Research Paper

Lanthanide (III) (La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) Ions Loaded in CeO₂ Support: Fundamental Natures, Hydrogen Reduction, and CO Oxidation Activities

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Abstract

The introduction of guest metal ions significantly change the nature of bare support materials. In this study lanthanide, Ln, (La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) ions were loaded into a cubic phase CeO₂ support by a hydrothermal method. Their fundamental characteristics were examined by scanning electron microscopy, transmission electron microscopy, optical microscopy, X-ray diffraction crystallography, and Raman spectroscopy. Their CO oxidation performances temperature were measured by temperature-programmed reaction mass spectrometry. It was found that the fundamental natures of the Ln-loaded catalysts were all dependent on the ionic radii of guest lanthanide metal ions. Higher CO oxidation activities were obtained for lanthanide metal ions with ionic radii closer to that of the host Ce⁴⁺ ion. The present results highlight that defects, particles sizes and surface active sites were affected from the matching of the host and guest-guest ionic radii.

Keywords: CeO₂, Lanthanide (III) ions, CO oxidation, Temperature programmed reduction

1. Introduction

Heterogeneous catalytic air purification such as catalytic carbon monoxide (CO) oxidation has extensively been researched using a model catalyst of cerium (IV) oxide (CeO₂) [1-7]. To achieve higher catalytic activity and understand the catalytic pathways many efforts have been devoted to develop various CeO₂ catalysts, test their catalytic activities, and employ density functional theory calculations [3]. CeO₂ shows convertible two oxidation states (Ce⁴⁺/Ce³⁺) and good oxygen release-acceptance ability over the surface under CO and O₂ environments [8-12]. Doping and loading guest metals (or their ions) into (or onto) have widely been employed to show significant alternation of the catalytic activity of a bare CeO₂ support [1-12]. Ha et al. prepared Au/CeO₂ cubes with exposed (100) surface and Au/CeO₂ octahedra with exposed (100) surface and showed a higher catalytic activity for Au/CeO₂ cubes, attributed to oxygen release capacity at the interface of Au and CeO₂(100) via the Mars-van Krevelen mechanism [3]. Papavasiliou et al. prepared CuO-CeO₂ catalysts, treated

under nitric acid solutions, and observed higher CO oxidation activity, attributed to higher oxygen vacancies, Cu⁺ species, and improved dispersion of active Cu species and reducibility of CeO₂ catalyst [14]. Vacancy formation is also known to be highly dependent on the dopant ionic radius [15-17]. Chen et al. employed diffuse reflectance infrared Fourier transformed spectroscopy to study surface species formed during CO oxidation over Au/CeO₂ catalysts and concluded that the chemisorbed CO was not greatly dependent on the Au particle size, whereas the carbonate, bicarbonate, and formate species were found to be strongly dependent on the size [4].

For the literature survey of lanthanide metal loaded CeO₂ catalysts [18-28], Zhang et al. prepared Pr-doped CeO₂ by a co-precipitation method, tested a Prins condensation-hydrolysis reaction of isobutene with HCHO, and observed a dependency of catalytic performance on Pr-doping induced oxygen vacancy [18]. Sutradhari et al. synthesized Sm-doped CeO₂ nanoparticle and applied to allylic oxidation of cyclohexene [23]. Hernandez et al. reported CO oxidation onset at around 300 °C for Ce_{1-x}Eu_xO_{2-x/2} catalyst, and found CO conversion of 70% at 375 °C for bare CeO₂ and

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85% for the catalyst with 10% wt Eu_2O_3 [20].

In this paper, lanthanide metal ions were first loaded into CeO_2 support to examine the effects of ionic radius on the fundamental natures and a catalytic activity. X-ray diffraction crystallographic data, Raman spectra, temperature-programmed reduction and CO oxidation profiles consistently showed that ionic radii of host-guest ions were very important for designing a catalyst.

II. Experimental details

For loading lanthanide (III) (La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) ions into CeO_2 nanoparticles, 10 mol% of Ln (III) (vs. Ce) was dissolved in 20.0 mL of 0.05 M cerium (III) nitrate hexahydrate (99%, Sigma-Aldrich) solution. La (III) nitrate hexahydrate (99%, Sigma-Aldrich), Pr (III) nitrate pentahydrate (99%, Sigma-Aldrich), Nd (III) nitrate (99%, Sigma-Aldrich), Sm (III) sulfate octahydrate (99.9%, Sigma-Aldrich), Eu (III) nitrate pentahydrate (99%, Sigma-Aldrich), Gd (III) nitrate hexahydrate (99%, Sigma-Aldrich), Tb (III) nitrate hydrate (99%, Sigma-Aldrich), Dy (III) nitrate hydrate (99%, Sigma-Aldrich), Ho (III) nitrate pentahydrate (99%, Sigma-Aldrich), Er (III) nitrate solution (0.1 M), Tm (III) nitrate pentahydrate (99%, Sigma-Aldrich), and Yb (III) nitrate pentahydrate (99%, Sigma-Aldrich) were used as received. Afterwards, 1.0 mL of 30% ammonia solution was added to obtained precipitates. After this process, the solution in a 100 mL Teflon-lined stainless autoclave was placed in an oven at 120 °C for 12 h. Upon finishing the reaction, the obtained powder samples were fully washed by ethanol and deionized water repeatedly and dried in an oven setting at 80 °C. The crystal phases of bare and Ln-loaded CeO_2 catalysts were examined using a PANalytical X'Pert Pro MPD diffractometer with $\text{Cu K}\alpha$ radiation. The surface morphology for the powder sample mounted on a Si substrate was examined using a Hitachi S-4800 scanning electron microscopy (SEM) system. The microstructure was examined using a Hitachi H-7600 transmission electron microscopy (TEM) system operated at 100 kV. A Bruker Senterra Raman spectrometer was used to obtain Raman spectra with a 514 nm laser line. A Quantachrome ChemBET TPR/TPD apparatus was used to obtain temperature programmed reduction (TPR) profiles for 20 mg catalyst under 5% H_2/He at a sample heating rate of 10 K/min. CO oxidation experiments under a condition of mixed CO (1%) and O_2 (2.5%) in N_2 were performed using a

10 mg catalyst at a heating rate of 20 K/min. CO_2 with reaction temperature were examined using a SRS RGA200 quadrupole mass spectrometer.

III. Results and discussion

Figure 1 displays the X-ray diffraction (XRD) patterns of unloaded CeO_2 and Ln-loaded CeO_2 powder samples. Several peaks were commonly found at around $2\theta = 28, 33, 47, 56, 59,$ and 69° , attributed to the (111), (200), (220), (311), (222), and (400) crystal planes of cubic phase CeO_2 (JCPDS # 034-0394). The I(111)/I(200) ratios show no critical difference for all the samples, but the width and the 2θ position were found to be dependent on the samples. Interestingly, the Sm-loaded sample showed several other smaller XRD peaks, indicating that Sm was not efficiently loaded into CeO_2 lattice.

Figure 2 displays the XRD 2θ positions of the (111) plane and the calculated crystallite sizes with the lanthanide metal ions. It is generally known that as the crystallite size becomes smaller the XRD peak becomes broader. Using the strongest peak at $2\theta = 28^\circ$ and the full-width at half maximum (FWHM) of the peak, the crystallite sizes were calculated using the well-known Scherrer's equation, d (crystallite size) = $k\lambda/\beta\cos\theta$, where k is shape factor, β is FWHM (deg), θ is Bragg diffraction angle, and λ is

Figure 1. (Color online) Powder X-ray diffraction patterns of unloaded CeO_2 and Ln-loaded CeO_2 catalysts. Inset shows the amplified XRD peaks for the (111) planes.

Figure 2. (Color online) Calculated crystallite sizes and 2θ peak positions of the (111) plane peaks for unloaded and Ln-loaded CeO₂ catalysts.

wavelength of X-ray [29]. Strain effect was not considered for the size estimation. The FWHM values for selected La, Eu, and Yb were estimated to be 0.42, 0.31, and 0.25°, respectively. The (111) peak was generally found to be shifted to a higher angle although it did not show a strict linear dependence. The shift to a higher angle is commonly known to be an indication of lattice contraction. Because the radius of the lanthanide ion is decreased with increasing the atomic number (well-known as lanthanide contraction) the lattice contraction can be expected with increasing the atomic number, as observed in the present result [30]. Ln³⁺ crystal ionic radius (pm) decreases with increasing the atomic number from 117.2 (La³⁺) to 100.8 pm (Yb³⁺) by lanthanide contraction [31]. Except for La³⁺, other ions show smaller ionic radius than that (101 pm) of Ce⁴⁺. The calculated crystallite sizes were found to be linearly increased from 18 nm for La-CeO₂ to 31 nm for Yb-CeO₂ with increasing the atomic number.

Figure 3 shows the photo images of all the powder samples, the selected SEM and TEM images of unloaded CeO₂ nanoparticles. For unloaded CeO₂, the size distributions were found to be 10–50 nm with an average size of ~23 nm. The average value is fairly close to the calculated particle size of ~20 nm. The corresponding HRTEM image shows clear lattice fringes with an interplanar distance of 0.31 nm. This distance is in good agreement with the (111) plane of cubic phase CeO₂ [23]. The unloaded powder sample is in yellowish white color. Based on the optical microscope images, the color of CeO₂ was changed very slightly upon Ln (III)-doping. However, the colors of the Tb-loaded and Pr-loaded samples were dramatically

Figure 3. (Color online) Optical microscope images show the color of unloaded and Ln-loaded CeO₂ catalysts. SEM and TEM images (bottom) of unloaded CeO₂. The inset (bottom right) shows HRTEM image of the CeO₂.

changed to light brown and reddish brown colors, respectively. The change in color was plausibly due to change in oxidation state from 3+ to 4+ for both metal ions [32,33]. For Pr oxide, Kang et al. observed brown color, attributed to an oxidation state of Pr (IV) [32]. For Tb oxide, Sohn reported brown color, attributed to charge transfer absorption of Tb (IV) [33]. In Fig. 2, Pr and Tb-loaded samples showed larger deviations from the linearity. This could be due to much smaller crystal ionic radii of Pr and Tb upon changing oxidation state from 3+ to 4+.

Figure 4 displays the CO oxidation profiles with temperature for unloaded and Ln-loaded CeO₂ catalysts. The CO oxidation onset was commonly observed at above 400 °C, but the onset position was dependent on the loaded lanthanide ions. For bare CeO₂, the onset was observed at 445 and 420 °C for the 1st and 2nd runs, respectively. The onset in the 2nd run was 25 °C lower than that in the 1st run. The enhancement of the catalytic activity was plausibly due to increase in crystallinity and exposure of active sites upon thermal CO oxidation reaction to 700 °C during the 1st run [9–11]. Most of the Ln-loaded CeO₂ samples (exception of Pr, Gd, and Ho) showed an enhancement in catalytic activity during the 2nd run, compared with that observed during the 1st run. The Nd-loaded CeO₂ showed the highest catalytic activity and the oxidation onset was observed at 424 and 410 °C for the 1st and 2nd runs, respectively. Hernandez et al.

Figure 4. (Color online) 1st and 2nd run CO oxidation onsets (top left) and 1st run CO oxidation profiles with temperature (top right) for unloaded CeO_2 and Ln-loaded CeO_2 catalysts. Change in oxidation onset compared with that of unloaded CeO_2 for the 1st and 2nd runs (bottom left). Difference in oxidation onset between the 1st and 2nd runs (bottom right).

prepared La-, Eu-, and Gd-loaded $Ce_{0.9}M_{0.1}O_{2-\delta}$ mixed oxides by a co-precipitation method and tested CO oxidation activity to show somewhat higher CO conversion rates but almost same CO oxidation onset temperature [27]. For Sm-loaded CeO_2 , the CO oxidation onset was found at 840 and 679 °C in the 1st and 2nd runs, respectively. The onset was extremely higher than those found in other samples. The extremely lower activity was due to Sm complex formed on CeO_2 , shown in the XRD patterns of Fig. 1. The significant deactivation upon Sm-loading needs further investigation. From Eu (atomic number of 63), the CO oxidation onset was found to be increased with increasing the atomic number of lanthanide ions. This is somewhat related with the particle size dependent on the atomic number displayed in Fig. 2.

TPR experiments were performed to verify surface and bulk oxygen reduction states. Figure 5 shows TPR profiles of unloaded and Ln-loaded CeO_2 catalysts. Two broad peaks were commonly observed at around 600 and 950 °C. The former peak at 600 °C and the latter peak at 970 °C were generally attributed to the reduction of surface oxygen and bulk CeO_2 [9-11]. It was clearly seen that Pr- CeO_2 showed the lowest surface reduction peak at 530 °C. Above the atomic number (59) of Pr, the surface reduction peak posi-

Figure 5. (Color online) Hydrogen TPR profiles of unloaded and Ln-loaded CeO_2 catalysts. Inset shows the peak position of the lower temperature peak.

tion was observed at higher temperatures. Based on the calculated particle sizes (Fig. 2), the catalyst with larger particles sizes showed a higher temperature surface reduction peak. For Sm-loaded CeO_2 , the surface reduction peak was dramatically diminished, instead a strong sharp peak was observed at 800 °C,

Figure 6. (Color online) Raman spectra (left panel) of bare and Ln-loaded CeO₂, and the selected expanded (10×) spectra (right panel). Inset shows the F_{2g} Raman peak position.

plausibly due to reduction of isolated Sm species as discussed above.

Figure 6 displays the Raman spectra of bare and Ln-loaded CeO₂ samples. A strong peak was commonly observed around 457–463 cm⁻¹ for all the samples. This has generally been assigned to F_{2g} vibration mode of the cubic fluorite-type structure [20]. For bare CeO₂, a strong peak was observed at 462 cm⁻¹. For Pr-CeO₂, the F_{2g} peak was found at 457 cm⁻¹, the lowest wavenumber compared with those for other samples. As discussed above, the Pr-CeO₂ sample showed the lowest surface reduction peak. At above the atomic number (59) of Pr, the F_{2g} peak was found to be shifted to a higher wavenumber with increasing the atomic number. This could be related with the ionic radius dependent CeO₂ crystal lattice [17,34]. Upon metal ion loading, additional Raman peaks were commonly observed between 500 and 650 cm⁻¹, attributed to oxygen vacancies (and/or crystal lattice distortions) created by metal doping [14,16,20,30]. Bare CeO₂, the defect-related Raman peak was found to be extremely weak. Mostly, two extra peaks were observed at 540 and 600 cm⁻¹. For Ho-, Eu-, and Pr-loaded CeO₂ samples, defect-related peaks were observed at 530 and 570 cm⁻¹ and much stronger than other samples. Interestingly, for only Tb- and Pr-loaded CeO₂ samples the defect related peaks were found at mid-position between the

two defect peaks. This could be related with an oxidation state of +4. For Ce_{0.9}Pr_{0.1}O_{2-δ} solid solution, Luo et al. reported an additional broad Raman peak at ~570 cm⁻¹, attributed to solid solution state formation [22]. This is in good consistent with the present result. Hernandez et al. observed a broad Raman peak at 532 cm⁻¹ for Ce_{1-x}Eu_xO_{2-x/2} mixed oxides between Eu₂O₃ contents of 3 and 17% wt [20,26]. The F_{2g} peak at 465 cm⁻¹ was reported to be shifted to a lower wavenumber for CeO₂ upon Eu-loading [20]. The literature is in good consistent with the present result. At higher weight %, Hernandez et al. also observed additional peak at 610 cm⁻¹, which was not observed in the present Eu-loaded CeO₂. For Er-loaded CeO₂, the Raman peaks were significantly different from others. Several strong multiple peaks were observed between 500 and 600 cm⁻¹ and attributed to ⁴S_{3/2} → ⁴I_{15/2} transitions of Er (III) ion [35,36].

IV. Conclusions

In summary, lanthanide ions were loaded into CeO₂ support to show the effects of ionic radius on the fundamental characteristics and catalytic CO oxidation properties. The XRD patterns (including calculated particle sizes), Raman peak profiles, TPR and CO oxidation profiles were found to be all dependent on

the lanthanide metal ions. The lanthanide ions with ionic radius closer to that of Ce^{4+} ion commonly showed higher CO oxidation activity. The present systematic research results highlight that matching of host-guest ionic radius was important to determine defects, particles sizes, and surface active sites.

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