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Preparation and characterization of $Ce_{1-x}Pr_xO_2$ supports and their catalytic activities[☆]

Kingkaew Chayakul Chanapattharapol [a,b,*], Somkiat Krachuamram [a,b], Ammarika Makdee [a], Preeya Unwiset [a], Sirihathai Srikwanjai [c]

[a] Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

[b] Center of Alternative Energy Research and Development, Khon Kaen University, Khon Kaen 40002, Thailand

[c] Department of Chemistry, Mahidol Wittayanusorn School, Salaya, Buddha Monthon, Nakhonpathom 73170, Thailand

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ABSTRACT

In this work, the addition of praseodymium (Pr) into ceria as a mixed oxide support in a form of $Ce_{1-x}Pr_xO_2$ ($x = 0.01$, 0.025, 0.050, 0.075 and 0.10) was prepared using a co-precipitation method. The structural and textural properties of the synthesized supports were characterized by X-ray diffraction (XRD), N_2 adsorption–desorption, Raman spectroscopy, H_2-temperature programmed reduction (H_2-TPR) and H_2-chemisorption. Upon addition of Pr, XRD patterns and Raman spectra indicated an enlargement of ceria unit cell and the characteristics Raman broad peak at 570 cm^{-1} which was attributed to the existence of oxygen vacancies in the ceria lattice. This indicated that some Ce^{4+} ions in ceria were replaced by larger Pr^{3+} cations. To evidence the incorporation of Pr^{3+} cations into ceria lattice, X-ray absorption near edge structure (XANES) was employed. The results showed that the oxidation states of Ce in mixed oxide supports were slightly lower than 4+ while those of Pr were still the same as a precursor salt. Therefore, the incorporation of Pr^{3+} into ceria lattice would lead to strain and unbalanced charge and result in oxygen vacancies. The reducibility of $Ce_{1-x}Pr_xO_2$ mixed oxide supports was investigated by H_2-TPR and temperature-resolved X-ray absorption spectroscopy experiment under reduction conditions. XANES spectra of Ce L_3 edges showed a lower surface reduction temperature (Ce^{4+} to Ce^{3+}) of $Ce_{0.925}Pr_{0.075}O_2$ than that of CeO_2 which agreed with H_2-TPR results. H_2-chemisorption indicated that Pr promoted the dispersion of the metal catalyst on the mixed oxide support and increased the adsorption site for CO. For WGS reaction, 1% Pd/mixed oxide support had higher WGS activity than 1% Pd/ceria. The increase of WGS activity was due to the increase of Pd dispersion on the support and the existence of oxygen vacancies produced from incorporation of Pr into the ceria lattice.

1. Introduction

Ceria (CeO_2) is one of the most widely used oxides as a catalysts support in various catalytic reactions. The most significant catalytic properties of ceria are its oxygen storage capability (OSC) and its fast redox ($Ce^{3+} \leftrightarrow Ce^{4+}$) cycle.[1] Because of these properties, it is usually used as catalyst support for several redox reactions, such as the reduction of sulfur dioxide to elemental sulfur by CeO_2 and Sn–Zr based catalysts,[2,3] Co_3O_4/CeO_2 and Ni–Ce mixed oxide for decomposition of N_2O,[4,5] Au/CeO_2 for oxidation of carbon monoxide and benzene[6,7] and soot combustion by rare earth doped CeO_2.[8,9] The catalytic activities of ceria-based support are due to its ability to change between the released (Ce_2O_3) and storage (CeO_2) forms during the reaction. Normally, ceria exhibits two kinds of oxygen species available for reaction, namely surface oxygen and bulk oxygen. To facilitate the changing between those two forms, creation of some defect inside ceria lattice is normally practiced. Many works reported that doping ceria with isovalent or aliovalent cations can enhance the OSC by improving the bulk reducibility or stabilize the thermal stability against sintering.[10–13] Reddy et al[14] reported that addition of isovalent (Zr^{4+}) into ceria lattice can create an extrinsic oxygen vacancies that enhance the oxygen mobility by facilitating the $Ce^{3+} \leftrightarrow Ce^{4+}$ redox process. J.S. Moura et al[15] found that the addition of aliovalent non-reducible cations such as lanthanum (La^{3+}) led to intrinsic oxygen vacancies. Other research has reported

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* Corresponding author. Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand. Fax: +66 432 02373.
E-mail address: kingkaew@kku.ac.th (K.C. Chanapattharapol).

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that doping aliovalent with variable valence cations such as terbium (Tb), praseodymium (Pr), Neodymium (Nd) can also produce intrinsic and extrinsic oxygen vacancies leading to an increase of oxygen mobility.[16,17]

Numerous studies have reported that ceria can exhibit remarkable redox properties when doped with rare earth cations and these mixed oxides should have interesting catalytic properties.[18–23] The doping of these rare earth cations can produce lattice defects which lead to an increase of bulk oxygen mobility. The addition of rare earth cations can also stabilize the fluorite-related structure of ceria and increase the thermal stability of ceria.[24] Among those elements that were frequently used as dopants for ceria, praseodymium has become of particular interest. The structure of Pr_6O_{11} is fluorite type and the ionic radius of Pr^{4+} (0.096 nm) is close to that of Ce^{4+} (0.097 nm). The mixed oxide of ceria–praseodymia exhibits a mixed oxidation states of Pr^{3+} and Pr^{4+} cations, moreover, in this mixed oxide, both elements can adopt 3+ and 4+ oxidation states and the anion vacancies are much mobile in this system.[25] Therefore ceria–praseodymia mixed oxide is currently used as a catalyst for many environmental applications such as automotive three-way catalysts,[26,27] N_2O oxidation,[28,29] CO oxidation[30,31] and soot combustion.[32,33] Many research groups studied the effect of Pr addition on ceria catalytic properties. Bensaid et al[34] studied the well-defined ceria–praseodymia nanostructured catalysts for soot oxidation. They proposed that more insertion of Pr into ceria lattice framework resulted in more cerium redox sites, thus increasing the oxygen vacancies. Bueno-Lopez et al[35] reported the effect of Pr addition on CeO_2 for volatile organic compound catalytic combustion. The results showed that upon addition of Pr, the mixed oxide catalysts exhibited a superior stability after three consecutive cycles. However, there are few reports on ceria–praseodymia mixed oxide for water gas shift reaction. X-ray absorption near edge structure (XANES) can be used to determine the reduction of metal oxide supports. In this work, we used time-resolved X-ray absorption spectroscopy to study the reduction of ceria and ceria–praseodymia mixed oxide. In our previous works,[36,37] we studied the doping of bimetallic RE–Co and RE–Ni on ceria for catalyzing water gas shift (WGS) reactions. We found that the addition of RE onto Co/CeO_2 and Ni/CeO_2 led to large increases of the WGS rate of reaction. The effects of RE on enhancing the WGS reaction rate were investigated by various techniques such as Raman spectroscopy and X-ray absorption near edge structure (XANES). We found that RE promoted partial reduction of surface ceria and provided oxygen vacancies that facilitated the redox process at the surface. Furthermore, XANES showed that electron densities were withdrawn from the d-state of Co and Ni to RE leading to easier bonding between metals and CO adsorbate in the elementary step which increased the WGS reaction.

In this work, we studied the preparation and characterization of $Ce_{1-x}Pr_xO_2$ ($x = 0.01, 0.025, 0.05, 0.075$ and 0.1) mixed oxide supports. The effect of Pr addition to ceria was investigated by X-ray diffraction, Raman spectroscopy, N_2 adsorption–desorption and H_2-temperature programmed reduction. X-ray absorption near edge structure was used to monitor the reducibility of the prepared mixed oxides. Moreover, $Ce_{1-x}Pr_xO_2$ mixed oxide was tested for catalytic activity for the WGS reaction by comparison between the activities of 1% Pd/CeO_2 and 1% $Pd/Ce_{0.925}Pr_{0.075}O_2$.

2. Experimental

2.1. Preparation of $Ce_{1-x}Pr_xO_2$ support and $Pd/Ce_{1-x}Pr_xO_2$

2.1.1. $Ce_{1-x}Pr_xO_2$ support preparation

The urea sol–gel method was used for CeO_2 support preparation which is similar to that of Kundakovic and Flytzani-Stephanopoulos.[38] An appropriate amount of metal salt ($Ce(NO_3)_3 \cdot 6H_2O$, 99%, Aldrich) and urea (H_2NCONH_2, 98%, Aldrich) were dissolved in deionized water. The mixture was stirred and heated until the salts dissolved. Ammonium hydroxide (NH_4OH, Aldrich) was added dropwise at the rate of 1 mL/min to obtain precipitate. The mixture was stirred and heated at ~100 °C for 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.

$Ce_{1-x}Pr_xO_2$ was also prepared using a urea sol–gel method. Nitrate salts of cerium ($Ce(NO_3)_3 \cdot 6H_2O$, 99%, Aldrich) and praseodymium ($Pr(NO_3)_3 \cdot 6H_2O$, 99%, Fluka) were dissolved in deionized water. Urea and ammonium hydroxide were added in similar manner as the preparation of CeO_2 as mentioned above. The amounts of Pr were 0.01 at.%, 0.025 at.%, 0.05 at.%, 0.075 at.% and 0.1 at.%.

2.1.2. Preparation of Pd on ceria and $Ce_{1-x}Pr_xO_2$

Ceria and $Ce_{1-x}Pr_xO_2$ supports were doped with Pd by an incipient wetness impregnation method using aqueous solutions of palladium nitrate ($Pd(NO_3)_2$, 99% Aldrich). The synthesized supports were impregnated with 1 wt% of the metal salt solution which was dried overnight at 110 °C and then calcined at 650 °C for 8 h.

2.2. Characterization

2.2.1. Standard characterization

The crystalline structure of mixed oxide supports were investigated by powder X-ray diffraction (XRD) using a Bruker XRD D8 Advance GX 280 diffractometer with Cu Kα radiation, 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°–80°. Lattice parameters were calculated using Bragg's equation and crystallite sizes were obtained from Scherrer's equation by using the (111) crystallographic plane.

The BET surface area of supports and catalysts were determined by N_2 adsorption–desorption isotherms at 77 K on an Autosorb 1-C instrument (Quantachrome). The samples were degassed under vacuum at 300 °C for 3 h prior to nitrogen adsorption measurement. The specific surface area of all samples was determined using the multipoint BET method and the average pore volume and diameter were determined at a relative pressure (P/P_o) near unity.

2.2.2. Raman spectroscopy

The Raman spectra were obtained by using a Jobin Yvon T64000 Raman spectrometer equipped with a BX51 Olympus optical microscope. The charge-coupled device (CCD) was used as a detector of a vibrational signal of prepared samples. The exciting wavelength from an Ar ion laser with an output power laser of 30 mW was 514.532 nm. The scanning range was 100–1300 cm^{-1}.

2.2.3. H_2-temperature programmed reduction (H_2-TPR)

The reduction properties of the samples were investigated by H_2-temperature programmed reduction (H_2-TPR) on an Autosorb 1-C instrument (Quantachrome). About 200 mg of sample was pretreated by helium at 120 °C (rate 10 °C/min) for 30 min. After pretreatment the gaseous mixture of 5% H_2 in 95% N_2 was flowed over the sample while the temperature was increased from 40 to 1000 °C at a rate of 10 °C/min. The products were analyzed using a thermal conductivity detector (TCD) and H_2-consumption was plotted as a function of temperature.

2.2.4. Inductively couple plasma-optical emission spectroscopy (ICP-OES) analysis for determination of Pd and Pr content

The samples (0.01–0.015 g) were dissolved in a mixture of 5% HCl, 5% H_2O_2 and deionized water. The calibration curves of each metal were determined by preparing the Pd and Pr solution in the range of 0–10 ppm. The samples solutions was analyzed by optima