

Steam Reforming of Ethanol over Co/Pr-CeO₂ Catalysts

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Abstract

Doping of Pr (5 and 10% loading) on Ce_{0.5}Co_{0.5}O₂ catalyst (assigned as Pr₅-Ce-Co and Pr₁₀-Ce-Co), used for steam reforming of ethanol (SRE), was prepared by incipient wetness impregnation method. The topic focused on the effect of the reduction pretreatment under 250 and 400 °C (assigned as H250 and H400). All samples were characterized by XRD, TPR and TEM. Catalytic performance of SRE was tested from 250 to 500 °C in a fixed-bed reactor. In the preliminary test, we found that the activity can be enhanced on increasing the content of Pr. Also, the reduction pretreatment can influence the distribution of products, i.e. the byproduct of acetone is higher than 30 % under H250, while, the CO byproduct is lower than 2 % under H400. According to the results, we suggested that the Co/Pr₁₀-CeO₂-H400 sample is a preferential SRE catalyst. The products varied with the increasing of reaction temperature, i.e. the acetaldehyde is oxidized to acetate and then, decomposes into CO₂ and methyl group. Further, the steam reforming of methyl and water gas shift reaction accompany as the temperature exceeds 375 °C. The hydrogen distribution approached 73% at 475 °C.

Keywords: Steam reforming of ethanol; Hydrogen production; Cobalt oxide.

1 Introduction

The current shortage of global energy and stringent emission regulations has stimulated interest in renewable energies. Fuel cells have been investigated as possible devices for conversion of chemical energy into electrical energy via the hydrogen and oxygen fuels. It provides clean and highly efficient electric power for both mobile and stationary applications [1]. Using of hydrogen as an energy carrier can sustain economic growth as well as reduce pollution and greenhouse gas emissions. From the renewable point, the use of ethanol is preferred because it can obtain from biomass that offers high hydrogen content, non-toxicity, safe storage and easy handling [2]. Production of hydrogen from the steam reforming of ethanol (SRE) reaction could favor the use of hydrogen as an alternative fuel, improving the difficulties of on-board hydrogen storage and distribution. Moreover, a high yield of hydrogen can be obtained from the SRE reaction [3–5].

The doping of Pr into the ceria lattice can enhance the redox property of the oxide support by creating more surface oxygen vacancies [6]. Pr-doping remarkably promoted the oxygen storage capacity (OSC) of ceria by facilitating the mobility of the surface oxygen species [7]. Praseodymium and cerium have many similar characteristics; the addition of Pr can depress the deactivation by the deposited carbon and decreases the CO production [8]. In this work, we aimed to prepare the Pr-Ce-Co catalysts by incipient wetness impregnation method to compare the effect of Pr on the SRE reaction.

2 Experimental

2.1 Preparation of catalyst

The cobalt-cerium composite oxide, with 1:1 molar ratio was prepared by co-precipitation-oxidation (CPO) method. Initially, a stoichiometric aqueous solution of cobalt nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Showa] and cerium nitrate [$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Showa] was mixed and stirred while a 6.4 M NaOH solution was added dropwisely to obtain precipitation. Then, a H_2O_2 solution was added drop-by-drop to oxidize the precipitant. The obtained suspension was filtered and washed seven times with DI water. Finally, it was dried at 110°C overnight. Meanwhile, the as-prepared sample was further calcined at 500°C for 2 h (assigned as Ce-Co).

The Pr-Ce-Co catalysts were prepared by wet impregnation method. Different Pr amounts (5 and 10% loading) from an aqueous solution of $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were prepared. The obtained samples were dried at 110°C for overnight and finally, calcined in air at 500°C for 3 h. The as-prepared catalysts were named as $\text{Pr}_5\text{-Ce-Co}$ and $\text{Pr}_{10}\text{-Ce-Co}$, being an indicative number of nominal Pr loading.

2.2 Characterization of catalysts

The BET surface area of the samples was measured using a Micromeritics ASAP 2012 analyzer by nitrogen adsorption at the boiling temperature of liquid nitrogen. XRD measurement was performed using a MAC Science MXP18 diffractometer with Cu K1 radiation ($\lambda = 1.5405 \text{ \AA}$) at 40 kV and 30 mA. The reduction behavior of the Pr-Ce-Co catalysts was studied by temperature programmed reduction (TPR). About 50mg of the sample was heated in a flow of 10% H_2/N_2 gas at a flow rate of $10 \text{ ml} \cdot \text{min}^{-1}$. During TPR, the temperature increased at a rate of $7^\circ\text{C} \cdot \text{min}^{-1}$ from room temperature to 900°C .

2.3 Evaluation of catalysts

The catalytic activities of the composite oxides towards the SRE reaction were performed at atmospheric pressure in a fixed-bed flow reactor. Catalyst in the amount of 100 mg was placed in a 4 mm i.d. quartz tubular reactor and held by glass-wool plugs. The feed of the reactants comprised a gaseous mixture of ethanol (EtOH), H_2O and

Ar. The composition of the reactant mixture ($\text{H}_2\text{O}/\text{EtOH}/\text{Ar} = 37/3/60 \text{ vol.}\%$) was controlled by an Ar stream flow (22 ml min^{-1}) through the saturator (maintained at 130°C) containing EtOH and H_2O . The gas hourly space velocity (GHSV) was maintained at $22,000 \text{ h}^{-1}$ and the $\text{H}_2\text{O}/\text{EtOH}$ molar ratio was 13. Prior to the reaction, the sample was activated by reduction with hydrogen at 250 and 400°C for 3 h (assigned H250 and H400). The SRE activity was tested stepwise by increasing the temperature from 250 to 500°C . The analysis of the reactants and all the reaction products was carried out online by gas chromatography with columns of Porapak Q and Molecular Sieve 5A to separate.

3 Results and discussions

Fig. 1 shows the TPR profiles of series Pr-Ce-Co catalysts. The Ce-Co sample presents three reduction peaks around 313°C (T_{r1}), 375°C (T_{r2}) and 487°C (T_{r3}). According to our previous study and literature reported [9], these peaks can be assigned as the reduction of: continuous reductive cobalt oxides, Co_3O_4 (T_{r1}), CoO (T_{r2}) and surface CeO_2 (T_{r3}) as shown in the following equations. The reduction peak of Ce-Co is similar with both $\text{Pr}_5\text{-Ce-Co}$ and $\text{Pr}_{10}\text{-Ce-Co}$ samples. The reduction temperature increases with the Pr content. The doped Pr can increase thermal stability, so we can observe the reduction signal shift to high temperature.

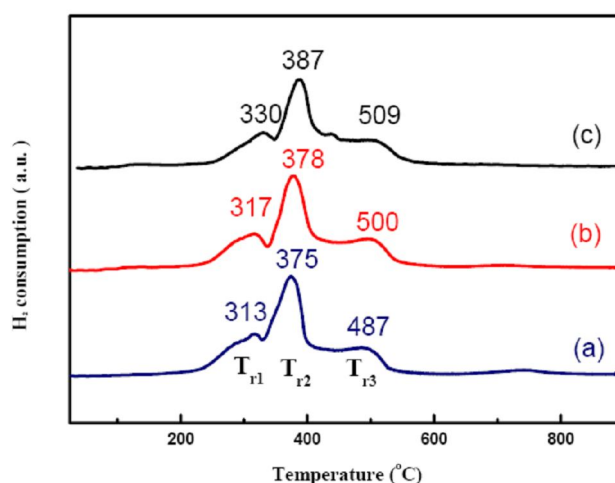


Figure 1 TPR profiles of (a) Ce-Co (b) $\text{Pr}_5\text{-Ce-Co}$ (c) $\text{Pr}_{10}\text{-Ce-Co}$.

Fig. 2 shows the XRD patterns of series Pr-Ce-Co catalysts. The diffraction patterns (111), (200), (220) and (311) of Pr-Ce-Co samples match the JCPDS 89-8436

identifying cerium oxide, CeO_2 with cubic structure. Comparison the (111) diffraction patterns of $\text{Pr}_5\text{-Ce-Co}$ and $\text{Pr}_{10}\text{-Ce-Co}$ with Ce-Co sample, the peak shifts slightly toward low angle. Also, the signal of Pr and/or PrO_x does not observe in $\text{Pr}_5\text{-Ce-Co}$ and $\text{Pr}_{10}\text{-Ce-Co}$ samples. This indicates that the doped Pr incorporates into the ceria lattice. The intensity of diffraction patterns of Co_3O_4 decreases with Pr loading. The calculated particle size become small (from 5.81 nm to 4.39 nm) indicates that the doped Pr can increase the dispersion.

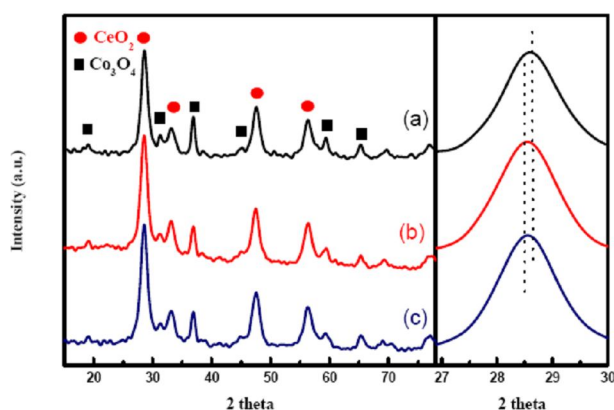


Figure 2 XRD patterns of (a) Ce-Co (b) $\text{Pr}_5\text{-Ce-Co}$ (c) $\text{Pr}_{10}\text{-Ce-Co}$.

Fig. 3 shows the ethanol conversion as well as the distribution of products at different reaction temperature over the $\text{Pr}_{10}\text{-Ce-Co-H250}$ catalyst. Ethanol is totally converted at 375 °C. Except the main products of H_2 and CO_2 , other byproduct of acetone approaches 40% at this temperature. Only minor C_2 (CH_3CHO) and C_1 (CH_4 and CO) species observes at temperature below 400 °C. Concentration of acetone increases with the temperature, then, decreases as the temperature exceeds 425 °C. At this temperature region, the concentration of H_2 and CO_2 increases rapidly and that of acetone decreases abruptly since the steam reforming of acetone is thermodynamically feasible under high temperature. According to the products distribution, the dehydrogenation of ethanol to form acetaldehyde then dehydrogenation into acetyl and/or oxidizes to the acetate intermediates which is the main reaction of SRE initially. As the temperature increases, C–C bond breaking occurs to form methyl group and carbon oxide (CO or CO_2). Further formation of the acetone byproduct comes from the combination of acetyl

and methyl group intermediates. Then, steam reforming of acetone accompanied with the increase of temperature to increase the concentration of H_2 and CO_2 . In the same time, the amount of CO also increases since the unfavorable direct decomposition of ethanol occurred that caused the slightly low of hydrogen and produced a great amount of CO .

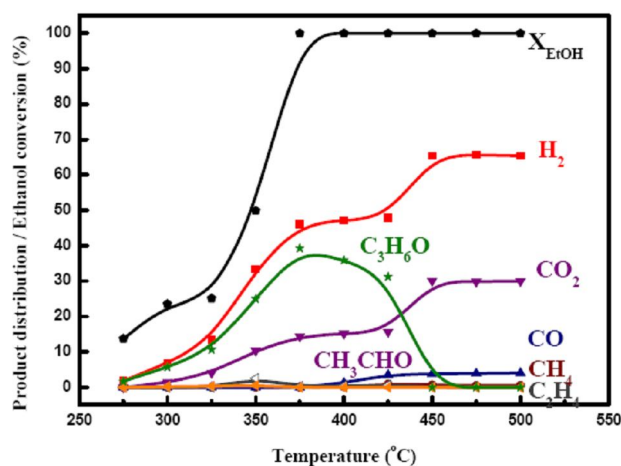


Figure 3 Catalytic performance in the SRE reaction over $\text{Pr}_{10}\text{-Ce-Co-H250}$ catalyst under $\text{H}_2\text{O}/\text{EtOH} = 13$ and $\text{GHSV} = 22,000 \text{ h}^{-1}$.

Fig. 4 shows the ethanol conversion as well as the distribution of products at different reaction temperature over the $\text{Pr}_{10}\text{-Ce-Co-H400}$ catalyst. Apparently, under high temperature pretreatment (H400), no influence of residue ion derived better activity and products distribution. The main products were acetaldehyde and hydrogen at low temperature, while, main products were H_2 and CO_2 . Only minor amounts of acetone (< 2%), CO (< 2%) and CH_4 (< 2%) were obtained. So, the hydrogen distribution approached 72%. Comparison the activity with the pretreatment condition, only 20% conversion arrived for H250 at 300 °C and 55% conversion for H400. In the same, totally converted at 375 °C for H250 and 350 °C for H400. Since the distribution of CO and CH_4 was lower, further water gas shift reaction (WGS), consecutive dehydrogenation of methyl and oxidation of carbon might be occurred.

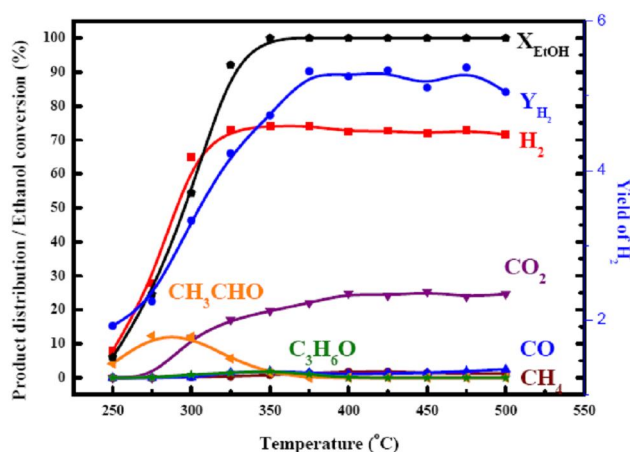


Figure 4 Catalytic performance in the SRE reaction over Pr_{10} -Ce-Co-H400 catalyst under $H_2O/EtOH = 13$ and $GHSV = 22,000 h^{-1}$.

4 Conclusions

The preliminary results showed that the influence of the residue ion on the sample was key point. The H400 samples had the better catalytic activity and products distribution than the H250 samples, i.e. the byproduct of acetone is higher than 30 % under H250, while, the CO byproduct is lower than 2 % under H400. The doped Pr enhanced the thermal stability and reduced the coke deposition. The Pr_{10} -Ce-Co-H400 sample shows the best catalytic performance with the less selectivity of acetone and CO.

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