

The Activity of M/Ce-Sm-O Mixed Oxide (M = Pt, Pd and Re)

for Water Gas Shift Reaction

การศึกษาประสิทธิภาพในการเร่งปฏิกิริยาของตัวเร่งปฏิกิริยา

M/Ce-Sm-O (M=Pt, Pd และ Re)

สำหรับปฏิกิริยา water gas shift

Pannipa Nachai (พรรณิภา นาชัย)* Sirihathai Srihwanjai (สิริหทัย ศรีขวัญใจ)*

Wirach Wongphathanakul (วิรัช ว่องพัฒนากุล)** Dr. Sunantha Hengrasmee (ดร. สุนันtha เฮงรัมย์)***

ABSTRACT

The influence of samarium on the water gas shift activities of noble metal Pt, Pd and Re on ceria was studied. Ceria supports were modified by doping Sm at various weight percents. The flow reactor was used to study the activity of the catalysts in temperature range 150–600°C. The feed gas composition was 5%CO, 10%H₂O and balance He, and the total flow rate was 100 mL/min. The %CO conversion was analyzed by on-line gas chromatography with TCD detector. 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 wt. % of Sm loading, 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, Raman spectroscopy, Temperature-Programmed reduction 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 H₂-TPR profiles of Re/Ce-Sm-O and Pd/Ce-Sm-O exhibited lowering of reduction temperature of surface oxygen which explained the activity enhancement of these catalysts. For Pt catalyst which possessed the highest activity, Pt played an important role in catalyzing the surface reduction of ceria and addition of Sm did not alter the reduction temperature of surface ceria. Thus, doping ceria with Sm did not improve the WGS activity of Pt catalyst.

* Student, Master of Science, Program in Physical Chemistry, Department of Chemistry, Faculty of Science, Khon Kaen University.

** Assistant Professor, Department of Chemistry, Faculty of Science, Khon Kaen University.

*** Associated professor, Department of Chemistry, Faculty of Science, Khon Kaen University.

บทคัดย่อ

ได้ศึกษาอิทธิพลของซมมาเรียมที่มีต่อประสิทธิภาพในการเร่งปฏิกิริยา WGS ของโลหะ Pt Pd และ Re บนตัวพวยซีเรียที่เติมซมมาเรียมที่มีปริมาณต่างๆ กัน โดยศึกษาประสิทธิภาพในการเร่งปฏิกิริยาในช่วงอุณหภูมิ 150 – 600 °C แก๊สที่ใช้เป็นสารตั้งต้นสำหรับปฏิกิริยา WGS ประกอบด้วยคาร์บอนมอนอกไซด์ 5% ไอน้ำ 10% และก๊าซฮีเลียม โดยมีอัตราการไหลทั้งหมดเป็น 100 mL/min ได้มีการวิเคราะห์เปอร์เซ็นต์การเปลี่ยนแปลงคาร์บอนมอนอกไซด์โดยใช้ gas chromatography ที่มี TCD เป็นตัวตรวจวัด การปรับแต่งซีเรียด้วยซมมาเรียมสามารถพัฒนาประสิทธิภาพในการเร่งปฏิกิริยาของ Pd และ Re โดยประสิทธิภาพในการเร่งปฏิกิริยาของ Re/Ce-Sm-O และ Pd/Ce-Sm-O เพิ่มขึ้นอย่างมากเมื่อเทียบกับ Re/CeO₂ และ Pd/CeO₂ ตามลำดับ แต่ประสิทธิภาพในการเร่งปฏิกิริยาของ Pt/Ce-Sm-O ยังคงเหมือนกับ Pt/CeO₂ ได้มีการปรับเปลี่ยนปริมาณของซมมาเรียม เพื่อหาประสิทธิภาพในการเร่งปฏิกิริยาสูงสุด พบว่าประสิทธิภาพในการเร่งปฏิกิริยาสูงสุดคือ 1% Sm โดยมวลและ 10% Sm โดยมวล สำหรับ Pd/Ce-Sm-O และ Re/Ce-Sm-O ตามลำดับ

ได้ศึกษาลักษณะทางกายภาพและทางเคมีของตัวเร่งปฏิกิริยาโดยใช้เทคนิคการเลี้ยวเบนของรังสีเอกซ์ สเปกโทรสโกปีรามาน อุณหภูมิรีดักชันและการวิเคราะห์พื้นผิว สเปกตรัมของการเลี้ยวเบนของรังสีเอกซ์แสดงให้เห็นว่าซมมาเรียมแทรกเข้าไปภายในโครงผลึกของซีเรีย ทำให้หน่วยเซลล์ขยายขนาดใหญ่ขึ้น และมีพื้นที่ผิวเพิ่มขึ้น โครงสร้างที่ผิดปกติภายในโครงผลึกซีเรียทำให้เกิดช่องว่างของออกซิเจน ผลการศึกษาจาก H₂-TPR ของ Re/Ce-Sm-O และ Pd/Ce-Sm-O แสดงการลดลงของอุณหภูมิรีดักชันของสารเร่งปฏิกิริยา ซึ่งลดความเสถียรของผลึก และผลึกจะถูกรีดิวซ์ได้ง่ายขึ้น สำหรับ Pt ซึ่งตามปกติมีประสิทธิภาพในการเร่งปฏิกิริยาสูงอยู่แล้ว การเติมซมมาเรียมลงบนซีเรียไม่ทำให้การเร่งปฏิกิริยา WGS ของ Pt ดีขึ้น เนื่องจาก Pt มีอันตรกิริยากับซีเรีย ทำให้ซีเรียถูกรีดิวซ์ได้ง่ายอยู่แล้ว การเติม Sm ลงบนซีเรียจึงไม่มีอิทธิพลเพิ่มขึ้นในการรีดิวซ์ซีเรีย

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

คำสำคัญ : ปฏิกิริยา water gas shift ซมมาเรียม อุณหภูมิรีดักชัน

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 dope Pt/CeO₂ catalysts with many metal cations, Kondarides and co-worker reported that the WGS activities of Pt/Ce-Me-O catalysts (Me=metal cations) depended on the nature of the dopants employed and the promotions affected the reducibility and oxygen ion mobility of the CeO₂

support (Panagiotopoulou et al., 2007). The incorporation of heterocations 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/CeO₂-Sm₂O₃ 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 factor, including increased BET surface area and total pore volume, decreased ceria particle size and enhanced reducibility (Tabakova et al., 2007).

In this thesis we are interested in studying the affect of addition of samarium dopant to ceria lattice. The catalytic activity of WGS of metals on ceria will be studied and compared with the WGS activity of same metals on Sm-doped ceria. We will select metals that possess different

activities for comparison. Pt/ceria is known to have excellent activity while Pd/ceria and Re/ceria are rather inactive and received less attention. Therefore, we decided to study the WGS activity of Pt, Pd and Re on Sm-doped ceria.

Experimental

1. Catalyst preparation

The urea gelation (UG) method for CeO₂ support preparation is similar to that used by Kundakovic and Flytzani-Stephanopoulos (Kundakovic & Flytzani-Stephanopoulos, 1998).

An appropriate amount of metal salt (Ce(NO₃)₃·6H₂O, 99%, Aldrich) and urea (H₂NCONH₂, 98%, Aldrich) were dissolved in deionized water. The mixture was stirred and heated until the salts were dissolved. Then ammonium hydroxide (NH₄OH, Aldrich) was added dropwise at the rate of 1 mL/min to obtain precipitate. The solution was stirred and heated at ~120 °C for 3.5 hours to remove NH₃ 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 hours.

Sm-doped ceria which is designated as Ce-Sm-O was prepared by urea gelation method. Nitrate salts of cerium (Ce(NO₃)₃·6H₂O, 99%, Aldrich) and samarium (Sm(NO₃)₃·6H₂O, 99%, Fluka) were dissolved in deionized water. Then urea and ammonium hydroxide were added in the similar manner with the preparation of CeO₂ as mentioned above.

After preparing the support, desired amount of Pt, Pd, and Re were added by impregnation method using aqueous solutions of (NH₃)₂Pt(NO₂)₂ (99%, Aldrich), Pd(NO₃)₂ (99%, Aldrich), and

NH_4ReO_4 (99%, Aldrich). Following impregnation, the catalysts were dried at 110°C for 12 hours and then calcined at 650°C for 8 hours.

2. Catalysts characterization

Perkin Elmer inductive coupled plasma optical emission spectrometer (optima 2100 DV) was used for confirm the amount of element.

Stock solutions contained 1000 mg/L of Pd, 83 mg/L of $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$, and 2000 mg/L of NH_4ReO_4 and $\text{N}_3\text{O}_9\text{Sm}.6\text{H}_2\text{O}$. The calibration standards were prepared by dilution of the stock solution with 5% HCl and 5% H_2O_2 (blank solution). Five points of calibration standards curve were used in following ranges of 0.5–10 mg/L of Pt, Pd, Re, and Sm.

Pt/Ce–Sm–O, Pd/Ce–Sm–O, or Re/Ce–Sm–O was dissolved in solution containing 5% HCl and 5% H_2O_2 . The solution was heated until completely dissolve. The dissolved samples were diluted to volume of 50 mL in volumetric flask with 5% HCl and 5% H_2O_2 .

The crystalline structure of catalysts were investigated by power X-ray diffraction (XRD) on Advance Series 2 X-ray Diffractometer with CuK_α radiation (0.15406 nm), operating at 40 kV and 40 mA. The analyses were carried out at 0.02° per step and 0.5 s per step over a 2θ range of $20\text{--}80^\circ$. The particle size was calculated from the X-ray line broadening, according to Scherrer's equation (Klug & Alexander, 1974).

$$D = 0.9\lambda / \beta \cos\theta$$

Where D is the particle size, λ is the wavelength of radiation used, β is the line broadening of the peak or full-width at half maximum and θ is the angle of the diffraction peak.

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 Raman spectra were obtained by using Jobin Yvon T64000 Raman spectrometer. The high efficiency of the charge-coupled device (CCD) detection means measurements can also be made with weak Raman signals. The exciting wavelength from an Ar ion laser with an output power laser of 30 mW was 514.532 nm. The scanning range was $100\text{--}1300\text{ cm}^{-1}$. The powder specimens were pressed to form disks before the measurement.

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 minutes. The reducing gas (5% H_2 /95% N_2) was purged from room temperature to 1000°C at the rate of $10^\circ\text{C}/\text{min}$.

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_2O , 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 :

$$\% \text{CO conversion} = \frac{\text{CO}_{in} - \text{CO}_{out}}{\text{CO}_{in}} \times 100$$

Results

1. Standard characterization

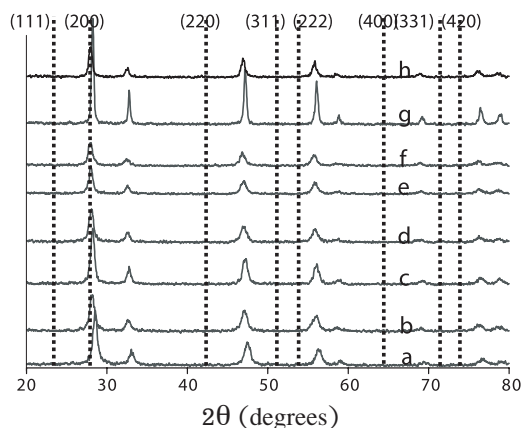


Figure 1 XRD pattern of

- (a) CeO_2 ,
- (b) $\text{Ce-5\%Sm-O}$,
- (c) $1\%\text{Pt/CeO}_2$,
- (d) $1\%\text{Pt/Ce-5\%Sm-O}$,
- (e) $1\%\text{Pd/CeO}_2$,
- (f) $1\%\text{Pd/Ce-5\%Sm-O}$,
- (g) $1\%\text{Re/CeO}_2$, and
- (h) $1\%\text{Re/Ce-5\%Sm-O}$.

The XRD patterns of CeO_2 , M/CeO_2 and M/Ce-Sm-O catalysts ($\text{M} = \text{Pt}, \text{Pd}, \text{and Re}$) 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 0.5412 nm (Table 1), in agreement with previous studies (Letichevsky et al., 2005). The absence of Sm_2O_3 reflection in Sm-doped ceria (Figure 1b) indicates that Sm^{3+} incorporates into subsurface region of CeO_2 lattice to form solid solution (Avgouropoulos and Ioannides, 2003). The

diffraction peaks of Sm-doped ceria appear at slightly lower diffraction angles when compared with the diffraction peaks of CeO_2 . The lower displacement indicates unit cell enlargement and the lattice parameters are calculated to be 0.5505 nm. The increase in lattice parameter indicates that Ce^{4+} ions are replaced by larger cations. Comparisons of ionic radii of Ce^{4+} (0.097 nm), Sm^{2+} (0.111 nm) and Sm^{3+} (0.108 nm) suggested that the dopant ions presented in the ceria lattice should be either Sm^{2+} or Sm^{3+} or combination of both. In order to determine the oxidation state of Sm, another advanced analytical technique such as XPS is needed. However, under calcinations temperature Sm should take higher oxidation state, Sm^{3+} . It should be mentioned that incorporation of $\text{Sm}^{2+}/\text{Sm}^{3+}$ in ceria lattice produces strain and unbalanced charges, therefore, oxygen vacancies are expected to form (Krishna et al., 2007).

Addition of noble metals (Pt, Pd, and 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 lattice parameters of metal on both support, CeO_2 and $\text{Ce-5\%Sm-O}$, are larger than the lattice parameter of ceria. In this case metal cations did not replace Ce^{4+} as in the case of Sm^{3+} . The ionic radii of metal cations are smaller than the ionic radii of Ce^{4+} . Replacement of Ce^{4+} by metal cations will result in small lattice parameters. The occurrence of unit cell expansion for M/CeO_2 ($\text{M} = \text{Pt}, \text{Pd}$ and Re) indicates strong metal-support interaction between metal and ceria solid solution, causing conversion of Ce^{4+} (0.097 nm) to larger Ce^{3+} (0.114 nm).

The average crystallite sizes of ceria and modified ceria, calculated from X-ray line broadening at $2\theta \sim 28^\circ$ using Scherrer's equation is compiled in Table 1 together with BET specific surface areas and average pore diameters. Doping CeO_2 with samarium leads to slight reduction of crystallite size. Smaller crystallite size is associated with increases of specific surface area. The increase of surface area with decreased pore diameters indicated that the supports are more porous with smaller pores and higher surface area. Dispersion of metal oxide on ceria lattice gives rise to larger crystallites with lower surface area. Large pore diameter indicates that metal oxide moves to occupy pore area and may block up small pores underneath. This in turn resulted in reduction of surface area. Sm^{3+} in $\text{M/Ce-5\%Sm-O}$ ($\text{M} = \text{Pt}$, Pd and Re) stabilizes the support by maintaining small crystallite size and high surface area.

Table 1 Surface area of various catalysts.

Catalysts	BET surface area (m^2/g)	average pore diameter (nm)	crystallite size (nm)	lattice parameter (nm)
CeO_2	64.28	13.48	13.59	0.5412
$\text{Ce-5\%Sm-O}$	95.43	13.32	13.43	0.5505
Pt/CeO_2	46.12	8.64	17.94	0.5464
$\text{Pt/Ce-5\%Sm-O}$	76.19	9.54	14.18	0.5490
Pd/CeO_2	47.08	7.47	19.59	0.5526
$\text{Pd/Ce-5\%Sm-O}$	71.38	5.31	17.89	0.5507
Re/CeO_2	23.35	5.60	23.55	0.5470
$\text{Re/Ce-5\%Sm-O}$	37.43	3.82	15.42	0.5538

2. Raman spectroscopy

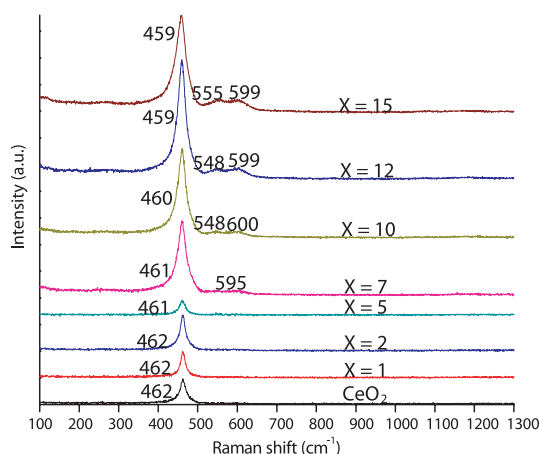


Figure 2 Raman spectra of CeO_2 and $\text{Ce-X\%Sm-O}$ ($X = 1, 2, 5, 7, 10, 12$ and 15).

Figure 2 displays the Raman spectra of CeO_2 and Ce-Sm-O mixed oxides. It can be seen that Raman spectrum of CeO_2 occurs at 462 cm^{-1} . This single sharp band at around 462 cm^{-1} is ascribed to the Raman active triply degenerate F_{2g} mode of CeO_2 (Luo et al., 2006). This can be viewed as a symmetric breathing mode of the oxygen atoms surrounding each cation. CeO_2 with a fluorite structure presents symmetrical stretching vibrations of CeO_8 vibrational unit and should be very sensitive to the oxygen sublattice disorder. In Ce-Sm-O samples F_{2g} mode exhibits systematic shift to lower energies with increased dopant concentration. Such a decrease in energy is consistent with dilatation of unit cell parameter due to the incorporation of large Sm^{3+} ions in cerium lattice. Besides the F_{2g} Raman mode there are two additional modes at $\sim 550 \text{ cm}^{-1}$ and $\sim 600 \text{ cm}^{-1}$. The Raman bands at $\sim 550 \text{ cm}^{-1}$ can be seen when the amount of Sm more than 7 wt. %. This mode

is assigned to the extrinsic oxygen vacancies introduced into the ceria lattice by substitution of Ce^{4+} ions with Sm^{3+} ions in order to keep charge neutrality (Radović et al., 2007). In addition, the intensity tends to increase with increasing Sm content. The Raman bands at $\sim 600\text{ cm}^{-1}$ can be ascribed to the intrinsic oxygen vacancies due to the nonstoichiometry of ceria nanopowders (Dohčević-Mitrović et al., 2006). The intensity of this mode increases with dopant concentration.

3. H_2 -Temperature Programmed Reduction

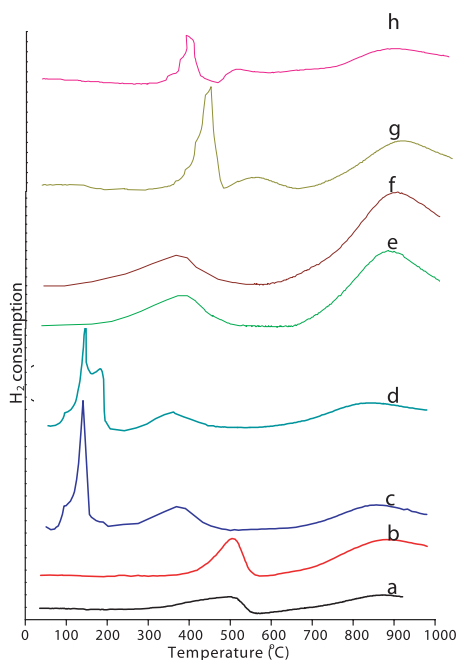


Figure 3 H_2 -TPR profile of

- (a) CeO_2 ,
- (b) $\text{Ce-5\%Sm-O}$,
- (c) $1\%\text{Pt/CeO}_2$,
- (d) $1\%\text{Pt/Ce-5\%Sm-O}$,
- (e) $1\%\text{Pd/CeO}_2$,
- (f) $1\%\text{Pd/Ce-1\%Sm-O}$,
- (g) $1\%\text{Re/CeO}_2$, and
- (h) $1\%\text{Re/Ce-10\%Sm-O}$.

The H_2 -TPR profile of CeO_2 and metals on samarium doped ceria are shown in Figure 3. The H_2 -TPR profile of CeO_2 (Figure 3a) 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_2 -TPR profile of Sm-doped ceria (Figure 3b) exhibits two broad peaks at 500°C and 860°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/CeO_2 (Figure 3c) catalysts are characterized by a low-temperature peak at 141°C , medium temperature features located at 368°C and the bulk reduction at 850°C . The consumption peak at 141°C is attributed to reduction of PtO_x species formed during the pre-oxidation step (Panagiotopoulou et al., 2006). The peak at 368°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 368°C .

The H_2 -TPR profile of $\text{Pt/Ce-5\%Sm-O}$ (Figure 3d) exhibited two PtO reduction peaks at 146°C and 180°C which indicated different

environment of Pt. The peak at 146 °C is similar to the reduction peak of Pt in the vicinity of ceria while the peak at 180 °C is probably due to the presence of Sm. The reduction peak of surface and bulk species appeared at the same position as the reduction peaks of Pt/ceria. This indicated that addition of Sm to Pt/CeO₂ does not alter the reduction behaviour of Pt catalyst.

PdO is known to be easily reduced even at room temperature. The reduction behaviour PdO depends on supports and precursors used in the preparation processes. (Bickford et al., 2005). Many papers (Ferrer et al., 2005) reported negative TPR peak below 100 °C due to thermal decomposition of palladium hydride which was formed in presence of hydrogen. Since the reduction process that consumed hydrogen occurred at temperature close to the decomposition process that produced hydrogen, a special instrument which can operate at low temperature is needed. Our instrument could not detect this behaviour. Anyway, a shift of surface reduction from 371 °C for Pd/CeO₂ to 356 °C for Pd/Ce-1%Sm-O can be detected (Figure 3e and 3f). This result indicated that addition of Sm made reduction of Pd catalyst slightly easier.

The H₂-TPR profile of 1%Re/CeO₂ (Figure 3g) exhibits a sharp peak at 425 °C, a small peak at 530 °C and a broad peak at 850 °C which can be assigned as reduction of ReO, surface ceria and bulk ceria, respectively. Addition of Sm to Re/ceria (Figure 3h) reduced the reduction temperature of ReO and surface ceria to 372 °C and 480 °C. This result also indicated that Sm lowered the reduction temperature of Re/ceria catalyst.

4. Catalytic activity

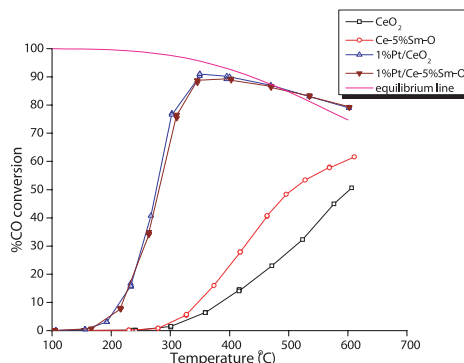


Figure 4 %CO conversion of CeO₂, Ce-5%Sm-O, 1%Pt/CeO₂ and 1%Pt/Ce-5%Sm-O.

Figure 4 compares activity of Pt on two supports, CeO₂ and Ce-Sm-O mixed oxide. The activity of the supports without catalyst is 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 CO₂ at temperature above 300 °C. The activity of Ce-Sm-O mixed oxide is slightly higher than that of CeO₂. Pt catalysts on both support, CeO₂ 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.

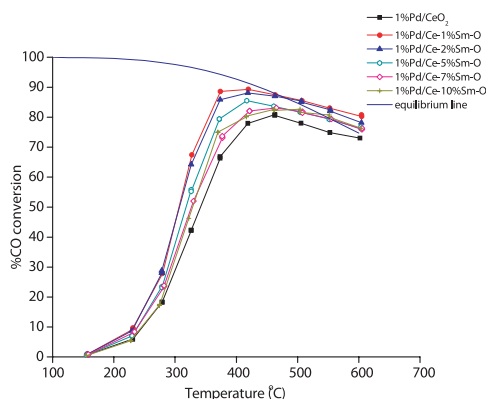


Figure 5 %CO conversion of 1%Pd/CeO₂ and 1%Pd/Sm-doped ceria.

Figure 5 illustrates the WGS activity of Pd/CeO₂ and Pd/Ce-Sm-O mixed oxide. For Pd/CeO₂ 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/CeO₂. The conversion started at about the same temperature but reached the maximum of 90 %conversion at 400 °C. When the weight percents of Sm loading were varied by 1, 2, 5, 7, and 10 wt. %, it was found that the most active catalyst was 1%Pd/Ce-1%Sm-O.

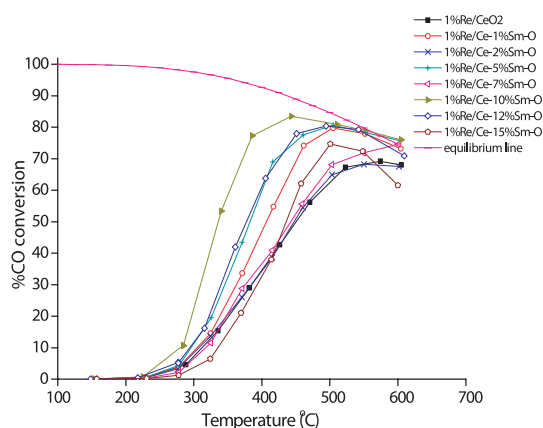


Figure 6 %CO conversion of 1%Re/CeO₂ and 1%Re/Sm-doped ceria.

Figure 6 compares the activity of 1%Re/CeO₂ and 1%Re/Ce-Sm-O mixed oxide. It can be seen that 1%Re/CeO₂ is not an active catalyst for WGS reaction. Addition of Sm to 1%Re/CeO₂ drastically increased the activity for WGS reaction. The CO conversion started above 200 °C and eventually reached the maximum of 85 %conversion at 450 °C. The most active activity was achieved when the percent loading of Sm was 10 wt. %.

Discussion

The effect of Sm³⁺ doping on ceria which is believed to enhance catalytic activity is investigated for WGS reaction. It was found that loading of 1% metal (Pd or Re) onto mixed oxide of ceria and samaria led to WGS activity enhancement. The XRD studies indicated that incorporation of Sm³⁺ into CeO₂ lattice gave rise to unit cell distortion. The replacement of Ce⁴⁺ by Sm³⁺ brought up unbalanced charges inside the lattice which facilitated oxygen vacancies. The present of oxygen vacancies resulted in more easily reduced surfaces and is evidenced by TPR profile. The lowering of surface reduction temperature was noticeable for Pd/Ce-Sm-O and Re/Ce-Sm-O. For the mixed oxide support loaded with 1% Pt, it is appeared on TPR profile that Pt, by itself, is very active in catalyzing surface reduction of ceria and addition of Sm³⁺ to ceria support could not promote further surface reduction. Therefore, Sm³⁺ was non-active in improving the catalytic activity of Pt/CeO₂ for WGS reaction.

When the weight percents of Sm³⁺ loading were varied by 1, 2, 5, 7, 10, 12, and 15%, it was found that the most active Pd catalyst was 1%Pd/Ce-1%Sm-O and the most active Re catalyst was 1%Re/Ce-10%Sm-O. The maximum activities were related directly to lowest surface reduction temperature (TPR profile is not shown here) and were not correlate with BET surface area. In fact, BET surface area was found to be highest for 1%Pd/Ce-7%Sm-O and 1%Re/Ce-2%Sm-O. Evidence seemed to point to the direction that the enhanced catalytic activity of Pd and Re on Ce-Sm-O mixed oxide support was mainly governed by surface oxygen vacancies and not by BET surface area.

Conclusion

We have illustrated that addition of Sm^{3+} ion to ceria support can enhance catalytic activity for WGS reaction of Pd and Re catalysts but the enhancement effect is negligible for Pt catalyst. The best activities were found for 1%Pd/Ce–1%Sm–O and 1%Re/Ce–10%Sm–O. The enhancement effect was due to surface oxygen vacancies which were produced by replacement of Ce^{4+} by Sm^{3+} . Incorporation of Sm^{3+} into ceria lattice gave rise to unit cell enlargement, crystallite size reduction and increased BET surface area. Unbalanced changes inside the lattice induced oxygen mobility. It is believed that oxygen transferring is an important step in WGS mechanism.

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References

- Avgouropoulos, G., and Ioannides, T. 2003. Selective CO oxidation over CuO-CeO_2 catalysts prepared via the urea-nitrate combustion method. *Appl Catal A: Gen* 244:155–67.
- Bickford, ES., Velu, S., and Song, C. 2005. Nano-structured CeO_2 supported Cu-Pd bimetallic catalysts for the oxygen-assisted water-gas-shift reaction. *Catal Today* 99:347–57.
- Choung, SY., Ferrandon, M., and Krause, T. 2005. Pt-Re bimetallic supported on $\text{CeO}_2\text{-ZrO}_2$ mixed oxides as water-gas shift catalysts. *Catal Today* 99:257–62.
- Dohčević-Mitrović, ZD., Šćepanović, MJ., Grujić-Brojčin, MU., Popović, ZV., Bošković, SB., Matovic, BM., Zinkevich, MV., and Aldinger, F. 2006. The size and strain effects on the Raman spectra of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ ($0 \leq x \leq 0.25$) nanopowders. *Solid State Commun* 137:387–390.
- Ferrer, V., Moronta, A., Sánchez, J., Solano, R., Bernal, S., and Finol, D. 2005. Effect of the reduction temperature on the catalytic activity of Pd-supported catalysts. *Catal Today* 107–8:487–92.
- Fu, Q., Kudriavtseva, S., Saltsburg, H., and Flytzani-Stephanopoulos, M. 2003. Gold-ceria catalysts for low-temperature water-gas shift reaction. *Chem Eng J* 93:41–53.
- Gorte, RJ., and Zhao, S. 2005. Studies of the water-gas-shift reaction with ceria-supported precious metals. *Catal Today* 104:18–24.
- Gómez-Sainero, LM., Baker, RT., Metcalfe, IS., Sahibzada, M., Concepción, P., and López-Nieto, JM. 2005. Investigation of $\text{Sm}_2\text{O}_3\text{-CeO}_2$ -supported palladium catalysts for the reforming of methanol: The role of the support. *Appl Catal A: Gen* 294:177–87.

- Klug, HP., and Alexander, LE. 1974. in: X-ray Diffraction Procedures, seconded, Wiley, New York, p. 642.
- Krishna, K., Bueno-López, A., Makkee, M., and Moulijn, JA. 2007. Potential rare earth modified CeO_2 catalysts for soot oxidation I. Characterisation and catalytic activity with O_2 . *Appl Catal B: Environ* 75:189-200.
- Kundakovic, Lj., and Flytzani-Stephanopoulos, M. 1998. Cu- and Ag-modified cerium oxide catalysts for methane oxidation. *J Catal* 179:203-21.
- Letichevsky, S., Tellez, CA., Avillez, RR., Silva, MIP., Fraga, MA., and Appel, LG. 2005. Obtaining CeO_2 - ZrO_2 mixed oxides by coprecipitation: role of preparation conditions. *Appl Catal B: Environ* 58:203-10.
- Li, Y., Fu, Q., and Flytzani-Stephanopoulos, M. 2000. Low-temperature water-gas shift reaction over Cu- and Ni-loaded cerium oxide catalysts. *Appl Catal B: Environ* 27:179-91.
- Luengnaruemitchai, A., Osuwan, S., and Gulari, E. 2003. Comparative studies of low-temperature water-gas shift reaction over Pt/CeO_2 , Au/CeO_2 , and $\text{Au/Fe}_2\text{O}_3$ catalysts. *Catal Commun* 4:215-21.
- Luo, MF., Yan, ZL., and Jin, LY. 2006. Structure and redox properties of $\text{Ce Pr}_{1-x}\text{O}_{2-\delta}$ mixed oxides and their catalytic activities for CO , CH_3OH and CH_4 combustion. *J of Mol Catal A: Chem* 260:157-162.
- Panagiotopoulou, P., Papavasiliou, J., Avgouropoulos, G., Ioannides, T., and Kondarides, DI. 2007. Water-gas shift activity of doped Pt/CeO_2 catalysts. *Chem Eng J*.
- Panagiotopoulou, P., Christodoulakis, A., Kondarides, DI., and Boghosian, S. 2006. Particle size effects on the reducibility of titanium dioxide and its relation to the water-gas shift activity of Pt/TiO_2 catalysts. *J Catal* 240:114-25.
- Radović, M., Dohčević-Mitrović, Z., Šćepanović, M., Grujić-Brojčin, M., Matović, B., Bošković, S., Popović, ZV. 2007. Raman study of Ba-doped ceria nanopowders. *Science of Sintering* 39:281-286.
- Ricote, S., Jacobs, G., Milling, M., Ji, Y., Patterson, PM., and Davis, BH. 2006. Low temperature water-gas shift: Characterization and testing of binary mixed oxides of ceria and zirconia promoted with Pt. *Appl Catal A: Gen* 303:35-47.
- Sadykov, VA., Kuznetsova, TG., Alikina, GM., Frolova, YV., Lukashevich, AI., Potapova, YV., Muzykantov, VS., Rogov, VA., Kriventsov, VV., Kochubei, DI., Moroz, EM., Zyuzin, DI., Zaikovskii, VI., Kolomiichuk, VN., Paukshtis, EA., Burgina, EB., Zyryanov, VV., Uvarov, NF., Neophytides, S., and Kemitz, E. 2004. Ceria-based fluorite-like oxide solid solutions as catalysts of methane selective oxidation into syngas by the lattice oxygen: synthesis, characterization and performance. *Catal Today* 93-5:43-53.
- Sato, Y., Soma, Y., Miyao, T., and Naito, S. 2006. The water-gas-shift reaction over Ir/TiO_2 and Ir-Re/TiO_2 catalysts. *Appl Catal A: Gen* 304:78-85.

- Tabakova, T., Idakiev, V., Papavasiliou, J., Avgouropoulos, G., and Ioannides, T. 2007. Effect of additives on the WGS activity of combustion synthesized CuO/CeO₂ catalysts. Catal Commun 8:101–6.
- Wang, JB., Shih, WH., and Huang, TJ. 2000. Study of Sm₂O₃-doped CeO₂/Al₂O₃-supported copper catalyst for CO oxidation. Appl Catal A: Gen 203:191–199.