$–ZrO$_2$ and that it can generate the oxygen vacancy sites even under reductive conditions. The mono-metal oxide of ZrO$_2$ showed no characteristic reduction peak; however, the mono-metal CeO$_2$ showed two distinctive reduction peaks at around 510 and 785 °C. On the other hand, the CeO$_2$–ZrO$_2$ mixed oxide supports showed only one main reduction peak at around 560–620 °C. Based on previous reports,\(^{29,30}\) the first reduction peak at around 560–620 °C indicates the reduction of surface oxygen species, and the second reduction peak at around 780 °C indicates the bulk partial reduction of CeO$_2$. As reported in previous work,\(^{31}\) the number of defect sites related with the oxygen vacancy sites generally increases with the increasing extent of zirconium insertion in the matrix of CeO$_2$ by improving oxygen mobility in the lattices. Therefore, the reduced reduction temperatures and the increased amounts of hydrogen consumption of the CeO$_2$–ZrO$_2$ mixed oxides seem to be mainly attributed to the increased oxygen mobility. In addition, CeO$_2$–ZrO$_2(4)$ showed the biggest reduction peak intensity of the maximum reduction peak, at a lower temperature of 560 °C. However, the observed maximum reduction peak of CeO$_2$–ZrO$_2(6)$ was at 575 °C and that of CeO$_2$–ZrO$_2(3)$ was at 620 °C. The observed lowest reduction temperature and the largest peak intensity of the CeO$_2$–ZrO$_2$ suggest the presence of larger amounts of surface oxygen species compared with other mixed metal oxide supports. The surface oxygen vacancy sites assigned to the anion vacancy may significantly influence the dispersion and the extent of platinum crystallite aggregation. The amounts of H$_2$ consumption on the CeO$_2$–ZrO$_2$ supports are also summarized in Table 2. The observed larger value of 8.4 μmol

Table 2  Physicochemical properties of Pt/CeO$_2$–ZrO$_2$ catalysts

<table>
<thead>
<tr>
<th>Notation</th>
<th>Sg (m$^2$ g$^{-1}$)</th>
<th>Ps (m$^2$ g$^{-1}$)</th>
<th>D (%)</th>
<th>dp(Pt) (nm)</th>
<th>T$_{max}$ (°C)</th>
<th>Consumed H$_2$ (μmol g$^{-1}$)</th>
<th>Consumed H$_2$ (μmol g$^{-1}$)</th>
<th>Raman$^d$</th>
<th>XPS$^e$</th>
<th>Ratio of Ce$^{3+}$/(Ce$^{4+}$ + Ce$^{5+}$)</th>
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<tr>
<td>Pt/ZrO$_2$</td>
<td>15.9</td>
<td>0.14</td>
<td>22.9</td>
<td>38.5</td>
<td>20.0</td>
<td>5.7</td>
<td>—</td>
<td>150/260</td>
<td>4.1/3.3</td>
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<tr>
<td>Pt/CeO$_2$–ZrO$_2(3)$</td>
<td>55.4</td>
<td>0.24</td>
<td>17.8</td>
<td>59.8</td>
<td>30.7</td>
<td>3.7</td>
<td>620</td>
<td>120/290</td>
<td>42.0/51.4</td>
<td>1.15/0.21</td>
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<tr>
<td>Pt/CeO$_2$–ZrO$_2(4)$</td>
<td>63.7</td>
<td>0.27</td>
<td>17.2</td>
<td>69.2</td>
<td>34.9</td>
<td>3.3</td>
<td>560</td>
<td>145/325</td>
<td>79.8/18.5</td>
<td>1.27/0.22</td>
</tr>
<tr>
<td>Pt/CeO$_2$–ZrO$_2(6)$</td>
<td>42.9</td>
<td>0.12</td>
<td>10.0</td>
<td>74.0</td>
<td>3.1</td>
<td>4.1</td>
<td>575</td>
<td>180/335</td>
<td>39.0/56.4</td>
<td>0.74/0.19</td>
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<tr>
<td>Pt/CeO$_2$</td>
<td>27.7</td>
<td>0.05</td>
<td>11.5</td>
<td>29.2</td>
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<td>2.1</td>
<td>610</td>
<td>150/300</td>
<td>3.0/78.2</td>
<td>0.03/0.16</td>
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$^a$ Sg represents surface area of Pt/CeO$_2$–ZrO$_2$ catalysts and Sg(sup) that of supports. $^b$ Ps represents pore volume and Ps the average pore size (diameter) of the Pt/CeO$_2$–ZrO$_2$ catalysts measured through N$_2$ sorption. $^c$ D represents the dispersion of metallic Pt, Sg(Pt) stands for the surface area of metallic Pt, and dp(Pt) for the crystallite size of metallic Pt measured through CO chemisorption of the fresh Pt/CeO$_2$–ZrO$_2$ catalysts. $^d$ The consumed amounts of H$_2$ from TPR were the amounts for all characterized temperature ranges on the supports from 50 to 900 °C, and those for below 500 °C for the Pt/CeO$_2$–ZrO$_2$ catalysts during TPR experiments. $^e$ The defect sites on the Pt/CeO$_2$–ZrO$_2$ were characterized using Raman spectroscopy analysis, by comparing the ratio of two peaks at ~460 cm$^{-1}$ (denoted as I$_{460}$) and at ~600 cm$^{-1}$ (denoted as I$_{600}$), which are assigned to the CeO$_2$ vibrations as the triply degenerate TO mode, and the defect-induced mode associated with oxygen vacancy sites of Ce$^{3+}$ ions. $^f$ The ratio of Ce$^{3+}$ and Ce$^{5+}$ was calculated through the deconvolution of the Ce 3d$_{3/2}$ peak at 881.6 eV for Ce$^{3+}$ and the shoulder peak at higher BE for Ce$^{5+}$ from the cerium oxides.
H₂ g_\text{cat}^{-1} on CeO₂–ZrO₂(4), which was obtained from the first reduction peak, can be attributed to the abundant presence of active oxygen species. The amounts of H₂ consumption were also found to be larger on the CeO₂–ZrO₂ mixed metal oxide supports, with a range of 4.1–8.4 μmol H₂ g_\text{cat}^{-1}, compared with that of the mono-metal oxide support of CeO₂, with a value of 2.8 μmol H₂ g_\text{cat}^{-1}. The larger value of H₂ consumption on CeO₂–ZrO₂(4) suggests a larger number of oxygen vacancy sites, which can strongly interact with the platinum crystallites by increasing the dispersion of active metals and by extensively forming Pt–O–metal oxide interactions at the oxygen vacancy defect sites.²²,³³

The Pt/CeO₂–ZrO₂ catalysts are shown in Fig. 3(B), showing new lower temperature reduction peaks below 200 °C, which were mainly attributed to the reduction of impregnated platinum crystallites on the CeO₂–ZrO₂ supports. For the Pt/CeO₂, two characteristic reduction peaks at around 300 and 765 °C were observed, and the first reduction peak at around 300 °C revealed that platinum crystallites strongly interacting with the surface of the CeO₂ support were formed, and the second reduction peak at around 765 °C can be attributed to the bulk reduction of the CeO₂ support. However, insignificant reduction peak intensities were observed for Pt/ZrO₂, with a weak intensity at 150 °C, which was assigned to the platinum crystallites supported on the ZrO₂. However, two characteristic maximum reduction peaks were observed in the ranges of 100–200 °C and 200–400 °C on the Pt/CeO₂–ZrO₂. The first reduction peak at a lower reduction temperature can be attributed to the reduction of bulk platinum crystallites on the surface the CeO₂–ZrO₂ supports, and the second peak at around 300 °C seems to be attributed to the reduction of the strongly interacting platinum crystallites on the CeO₂–ZrO₂ supports.²⁹–³⁴ However, the intensity of the first reduction peak on Pt/CeO₂–ZrO₂(4) was found to be much larger than the other catalysts at the temperature of 145 °C. These findings also suggest that the oxygen vacancy sites on the CeO₂–ZrO₂ can greatly alter the platinum dispersion by strongly interacting with the oxygen vacancy sites of the supports, and CeO₂–ZrO₂(4) seems to be optimum to obtain a higher dispersion of platinum crystallites and a moderate interaction with the oxygen vacancy defect sites. The amounts of H₂ consumption on the Pt/CeO₂–ZrO₂ can further support the above phenomena, and the results are summarized in Table 2. The larger value of 79.8 μmol H₂ g_\text{cat}^{-1}, which is assigned to the first reduction peak, was observed for Pt/CeO₂–ZrO₂(4). In addition, the amounts of hydrogen consumption of the first reduction peak of the Pt/CeO₂–ZrO₂ were found to be 4.1–79.8 μmol H₂ g_\text{cat}^{-1}, and the value was small on the Pt/ZrO₂. Even though somewhat larger value of 78.2 μmol H₂ g_\text{cat}^{-1} was observed on the Pt/CeO₂, the catalyst seems to be less reducible than other catalysts due to its higher temperature reduction behavior above 300 °C. The second reduction peaks, which can be assigned to the strongly interacting platinum crystallites, were observed in similar temperature ranges above 200 °C; however, the total amounts of hydrogen consumption (7.9–98.3 μmol H₂ g_\text{cat}^{-1}) were found to be maximized on Pt/CeO₂–ZrO₂(4), except for the Pt/CeO₂. Therefore, similarly to the characteristics of the supports, the larger value of total hydrogen consumption on Pt/CeO₂–ZrO₂(4) suggests the presence of larger numbers of oxygen vacancy sites, enhancing the dispersion of the strongly interacting platinum crystallites.

To further verify the catalyst stability and activity, the used Pt/CeO₂–ZrO₂ catalysts were further analyzed using XRD, Raman, CO chemisorption, and TEM analyses. From the XRD patterns of the used Pt/CeO₂–ZrO₂ as shown in Fig. 2(B), the peak assigned to the platinum crystallites (at around 2θ = 39.9°) became more sharp compared with that of the fresh Pt/CeO₂–ZrO₂, which suggests significant aggregation of platinum crystallites. However, the variations in the peak intensities of the CeO₂–ZrO₂ supports before and after reaction were found to be less significant, which suggests that the phases of the CeO₂–ZrO₂ mixed metal oxide supports remained stable under the APR reaction conditions. Even though the lattice parameters of the respective CeO₂ and ZrO₂ phases of the used Pt/CeO₂–ZrO₂ were found to be similar to the fresh catalysts (not shown here), the crystallite sizes of the cubic-CeO₂ or tetragonal-ZrO₂, assigned to 2θ = 29° were greatly increased, especially on the mono-metal oxide supports of Pt/ZrO₂ and Pt/CeO₂, increasing from 14.4 to 26.6 nm and 13.0 to 17.4 nm after the APR reaction, respectively, as summarized in ESI Table S2. However, the variations in the crystallite sizes of the cubic-CeO₂ or tetragonal-ZrO₂ of Pt/CeO₂–ZrO₂(4) showed an insignificant aggregation.
showing a size of 6.7 nm on the used catalyst compared to that of 6.2 nm on the fresh one. In general, the aggregation of the crystallites of the supports has been known to be less significant on the CeO$_2$–ZrO$_2$ mixed oxide supports.\textsuperscript{34–36} The mono-metal oxide of ZrO$_2$ also showed a phase transformation from tetragonal to monoclinic ZrO$_2$ phase after the APR reaction due to the aggregation of crystallites and coke formation under the APR reaction conditions, especially on Pt/CeO$_2$, showing a new peak assigned to the CeCO$_3$OH phase and a large peak for coke. The degree of the diffraction peak shifts of the cubic-CeO$_2$ or tetragonal-ZrO$_2$ assigned to 2θ = 29° before and after the APR reaction were found to be smaller for Pt/CeO$_2$–ZrO$_2$(4) than other catalysts, as shown in ESI Table S2, which may be assigned to the formation of solid solutions such as Zr$_{0.84}$Ce$_{0.16}$O$_2$ and Zr$_{0.4}$Ce$_{0.6}$O$_2$ phases.\textsuperscript{32} This observation also suggests the thermally stable CeO$_2$–ZrO$_2$ phase formation on the CeO$_2$–ZrO$_2$(4) support. The phase transformations also greatly altered the numbers of oxygen vacancy defect sites on the CeO$_2$–ZrO$_2$ mixed oxide supports.\textsuperscript{32–34} These positive effects of the CeO$_2$–ZrO$_2$ mixed oxides can further enhance the thermal stability of the impregnated platinum crystallites by forming strong metal–support interactions during the APR reaction as well. Therefore, Pt/CeO$_2$–ZrO$_2$(4), having a larger number of oxygen vacancy defect sites, seems to show an insignificant aggregation of nano-sized platinum crystallites, forming a stronger interaction with the vacant sites on the CeO$_2$–ZrO$_2$(4) surface as confirmed by TPR, chemisorption and XRD analyses. In addition, the redox properties of CeO$_2$–ZrO$_2$(4), having larger defect sites as confirmed by the TPR experiments on the CeO$_2$–ZrO$_2$ supports by forming thermally stable small platinum crystallites, can also increase the activity of the WGS reaction by easily desorbing the adsorbed CO molecules and by the facile cleavage of C–O bonds.\textsuperscript{17,26,38,39} Therefore, the thermally stable platinum crystallites on Pt/CeO$_2$–ZrO$_2$(4) seem to be responsible for the higher conversion of EG at steady-state.

This hypothesis was also verified by using TEM analysis of the fresh and used Pt/CeO$_2$ and Pt/CeO$_2$–ZrO$_2$(4), as shown in Fig. 4, and the platinum crystallite sizes on the fresh catalysts were well matched with the results of the CO chemisorption. The average crystallite sizes of platinum on the fresh Pt/CeO$_2$ were found to be ~6 nm with a broad size distribution in the range of 4–10 nm, and the average crystallite sizes of platinum were significantly increased up to an average size of ~10 nm with a size distribution of 4–14 nm on the used catalyst. However, the average platinum crystallite sizes on the fresh Pt/CeO$_2$–ZrO$_2$(4) were found to be ~3 nm with a narrow distribution of 2–6 nm, and the crystallite sizes of platinum on the used catalyst were increased up to ~7 nm with a homogeneous size distribution in the range of 4–12 nm, even after the APR reaction. The diminished aggregation of platinum crystallites on Pt/CeO$_2$–ZrO$_2$(4) after the reaction seems to be responsible for the stable catalytic activity for 20 h on stream as shown in Fig. 1. The effects of the surface properties of the CeO$_2$–ZrO$_2$ on the aggregation of platinum crystallites explain well the observed higher catalytic activity on Pt/CeO$_2$–ZrO$_2$(4), possibly due to the suppressed aggregation through the formation of stable platinum crystallites with the oxygen vacancy defect sites on the CeO$_2$–ZrO$_2$(4) support during the APR reaction.

In summary, the EG conversion to gaseous products and the surface areas of the metallic platinum crystallites were plotted in terms of the molar ratios of Ce/(Ce + Zr) as shown in Fig. 5. The conversion of EG was found to be maximized on Pt/CeO$_2$–ZrO$_2$(4), which has a larger number of oxygen vacancy defect sites, and it was also directly correlated with the surface area of metallic platinum species with the volcano plot. The higher catalytic activity was mainly attributed to the higher dispersion of platinum crystallites, which strongly interact with the oxygen vacancy sites on the CeO$_2$–ZrO$_2$(4) support, which concomitantly enhanced the thermal stability of the platinum crystallites even under the APR reaction conditions, showing a stable activity at steady-state. In addition, the formation of the strongly interacting platinum crystallites on the oxygen vacancy defect sites can also suppress the aggregation of platinum crystallites. The properly designed CeO$_2$–ZrO$_2$ support can change the thermal stability of the support and the active platinum metals.

![Fig. 4 TEM images of (A) Pt/CeO$_2$ and (B) Pt/CeO$_2$–ZrO$_2$(4) catalysts (1) before and (2) after APR reaction.](image)

![Fig. 5 Correlation of catalytic activity (EG conversion to gas) and surface area of metallic platinum in terms of molar ratio of Ce/(Ce + Zr) of the Pt/CeO$_2$–ZrO$_2$ catalysts.](image)
as well, and it can enhance the catalytic activity by reducing the catalytic deactivation through the aggregation mechanism of the supported platinum species at the very beginning of APR reaction.

3 Conclusions

A higher catalytic activity for the aqueous-phase reforming reaction of ethylene glycol to selectively generate hydrogen was observed on the platinum supported CeO$_2$–ZrO$_2$ mixed oxide catalyst at an optimal molar ratio of Ce/(Ce + Zr) = 0.4. The main role of the CeO$_2$–ZrO$_2$ support was found to be to alter the dispersion of active platinum crystallites and the metal-support interaction by forming the strongly interacting platinum species on the oxygen vacancy defect sites, which is responsible for the catalytic stability. The different numbers of oxygen vacancy defect sites on the CeO$_2$–ZrO$_2$ mixed oxides significantly altered the dispersion and stability of the platinum crystallites. The volcano plots of the catalytic activity and the platinum surface areas in terms of Ce/(Ce + Zr) molar ratios were explained well by the total numbers of oxygen vacancy defect sites on the CeO$_2$–ZrO$_2$ mixed oxides. A higher dispersion of platinum crystallites with a greater surface area and thermal stability was observed on Pt/CeO$_2$–ZrO$_2$(4) and it also showed a higher conversion of ethylene glycol.

4 Experimental section

4.1 Preparation of Pt/CeO$_2$–ZrO$_2$ catalysts and activity test

The CeO$_2$–ZrO$_2$ mixed oxides were synthesized using the sol–gel method, and the molar ratios of Ce/(Ce + Zr) were varied from 0 to 1 to change the surface properties of CeO$_2$–ZrO$_2$. In detail, the CeO$_2$–ZrO$_2$ supports were prepared by using two metal precursors of cerium(III) nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O, Aldrich) and zirconium(IV) oxychloride octahydrated (ZrOCl$_2$·8H$_2$O, Kanto) simultaneously. The two metal precursors were fixed to 1 : 10 : 10 for the preparation of ZrO$_2$ and for the CeO$_2$–ZrO$_2$ supports. The powder was obtained and was further dried at 80 °C overnight, followed by calcining again at 350 °C for 4 h. The final platinum-impregnated CeO$_2$–ZrO$_2$ catalysts were denoted as Pt/CeO$_2$–ZrO$_2$(x), where x represents the molar ratios of Ce/(Ce + Zr) × 10 of the CeO–ZrO$_2$ supports.

The APR reaction was carried out in a fixed-bed tubular reactor with 0.3 g catalyst at T = 250 °C and P = 4.5 MPa. Prior to the reaction, the Pt/CeO$_2$–ZrO$_2$ was reduced under the flow of 10 vol% H$_2$ balanced with N$_2$ at 350 °C for 2 h. The catalytic activities of Pt/CeO$_2$–ZrO$_2$ were tested, using 10 wt% aqueous EG solution with a feeding rate of 0.1 mL min$^{-1}$ using an HPLC pump, and N$_2$ was fed in to maintain the reaction pressure and used as an internal standard gas with a flow rate of 30 mL min$^{-1}$, for around 20 h on stream. Effluent gaseous products were analyzed using an on-line gas chromatograph (GC, Young-Lin 6500GC) equipped with a thermal conductivity detector (TCD) connected to a Carboxen 1000 packed-column and with a flame ionization detector (FID) connected to a HP-LOT/Q capillary column. The carbon conversion of EG and selectivities for H$_2$, CO, CO$_2$ and hydrocarbons were calculated by using the following equations based on mol%:

(a) Carbon conversion to gaseous products (mol%) = (moles of C atoms in gaseous products/moles of C atoms in EG reactant) × 100

(b) Selectivity (mol%) = (moles of selected product in a gas-phase/total moles of carbons (and hydrogen) in gas phase) × 100

4.2 Catalyst characterization

The Pt/CeO$_2$–ZrO$_2$ catalysts were characterized by using powder X-ray diffraction (XRD), nitrogen sorption, temperature programmed reduction with hydrogen (H$_2$-TPR), CO chemisorption, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and TEM analysis on the fresh and used catalysts.

The nitrogen sorption isotherms at −196 °C in a constant-volume adsorption apparatus (Micromeritics ASAP-2020) were used to measure the Brunauer–Emmett–Teller (BET) surface areas, pore volumes and average pore diameters of the Pt/CeO$_2$–ZrO$_2$ catalysts, and the CeO–ZrO$_2$ supports as well.

The dispersion, surface area, and crystallite size of the metallic platinum crystallites in the Pt/CeO$_2$–ZrO$_2$ were further characterized by CO chemisorption at 50 °C under a static condition using the BELCAT-B instrument, because the H$_2$ probe molecule can possibly react with the active vacant surfaces of CeO$_2$–ZrO$_2$ after pretreatment. Prior to CO adsorption measurement, the as-prepared 0.5 g catalyst was reduced in situ at 350 °C for 0.5 h under a flow of 10 vol% H$_2$ balanced with Ar. The surface area of metallic platinum crystallites was calculated by assuming a CO/Pt stoichiometry of 1.0.

Powder XRD patterns were obtained on the fresh and used Pt/CeO$_2$–ZrO$_2$ by using a Bruker D8 ADVANCE X-ray diffractometer equipped with Cu-K$_\alpha$ radiation (operating conditions were 40 kV, 40 mA, and scanning rate of 4° min$^{-1}$ from 20 to 80°) to identify the crystalline phases of CeO$_2$, ZrO$_2$ and Pt species. The crystallite sizes of CeO$_2$ and ZrO$_2$ were calculated using the
values of full width at half maximum (FWHM) of the most intense diffraction peak, and the lattice parameters were calculated using Bragg’s equation.

H2-TPR experiments were carried out using an AutoChemII 2920 instrument supplied by Micromeritics to elucidate the reduction behaviors of the Pt/CeO–ZrO2 catalysts and CeO–ZrO2 supports by measuring the amount of the consumed hydrogen on the fresh Pt/CeO–ZrO2. A 0.1 g sample of the Pt/CeO–ZrO2 was preheated in a quartz reactor at 300 °C for 1 h under a flow of He gas to remove the adsorbed contaminants and water and then cooled down to 50 °C. The reduction behaviors and reducibility of the Pt/CeO–ZrO2 were measured in the temperature range of 50 to 950 °C under a flow of 5 vol% H2 balanced with Ar, with a heating rate of 10 °C min⁻¹.

The electronic states and binding energies (BE) of Ce 3d₅/₂ assigned to 881.6 eV for cerium oxide on the fresh Pt/CeO–ZrO2 were characterized before and after the APR reaction with a deconvolution of the Ce 3d₅/₂ peak at 881.6 eV for Ce⁴⁺ ions and the shoulder peak at higher BE for Ce⁴⁺ species from the cerium oxides.

The variation of the surface morphologies and the local distribution of crystallites on Pt/CeO–ZrO2(0) and Pt/CeO–ZrO2(4) were characterized before and after the APR reaction using a Tecnai G2 transmission electron microscope (TEM) operating at 200 kV. The TEM sample was prepared on a carbon-coated copper grid using a fine powder sample dispersed in ethanol solvent.

The defect sites on the Pt/CeO–ZrO2 were characterized using Raman spectroscopy analysis, which was conducted under ambient conditions using a Bruker FRA106/S with a Nd:YAG excitation laser (wavelength of 1064 nm) and optical power of 300 mW at the sample position, by comparing the ratio of two peaks at ~460 cm⁻¹ (denoted as I₄₀₀) and at ~600 cm⁻¹ (denoted as I₆₀₀), which are assigned to the CeO₂ vibrations as the triply degenerate TO mode, and the defect-induced mode associated with oxygen vacancy sites of Ce⁵⁺ ions.⁴⁰

Acknowledgements

This study was financially supported by the grant from the Industrial Source Technology Development Programs (20132010201750) of the Ministry of Knowledge Economy (MKE) of Korea. The authors would like to acknowledge the financial support from the National Research Foundation of Korea (NRF-2014R1A1A2A16055557). This work was also financially supported by the R&D Center for Valuable Recycling (Global-Top R&D Program) of the Ministry of Environment (Project no. GT-14-C-01-038-0). This work was also supported by an institutional program grant (2E25404-15-021) from the Korean Institute of Science and Technology.

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