The activity of M/Ce-Sm-O (M=Pt, Pd, Re) mixed oxide for Water Gas Shift (WGS) reaction.

ABSTRACT

The influence of samarium on the water gas shift activities of noble metal Pt, Pd and Re on ceria was studied. Modification of ceria with samarium significantly improved the activity of the Pd and Re catalysts. The activities of Re/Ce-Sm-O and Pd/Ce-Sm-O were greatly enhanced when compared with the activities of Re/CeO₂ and Pd/CeO₂, respectively. The activity of Pt/Ce-Sm-O remained the same with that of Pt/CeO₂. By varying the Sm loading (1, 2, 5, 7 and 10 wt.%), it was found that the maximum catalytic activity was achieved at 1 wt.% for Pd/Ce-Sm-O and 10 wt.% for Re/Ce-Sm-O. The catalysts were characterized by X-ray diffraction (XRD), Temperature-Programmed reduction (TPR) and surface area analysis. XRD pattern indicated that Sm³⁺ incorporated into subsurface region of CeO₂ lattice to form solid solution, gave rise to unit cell enlargement, and increased specific surface area. The structural distortions inside ceria lattice produced strain into the oxide lattice and facilitated oxygen vacancies formation. The results agreed well with H₂-TPR profiles which exhibited lowering of reduction temperature that explained the activity enhancement of the catalysts.

Key Words: Water gas shift reaction, Samarium, Temperature-programmed reduction

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Background and Significance
Water gas shift (WGS) is an important step in fuel processors for preliminary CO elimination and additional hydrogen generation prior to the final CO clean up stage. The presence of CO causes detrimental effects on the anode catalyst of the fuel cell (Choung et al., 2005). Studies of water gas shift mechanism tend to favor regenerative mechanism which is based on oxidation-reduction cycles of catalysts (Gorte & Zhao, 2005). Ceria is a good choice as a support of both noble metal and base metal catalysts because it promotes metal dispersion and possesses oxygen storage properties (Luengnaruemitchai et al., 2003). Addition of some rare-earth metal cations to ceria lattice are reported to enhance the oxygen storage capacity of ceria (Fu et al., 2003). Zirconia-ceria mixed oxide supports are widely studied and reported. In an attempt to doped Pt/CeO$_2$ catalysts with mixed metal cations, Kondarides et al. reported that the WGS activities of Pt/Ce-Me-O catalysts (Me=metal cations) depended on the nature of the dopants employed and the promoters affected the reducibility and oxygen ion mobility of the CeO$_2$ support (Panagiotopoulou et al., 2007). The incorporation of heterocausations causes structural distortion inside ceria, producing strain into the oxide lattice and facilitating oxygen vacancies formation.

Samarium is one of the possible dopants to modify structural and chemical properties of ceria because the ionic radius and electronegativity of samarium is close to those of ceria. Significant enhancement of catalytic activity for CO oxidation of copper supported on samarium doped ceria was reported (Wang et al., 2000). The activity enhancement was concluded to be governed by the surface oxygen vacancies and interfacial active centers formed, and not by the dispersion and BET surface area. On the other hand, Pd/CeO$_2$-Sm$_2$O$_3$ catalyst was found to be very active in the production of hydrogen by steam reforming of methanol (Gómez-Sainero et al., 2005). In this study, the authors interpreted the activity enhancement as a consequence of higher dispersion and more favorable distribution of Pd particles. Recently, samarium-doped ceria was studied for WGS reaction. Tabakova et al. reported highly active CuO/Sm-doped ceria catalysts for WGS reaction and concluded that the better performance of Sm-doped ceria can be attributed to various factors, including increased BET surface area and total pore volume, decreased ceria particle size and enhanced reducibility (Tabakova et al., 2007).

In this study, we report on WGS activity of Pt, Pd and Re catalysts supported on Sm-doped-ceria. The catalysts will be characterized by H$_2$-TPR, BET and XRD techniques.

Experimental
1. Catalyst preparation
The urea gelation (UG) method for Ce-Sm-O support preparation is similar to that used by Kundakovic and Filtyzani-Stephanopoulos (Kundakovic & Filtyzani-Stephanopoulos, 1998). An appropriate amount of metal salt Ce(NO$_3$)$_3$.6H$_2$O and Sm(NO$_3$)$_3$.6H$_2$O were dissolved in deionized water. The mixture was stirred and heated until the salts were dissolved. Urea (H$_2$NCONH$_2$, 98%, Aldrich) was dissolved in deionized water and then added to the metal salt solution. Then ammonium hydroxide (NH$_4$OH, Aldrich) was added dropwise at the rate of 1 ml/min to obtain precipitate. The solution was stirred and heated at ~120 °C. The suspension was boiled for another 3.5 h to remove NH$_3$ and to age the support. The filtered support was dried overnight at 110°C in an oven and then calcined at 450 °C for 4 h.

After preparing the support, desired amount of Pt, Pd, and Re were added by impregnation method using aqueous solutions of (NH$_4$)$_2$Pt(NO$_3$)$_2$ (99%, Aldrich), Pd(NO$_3$)$_2$ (99%, Aldrich), and NH$_4$ReO$_4$ (99%, Aldrich). Following impregnation, the catalysts were dried at 110°C for 12 h and then calcined at 650°C for 8 h.

2. Catalysts characterization
The BET surface area of support and catalysts were determined by N$_2$ adsorption-desorption isotherms at 77.3 K on Quantachrome NOVA 1200e instrument.

The redox properties of the catalysts were investigated by H$_2$-Temperature Programmed Reduction (H$_2$-TPR) on Quantachrome Autosorp-1-C instrument. About 0.20 g of sample was loaded in the reactor. High purity helium gas was purged into the reactor at 120 °C for 30 min. The reducing gas (5%H$_2$/95%N$_2$) was purged from room temperature to 1000 °C at the rate of 10 °C/min.

The crystalline structure of catalysts were investigated by power X-ray diffraction (XRD) on Advance Series 2 X-ray Diffractometer with CuK$_\alpha$ radiation (0.15406 nm), operating at 20 kV and 5 mA. The analyses were carried out at 0.02° per step and 0.5 s per step over a 2θ range of 20-80°. The particle sizes was calculated from the X-ray line broadening, according to Scherrer’s equation (Klug & Alexander, 1974).

\[ D = \frac{0.9\lambda}{\beta\cos\theta} \]

Where D is the particle size, \( \lambda \) is the wavelength of radiation used, \( \beta \) is the line broadening of the
peak or full-width at half maximum and \( \theta \) is the angle of the diffraction peak.

3. Catalytic activity measurements

The 20 mg catalyst was loaded in a Pyrex fixed bed flow reactor. The feed gas composition was 5\% CO, 10\% H\(_2\)O, balanced He and total flow rate was 100 ml/min. The reactants and products were analyzed by on-line gas chromatography with TCD detector (Agilent Technologies 6890N). The column utilized in the chromatograph is a Hayesap D, 80/100 mesh, 10 Ft x 1/8 inch stainless-steel packed column. The %CO conversion was calculated by:

\[
\text{% CO conversion} = \frac{CO_{\text{in}} - CO_{\text{out}}}{CO_{\text{in}}} \times 100
\]

Results and discussion

1. Standard characterization

![Figure 1 XRD pattern of (a) CeO\(_2\), (b) Sm-doped ceria, (c) 1\%Pt/CeO\(_2\) and (d) 1\%Pt/Sm-doped ceria (e) 1\%Pd/CeO\(_2\) (f) 1\%Pd/Sm-doped ceria (g) 1\%Re/CeO\(_2\) and (h) 1\%Re/Sm-doped ceria.](image)

The XRD patterns of CeO\(_2\), M/CeO\(_2\) and M/Ce-Sm-O catalysts are displayed in Figure 1. The fluorite oxide-type diffraction of CeO\(_2\) is observed in all samples. CeO\(_2\) appears to be phase-pure with cubic crystallography. The lattice constant calculated from (111) crystallographic plane is found to be equal to 0.5405 nm (Table 1), in agreement with previous studies (Letichevsky et al., 2005). The absence of Sm\(_2\)O\(_3\) reflection in Sm-doped ceria (Figure 1b) indicates that Sm\(^{3+}\) incorporates into subsurface region of CeO\(_2\) lattice to form solid solution (Avgyouropoulos & Ioannides, 2003). The ionic radii of Sm\(^{3+}\) (0.098 nm) which is larger than that of Ce\(^{4+}\) (0.088 nm) gives rise to unit cell enlargement of ceria lattice. As the result of unit cell enlargement, the diffraction peaks are displaced to lower diffraction angles. It should be mentioned that incorporation of Sm\(^{3+}\) cation into ceria lattice produces strain and unbalanced charges, therefore, oxygen vacancies are expected to form (Krishna et al., 2007). Addition of noble metals (Pt, Pd, Re) did not cause any observable shift in the XRD reflections of both ceria and doped sample. This also suggests that metal oxides are highly dispersed on the surface of the supports (Sato et al., 2006).

The average crystallite sizes of ceria and modified ceria, calculated from X-ray line broadening at 20 \( \sim \) 28\(^\circ\) using Scherrer’s equation is compiled in Table 1 together with BET specific surface areas. Doping CeO\(_2\) with 5 wt.% samarium leads to slight reduction of crystallite size. The result indicates that Sm\(^{3+}\) inhibits the crystal growth of ceria. Smaller crystallite size is associated with increases of specific surface area. Similar results are observed for samples with noble metal loading. Sample with noble metals loaded on samarium-doped ceria have particle sizes smaller than those with noble metals loaded on bare ceria.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>BET surface area(^a) (m(^2)/g)</th>
<th>particle size(^b) (nm)</th>
<th>lattice parameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO(_2)</td>
<td>81.35</td>
<td>13.49</td>
<td>0.5405</td>
</tr>
<tr>
<td>Ce-5%Sm-O</td>
<td>95.43</td>
<td>13.43</td>
<td>0.5505</td>
</tr>
<tr>
<td>1%Pt/CeO(_2)</td>
<td>46.12</td>
<td>17.94</td>
<td>0.5464</td>
</tr>
<tr>
<td>1%Pt/Ce-5%Sm-O</td>
<td>76.19</td>
<td>14.18</td>
<td>0.5490</td>
</tr>
<tr>
<td>1%Pd/CeO(_2)</td>
<td>47.08</td>
<td>19.59</td>
<td>0.5526</td>
</tr>
<tr>
<td>1%Pd/Ce-5%Sm-O</td>
<td>71.38</td>
<td>17.89</td>
<td>0.5507</td>
</tr>
<tr>
<td>1%Re/CeO(_2)</td>
<td>23.35</td>
<td>23.55</td>
<td>0.5470</td>
</tr>
<tr>
<td>1%Re/Ce-5%Sm-O</td>
<td>37.43</td>
<td>15.42</td>
<td>0.5538</td>
</tr>
</tbody>
</table>

\(^a\) Determined by N\(_2\) adsorption-desorption measurements.
\(^b\) Calculated by X-ray line broadening method using Debye-Scherrer equation.

Table 1 Surface areas of various catalysts.
2. H\textsubscript{2}-Temperature Programmed Reduction (H\textsubscript{2}-TPR)

![H\textsubscript{2}-TPR profile](image)

**Figure 2** H\textsubscript{2}-TPR profile of (a) CeO\textsubscript{2}, (b) Sm-doped ceria, (c) 1\%Pt/CeO\textsubscript{2} and (d) 1\%Pt/Sm-doped ceria. (e) 1\%Pd/CeO\textsubscript{2}, (f) 1\%Pd/Sm-doped ceria (g) 1\%Re/Sm-doped ceria.

The H\textsubscript{2}-TPR profile of CeO\textsubscript{2} and metals on samarium doped ceria are shown in Figure 2. The H\textsubscript{2}-TPR profile of CeO\textsubscript{2} (Figure 2a) exhibits two broad peaks at 510 °C and 850 °C. The peak at 510 °C is assigned to reduction of surface-capping oxygen of ceria, and the peak at 850 °C is assigned to reduction of bulk ceria (Ricote et al., 2006).

The H\textsubscript{2}-TPR profile of Sm-doped ceria (Figure 2b) exhibits two broad peaks at 400 °C and 830 °C. Incorporation of Sm into ceria lattice increases reducibility in the middle temperature range and move the peak down. The effect is apparently due to appearance of anion vacancies in the surface lattice (Sadykov et al., 2004). The shift of bulk reduction at high temperature is not pronounce which probably indicates that Sm cation are mainly localized at the surface layers. The segregation of dopant cations of the surface and domain boundaries of ceria is a well known phenomenon.

The TPR profiles of Pt/Sm-doped ceria (Figure 2c) catalysts are characterized by a low-temperature peak at 148 °C, medium temperature features located at 375 °C and the bulk reduction at 850 °C. The consumption peak at 148 °C is attributed to reduction of PtO\textsubscript{2} species formed during the pre-oxidation step (Panagiotopoulou et al., 2006). The peak at 375 °C is attributed to the Pt-catalyzed reduction of the surface shell of ceria (Li et al., 2000). It is interesting to note that addition of Pt to ceria support significantly shifts the reduction temperature of surface ceria from 510 °C to 375 °C.

The H\textsubscript{2}-TPR of Pt/Sm-doped ceria indicated that modification of ceria support with samarium cations does not affect the reduction temperature of PtO\textsubscript{2}. Furthermore, the reduction peak of surface ceria which appeared at 375 °C is moved up to 450 °C and this indicated that Sm made the support more difficult to reduced.

PdO is known to be an easily reducible oxide, even at room temperature, depending on the supports or precursors used in the preparation of catalysts (Bickford et al., 2005). The profile for 1\%Pd/CeO\textsubscript{2} (Figure 2e) exhibits two broad peaks at 356 °C and 863 °C. A broad reduction peak at 356 °C indicates a strong interaction between the Pd phase and the support. A narrow reduction peak at temperatures below 100 °C can’t be detected here in any case. This temperature indicates that weak interaction occurred between Pd and the support (Ferrer et al., 2005). Doping ceria with Sm shift the reduction temperature of surface ceria in the vicinity of Pd from 356 °C to 376 °C. The stability toward reduction of the Sm-containing catalyst evidenced by the large broad reduction peaks at high temperatures.

The H\textsubscript{2}-TPR profile of 1\%Re/CeO\textsubscript{2} (Figure 2g) exhibits a sharp peak at 425 °C, a small peak at 540°C and a broad peak at 850 °C which can be assigned as reduction of ReO\textsubscript{2}, surface ceria and bulk ceria, respectively.

When H\textsubscript{2}-TPR of Re/CeO\textsubscript{2} (Figure 2g) is compared with H\textsubscript{2}-TPR of Pt/CeO\textsubscript{2} (Figure 2c), it is clear that addition of Pt to ceria support gives rise to lowering of reduction peak of surface ceria (510 °C → 375 °C). This is not the case for Re, addition of Re to ceria does not lead to lowing of reduction temperature of surface ceria and this may be accounted for low WGS activity of Re/CeO\textsubscript{2}. Drastic increase in WGS activity of Re/Ce-Sm-O mixed oxide can be explained by H\textsubscript{2}-TPR of Re/Ce-Sm-O mixed oxide (Figure 2h). Doping ceria with 5\%Sm shift the reduction temperature of ReO\textsubscript{2} from 425 °C to 350 °C. Furthermore, reduction temperature of surface ceria and bulk ceria also slightly lower to 500 °C and 830 °C, respectively.
3. Catalytic activity

Figure 3 %CO conversion of 1%Pt/CeO$_2$, 1%Pt/Sm-doped ceria, CeO$_2$ and Sm-doped ceria.

Figure 3 compares activity of Pt on two supports, CeO$_2$ and Ce-Sm-O mixed oxide. The activity of the supports without catalyst are also shown for comparison. It appears that ceria support and Ce-Sm-O mixed support have weak WGS activity and start to convert CO to CO$_2$ at temperature above 300 °C. The activity of Ce-Sm-O mixed oxide is slightly higher than that of CeO$_2$. Pt catalysts on both support, CeO$_2$ and Ce-Sm-O mixed oxide, showed equally active activity. The CO conversion started to occur below 200 °C and raised up quickly to reach maximum of 90 %conversion at about 350 °C. Above 350 °C the activity reaches equilibrium and slightly decreases.

Figure 4 %CO conversion of 1%Pd/CeO$_2$, 1%Pd/Sm-doped ceria, CeO$_2$ and Sm-doped ceria.

Figure 4 illustrates the WGS activity of Pd/CeO$_2$ and Pd/Ce-Sm-O mixed oxide. Activity of Pd/CeO$_2$ is less than activity Of Pt/CeO$_2$ (figure 1). For Pd/CeO$_2$ the conversion started at 150 °C and raise up slowly to reach the maximum of 80 %conversion at 450 °C. However, the activity of Pd/Ce-Sm-O mixed oxide is slightly higher than the activity of Pd/CeO$_2$. The conversion started at about the same temperature but reached the maximum of 85 %conversion at 400 °C.

Figure 5 %CO conversion of 1%Re/CeO$_2$, 1%Re/Sm-doped ceria, CeO$_2$ and Sm-doped ceria.

Figure 5 compares the activity of 1%Re/CeO$_2$ and 1%Re/Ce-5%Sm-O mixed oxide. It can be seen that 1%Re/CeO$_2$ is not an active catalyst for WGS reaction. Addition of 1%Re to CeO$_2$ support only slightly increased the activity of CeO$_2$ support. In fact, the activity of Re/CeO$_2$ was even lower than the activity of Ce-Sm-O mixed oxide support without noble metal. Addition of 1%Re to Ce-Sm-O mixed oxide drastically increased the activity for WGS reaction. The CO conversion started above 200 °C and eventually reached the maximum of 80 %conversion at 500 °C.

Similar activities were tested for catalysts prepared by co-impregnation of 1%Re and 5%Sm onto ceria support for comparison. The results showed that the activities of catalysts prepared by impregnation of 1%Re on Ce-Sm-O mixed oxide are thee same as those prepared by co-impregnation of 1%Re and 5%Sm onto pure ceria support.

4. Conclusion

4.1 The activities of Re/Ce-Sm-O and Pd/Ce-Sm-O were greatly enhanced up on addition of Sm$^{3+}$ to ceria support.

4.2 The activity of Pt/Ce-Sm-O remained the same with that of Pt/ CeO$_2$.

4.3 By varying the Sm$^{3+}$ loading (1, 2, 5, 7 and 10 wt.%), it found that the maximum catalytic activity was achieved at 1 wt.% for Pd/Ce-Sm-O and 10 wt.% for Re/Ce-Sm-O.

4.4 Sm doping increased BET surface area and inhibited crystal growth of ceria.

4.5 Sm$^{3+}$ gives rise to unit cell enlargement of ceria lattice.
4.6 The addition of Sm led to improve reducibility and enhance their activity.

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References


