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The effect of accessible oxygen over $\text{Co}_3\text{O}_4\text{--CeO}_2$ catalysts on the steam reforming of ethanol

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ABSTRACT

The effect of accessible oxygen on the steam reforming of ethanol (SRE) over $\text{Co}_3\text{O}_4\text{--CeO}_2$ catalysts was investigated. Both equal molar ratio of $\text{Co}_3\text{O}_4\text{--CeO}_2$ catalysts were prepared by hydrothermal co-precipitation (H), and hydrothermal ultrasonic-assisted co-precipitation (UH) methods and characterized through X-ray diffraction (XRD), in situ temperature programmed reduction/temperature programmed oxidation (TPR/TPO), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and elemental analysis (EA) techniques at various stages of the catalyst. The results indicated that the incorporation of cobalt ion into the ceria lattice could increase the dispersion of catalyst, oxygen vacancies and promote the oxygen-storing and releasing capability of ceria, especially over the catalyst prepared by ultrasonic-assisted method. The accessible oxygen played an important role on the SRE reaction and resistant to carbon deposition. The Co–Ce (UH) catalyst was more active and selective in the SRE reaction, where ethanol was fully converted and hydrogen selectivity (S_{H_2}) was about 70% at 400 °C under $\text{H}_2\text{O}/\text{EtOH}$ molar ratio of 13.0 and gas hourly space velocity (GHSV) of 22,000 h^{-1} . The high oxygen storage capacity (OSC) and high accessible oxygen for the Co–Ce (UH) catalyst allowed oxidation/gasification of deposited carbon as soon as it formed, and less coke was detected.

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Introduction

Hydrogen is a promising candidate for future energy, which is essential reactant in the application of fuel cell with the sole product of water. A large feedstock of hydrogen is currently produced from the steam reforming of fossil fuels, which may generate harmful gases to human and environment. Searching the renewable energy has become critical on the world. As an energy source, hydrogen can be obtained from the

renewable biomass by steam reforming of ethanol (SRE) using an adequate catalyst. The evolved carbon dioxide after the process can be absorbed by the plants under photosynthesis forming a closed carbon cycle without generating more greenhouse gas to the earth. The bioethanol was produced with great amount of water after the fermentation of sugar, which obtained from the biomass [1]. Since the SRE requires water to kick off the reaction, imitating bioethanol obtained from biomass fermentation could save lots of money and energy for purification of crude bioethanol.

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The SRE is a typical process for the production of hydrogen with the advantage of high hydrogen yield but it suffers from a low reaction rate and an easy deactivation with the sintering of catalyst and/or the coke formation. Development of highly active and stable catalysts for steam reforming of bioethanol to produce hydrogen has become a real challenge for the green energy source industry. Noble metals such as, Rh, Pt, Pd, Ru have been proved with high activity and strong capability for C–C cleavage [2–9], but the high costs would limit their application on large scale. Base metals, represented by Ni, Co, etc., have been reported to possess excellent performance on the SRE due to its high C–C bond cleavage activity and low expenses while deactivated preferably by the carbon deposition. Therefore, many studies on Co-based catalysts have been carried out in order to improve their performance [10–40].

Carbon deposits are produced preferably on Ni and Co catalysts. Redox supports like ceria and ceria-containing mixed oxides have been proposed to remove the deposited carbon due to their high oxygen storage capacity (OSC) [41,42]. The major role of oxygen storage materials is to store oxygen under excess oxygen condition and release it under deficient oxygen condition on the basis of the reversible redox reaction between Ce^{4+} and Ce^{3+} causing by the formation of oxygen vacancies. The OSC can improve active phase redox properties and stability of catalyst via the increase of the metal-support interaction and the gasification of the carbonaceous deposits [20,43–45]. However, ceria sinters and/or forms stable solid solution with metal oxides, i.e., Al_2O_3 , when the process is performed at high temperature [46] leading to the loss of OSC and further the deactivation of catalytic activity. It has been demonstrated that partial replacement of the ceria lattice with foreign transition metals or lanthanides by facilitating the mobility of the surface and/or subsurface oxygen species is known to enhance the thermal stability and prolongation of redox cycles of pure CeO_2 [47–50]. There are several reports regarding binary Ce-Pr-O or ternary Ce-Zr-Pr-O systems which evidence an increase in the OSC and catalytic properties in comparison with the individual Ce and Pr systems [47–49]. In the Co-based catalysts studied, Song and Ozkan [43] proposed that the high SOC and high oxygen mobility over ceria-supported samples can suppress carbon deposition. da Silva et al. [20] studied the performance of Co/CeO₂ catalyst for the oxidative steam reforming of ethanol. They reported that the higher oxygen mobility of high ceria surface area promoted the removal of carbon deposition. In the SRE reaction, Wang et al. [51] confirmed that the Co₃O₄/CeO₂ catalyst prepared by co-precipitation was more active and beneficial for resistance to carbon deposition than the impregnation method. Soykal et al. [52] investigated the effect of ceria and cobalt particle size on Co/CeO₂ catalysts in ethanol steam reforming. They found the superior performance of the cobalt catalysts supported on nanoparticles is due to a combination of factors, including increased reducibility and a difference in relative abundance of redox sites on the surface.

Ultrasonic irradiation can induce the formation of particles with much smaller size and well-dispersion than other methods. In the synthesis of colloid CeO₂-ZrO₂, Guo et al. [53] found that CeO₂-ZrO₂ prepared by ultrasound had better OSC properties than hydrothermal samples. In this paper, we

prepare Co₃O₄-CeO₂ catalysts with hydrothermal co-precipitation and hydrothermal ultrasonic-assisted co-precipitation, respectively, and it is found that the ultrasonic-assisted sample [Co-Ce (UH)] exhibits higher OSC and derives a better catalytic performance on the SRE reaction at low temperature and less carbon deposition. The oxygen vacancies and OSC properties are examined through characterization studies by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and in situ temperature programmed reduction/temperature programmed oxidation (TPR/TPO) techniques.

Experimental

Catalyst preparation

The Co₃O₄-CeO₂ catalysts with equal molar ratio were prepared by hydrothermal co-precipitation (H) and hydrothermal ultrasonic-assisted co-precipitation (UH) methods with about 15.0 mL of 2.9 M NaOH as precipitant from the precursors of Co(NO₃)₂·6H₂O and Ce(NO₃)₃·6H₂O, which were denoted as Co-Ce (H) and Co-Ce (UH), respectively. Initially, precursors and precipitant were added into 50.0 mL deionized water simultaneously with and without 480 W ultrasonic-assisted in the beaker at RT for 15 min. Then, the suspended solution was transferred individually to autoclave and heated at 200 °C for 24 h. After cooling to the room temperature, the solution was filtrated and washed with deionized water until pH 7–8. Following the drying at 100 °C for 12 h, the catalyst was calcined at 450 °C for 3 h. The Ce (H) and Ce (UH) supports as a blank were prepared with the same procedure for further study.

Catalyst characterization

The metal loading of catalysts was determined by the atomic-emission technique (ICP-AES) using a Perkin Elmer Optima 3000 DV. X-ray diffraction (XRD) measurements were performed using a Bruker D2 Phaser diffractometer with Cu K_{α1} radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 30 mA, employing a scan of $0.05^\circ \text{ s}^{-1}$ from 10° to 80° . The particle size was calculated by Scherrer equation with the diffraction profiles of XRD. The morphology and lattice profiles of the catalysts were studied by using high resolution transmission electron microscopy (HR-TEM) with FEI Tecnai G² operated at 200 kV. Fast Fourier Transform (FFT) was obtained to determine the d-spacing corresponding to which crystalline species. X-ray photoelectron spectroscopy (XPS) was utilized to identify the surface nature of the catalysts by ESCALAB 250 (Vacuum Generators) using AlK radiation (15 kV). The charge neutralizer was operated at a current of 2.0 A and a filament bias of 2.3 V. Prior to XPS recording, all samples were ground with 30% by weight of graphite powder and made into thin pellets to avoid development of any charging on the samples while XPS recording. All binding energies (BE) were referenced to the adventitious C 1s line at 284.6 eV. This reference gave BE values with an accuracy of $\pm 0.1 \text{ eV}$. The peaks fitting were carried by CasaXPS software with parameters of Gaussian/Lorentzian, GL (20). The reduction/oxidation behavior of catalysts was studied by

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