Praseodymium-doped $\text{Ce}_{0.5}\text{Co}_{0.5}\text{O}_2$ Catalyst for Use on the Ethanol Steam Reforming to Produce Hydrogen

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Keywords: Ethanol steam reforming; Hydrogen production; $\text{Ce}_{0.5}\text{Co}_{0.5}\text{O}_2$ catalyst.

Abstract. The catalytic performance of ethanol steam reforming (ESR) reaction was investigated on a praseodymium (Pr) dopant to modify $\text{Ce}_{0.5}\text{Co}_{0.5}\text{O}_2$ catalyst. The $\text{Ce}_{0.5}\text{Co}_{0.5}\text{O}_2$ catalyst was prepared by co-precipitation-oxidation method with NaOH precipitant and H_2O_2 oxidant. Doped 5 and 10 wt% Pr ($\text{Pr}_5\text{-Ce-Co}$ and $\text{Pr}_{10}\text{-Ce-Co}$) catalysts were prepared by an incipient wetness impregnation method and reduced at 250 and 400 °C (H250 and H400). All samples were characterized by using XRD, TPR, BET, EA, TG and TEM techniques at various stages of the catalyst. The results indicated that the doped Pr improved the activity and products distribution, and depressed the deposited carbon. The $\text{Pr}_{10}\text{-Ce-Co-H400}$ sample was a highly active and stable among these catalysts, where the hydrogen distribution approached 72% at 475 °C and only minor C_1 (CO and CH_4) species were detected. In addition, the ethanol conversion still remained complete, and the selectivity of hydrogen exceeded 70% during a 100 h time-on-stream test at 400 °C. The high oxygen storage capacity (OSC) and high accessible oxygen for this catalyst allowed oxidation/gasification of deposited carbon as soon as it formed, and less coke was detected.

1. Introduction

The current shortage of global energy and stringent emission regulations has stimulated interest in renewable energy. Fuel cells have been investigated as possible devices for conversion of chemical energy into electrical energy via hydrogen and oxygen fuels. They provide clean and highly efficient electric power for both mobile and stationary applications [1]. Use of hydrogen as an energy carrier can sustain economic growth as well as reduce pollution and greenhouse gas emissions. From the renewable standpoint, the use of ethanol is preferred because it can be obtained from biomass that offers high hydrogen content, non-toxicity, safe storage and easy handling [2]. Production of hydrogen from the ethanol steam reforming (ESR) 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 an ESR reaction [3–5].

In spite of reportedly high activity and selectivity, Co-based catalysts are not immune to the problem of deactivation [3, 6–11] by deposited carbon. However, cobalt is low-cost and can be used instead of the noble metals to study the ESR reaction. Noble metal-supported catalysts have exhibited catalytic ability in the ESR reaction. Ceria (CeO_2), in particular, has been widely used in the ESR reaction; its use is attributed to high reducibility and an oxygen storage-release capacity. So, the gasification of deposited carbon can be easily removed, preventing the deactivation of the catalyst under steam conditions [12]. A ceria-supported catalyst also can promote the water gas shift (WGS) reaction which leads to a low CO production and a high H_2 yield [13]. Moreover, ceria improves the dispersion of the active phase and formation of a solid solution [14]. Ceria-supported Pt, Ir and Co catalysts have shown significant activity over the ESR reaction [12, 15–20].

The doping of Pr into the ceria lattice can enhance the redox property of the oxide support by creating more surface oxygen vacancies [21]. The doped Pr remarkably promotes the oxygen storage capacity (OSC) of ceria by facilitating the mobility of the surface oxygen species [22, 23]. Praseodymium and cerium have many similar characteristics, i.e. the addition of Pr can depress

deactivation by deposited carbon and decrease CO production [24]. In this work, we aimed to prepare Pr-Ce-Co catalysts by an incipient wetness impregnation method to compare the effect of Pr and pretreatments on the ESR reaction.

2. Experimental

A cobalt-cerium composite oxide, with a 1:1 molar ratio, was prepared by a 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 dropwise to obtain precipitation. Then, an 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 3 h (assigned as Ce-Co). The Pr-Ce-Co catalysts were prepared by the incipient wetness impregnation method with different Pr loadings (5 and 10% from the $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ precursor). The obtained samples were dried at 110 °C 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 indicative numbers of nominal Pr loading.

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 $K_{\alpha 1}$ radiation ($\lambda = 1.5405 \text{ \AA}$) at 40 kV and 30 mA. Reduction behavior of the Ce-Co and Pr-Ce-Co catalysts was studied by temperature programmed reduction (TPR). A sample of about 50 mg was heated from room temperature to 900 °C using 10% H_2/N_2 at a flow rate of 10 mL/min and a ramp rate of 7 °C/min. Morphology of the catalysts was observed using a transmission electron microscope (TEM, JEOL, JEM-2010) with an acceleration voltage of 80 to 200 kV. The ICP-AES technique was used to determine the actual content of metals in the composite oxide using a Varian VISTA-PRO AXCCD-Simultaneous ICP-AES spectrophotometer. Physical characterization of series Pr-Ce-Co catalysts is listed in Table 1.

Catalytic activities of the composite oxides towards the ESR reaction were performed at atmospheric pressure in a fixed-bed flow reactor. A 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 hourly gas 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 pretreatment by reduction with hydrogen at 250 and 400 °C for 3 h (assigned as H250 and H400). The ESR activity was tested stepwise by increasing the temperature from 275 to 500 °C. Analysis of the reactants and products was carried out online by gas chromatography with columns of Porapak Q and Molecular Sieve 5A used to separate. The evaluation of ESR activity for all samples depends on the conversion of ethanol (X_{EtOH}) and the distribution of products (mol%).

3. Results and discussion

The reducibility and oxygen storage capacity of the catalysts were examined by the TPR/TPO cycle process. The TPR profiles of Ce-Co and Pr-Ce-Co catalysts are shown in Fig. 1(A). All samples present three apparent reduction peaks indicating the reduction of Co_3O_4 and CeO_2 . Peaks 1 ($T_{r1} \sim 310 \text{ °C}$) and 2 ($T_{r2} \sim 380 \text{ °C}$) are referred to the sequent reduction of Co_3O_4 into CoO and from CoO to metallic Co [12, 25], and peak 3 ($T_{r3} \sim 490 \text{ °C}$) corresponds to the reduction of capping oxygen reduction of sub-surface oxygen of CeO_2 while accompanied little reduction of sub-surface oxygen locating around 750 °C [26, 27]. This demonstrates that the dissociated hydrogen is able to spill over from the Co to the CeO_2 surface and further reduce it at a lower

temperature. Noticeably, the three reduction peaks shift to a higher temperature with the increase of Pr loading, which may be due to the increase of thermal stability created by the doped Pr into the composite oxide. Moreover, a weak reduction signal on the Pr-Ce-Co catalysts around 120 °C is attributed to the composite oxide acts effectively with the Pr-dopant to form more mobile oxygen species which reduces at lower temperature, is consistent with previous reports [28, 29]. In order to evaluate the OSC contribution, we choose the TPR/TPO cycle process. After the 1st TPR process, TPO analysis was subsequently conducted to 200 °C for 1 h. The amount of O₂ uptake is observed higher over the Pr₁₀-Ce-Co catalyst (158 $\mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}$) in Fig. 1(B), indicating the optimal Pr-doped catalyst possessed better OSC, suggesting a role for the insertion of Pr in facilitating a large number of accessibility of oxygen from the ceria lattice.

Fig. 1(C) shows the XRD patterns of Ce-Co and Pr-Ce-Co catalysts. The major diffraction lines of CeO₂ and Co₃O₄ occur at a 2 θ value around 29° and 37.3°, which correspond to the (111) plane of CeO₂ (JCPDS 34-0394) and the (311) plane of Co₃O₄ (JCPDS 42-1467). All diffraction patterns of CeO₂ are shifted to lower angle after the adding of praseodymium, and it was due to larger Pr³⁺ (1.13 Å) and/or Pr⁴⁺ (0.99 Å) incorporated into Ce⁴⁺ (0.92 Å) with following lattice expansion, which indicates that the Pr-dopant is incorporated into the CeO₂ lattice [24, 30]. The intensity of Co₃O₄ diffraction patterns decreases with Pr loading. The particle sizes of Co₃O₄ in the Ce-Co, Pr₅-Ce-Co and Pr₁₀-Ce-Co catalysts, calculated by the Debye-Scherrer formula, according to the (311) diffraction peak are 11.7, 9.3 and 7.7 nm, respectively (lists in 6th column in Table 1). This indicates that the doped Pr could increase the dispersion of active species.

Fig. 1. (A) TPR profiles; (B) Oxygen uptakes during TPO after 1st TPR process; (C) XRD patterns of (a) Ce-Co (b) Pr₅-Ce-Co (c) Pr₁₀-Ce-Co.

Table 1. Physical characterization of Ce-Co and Pr-Ce-Co catalysts.

Sample	ICP (%)			Surface area (m ² /g)	Partical size (nm)	
	Pr	Co	Ce		Co ₃ O ₄ [*]	CeO ₂ ^{**}
Ce-Co	--	20.5	46.6	85	11.7	6.0
Pr ₅ -Ce-Co	3.54	23.1	43.5	80	9.3	6.2
Pr ₁₀ -Ce-Co	7.07	20.5	40.0	79	7.7	6.9

^{*}Calculated from the (311) plane. ^{**}Calculated from the (111) plane.

The catalytic performance of Ce-Co and Pr-Ce-Co catalysts on the ethanol steam reforming reaction under different reduction pretreatments is demonstrated in Fig. 2 and Fig. 3. Fig. 2(A) shows the ethanol conversion as well as the distribution of products over the Pr₁₀-Ce-Co-H250 catalyst. Ethanol is totally converted at 375 °C. Apart from the main products of H₂ and CO₂, other byproducts of acetone approach 40% at this temperature. Only minor C₂ (CH₃CHO and C₂H₄) and C₁ (CH₄ and CO) species are observed at temperatures below 400 °C. The selectivity of acetone increases when the temperature increases. At the temperature increases to 400 °C, the concentration of H₂ and CO₂ increases rapidly and that of acetone has decreased gradually since the steam reforming of acetone is thermodynamically feasible under high temperature [31]. According to the products distribution, the dehydrogenation of ethanol forms acetaldehyde, then dehydrogenation into acetyl and/or oxidizes to the acetate intermediates, which is the main reaction of ESR initially. Further, the C–C bond breaking occurs to form a methyl group and carbon oxide species (CO or CO₂) with the increase of temperature. Formation of acetone comes from the combination of acetyl and methyl group intermediates. Then, steam reforming of the acetone accompanied simultaneously with temperature to elevate the concentrations of H₂ and CO₂. At the same time, the amount of CO increases because of the unfavorable direct decomposition of ethanol occurs.

Fig. 2(B) compares the Ce-Co and Pr-Ce-Co catalysts on the SRE conversion and products distribution under 250 °C reduced pretreatment (H250). Although the Ce-Co catalyst possesses preferential activity, while the durability is worse than the Pr-doped catalysts. Since the Pr-dopant could enhance the thermal stability of a Ce-Co sample, the temperature of the complete ethanol conversion shifts to higher than that of Ce-Co catalyst. The direct decomposition of ethanol accompanies over the H250 pretreatment catalysts at high temperatures that increase the concentration of CO. The doped Pr with a Pr(NO₃)₃·6H₂O precursor was difficult to reduce the nitrate ion completely under 250 °C. Under this condition, amounts of acetone might be attributed to the residue ion, i.e. NO₃[−], and influences the hydrogen distribution only approached 65%.

Fig. 2. (A) Catalytic performance in the ESR reaction over $\text{Pr}_{10}\text{-Ce-Co-H250}$ catalyst; (B) Ethanol conversion and products distribution for ESR reaction over Ce-Co and Pr-Ce-Co catalysts: (a) ethanol conversion (b) H_2 distribution (c) $\text{C}_3\text{H}_6\text{O}$ distribution (d) CO distribution.

Fig. 3(A) shows the ethanol conversion, as well as the distribution of products, over the $\text{Pr}_{10}\text{-Ce-Co-H400}$ catalyst. Apparently, under high temperature reduced pretreatment (H400), no influence of residue ion derives better activity and products distribution. The main products are acetaldehyde, H_2 and CO_2 at low temperature, with only minor amounts ($< 2\%$) of acetone, CO and CH_4 . According to the products distribution, since the distribution of CO and CH_4 was low, further WGS reaction, the consecutive dehydrogenation of methyl and oxidation of carbon, might occur. The $\text{Pr}_{10}\text{-Ce-Co-H400}$ catalyst shows a higher catalytic performance and hydrogen selectivity than the $\text{Pr}_{10}\text{-Ce-Co-H250}$ catalyst.

Fig. 3(B) compares the Ce-Co and Pr-Ce-Co catalysts on the SRE conversion and products distribution under 400°C reduced pretreatment (H400). Under this condition, no influence of residue ion derives the hydrogen distribution approaching 70% as the ethanol completes conversion. Comparing the acetone distribution, the concentration drops from 40% to 2% for the H250 and H400 pretreatment over the $\text{Pr}_{10}\text{-Ce-Co}$ sample.

Fig. 3. (A) Catalytic performance in the ESR reaction over $\text{Pr}_{10}\text{-Ce-Co-H400}$ catalyst; (B) Ethanol conversion and products distribution for ESR reaction over Ce-Co and Pr-Ce-Co catalysts: (a) ethanol conversion (b) H_2 distribution (c) $\text{C}_3\text{H}_6\text{O}$ distribution (d) CO distribution.

Fig. 4 shows TEM images of fresh and used H400 catalysts. It is clear that more deposited coke around the Ce-Co-H400 [Fig. 4(a)] and $\text{Pr}_5\text{-Ce-Co-H400}$ [Fig. 4(b)] catalysts than the used $\text{Pr}_{10}\text{-Ce-Co-H400}$ [Fig. 4(c)] catalyst, suggesting that formation of deposited carbon could be eliminated easily by the accessible oxygen enhanced by the more formation of oxygen vacancies over $\text{Pr}_{10}\text{-Ce-Co-H400}$ catalyst. The deposited coke is also analyzed by EA and TG, and shows in the Table 2. With the EA analysis, the carbon content of used $\text{Pr}_5\text{-Ce-Co-H400}$ and $\text{Pr}_{10}\text{-Ce-Co-H400}$ samples is 1.1% and 0.6%, respectively. The TG analysis (not shown) also reinforces the analysis of EA results, where weight loss occurs at 400°C, which is attributed to the burning of the deposited coke. Apparently, the $\text{Pr}_{10}\text{-Ce-Co-H400}$ catalyst shows higher catalytic performance and hydrogen selectivity than the $\text{Pr}_{10}\text{-Ce-Co-H250}$ catalyst. Hydrogen distribution can approach 72% under 475 °C and only minor C_1 (< 2% of CO and CH_4) species are detected over the $\text{Pr}_{10}\text{-Ce-Co-H400}$ catalyst. For smaller amounts of Pr loading, a lower ethanol complete conversion temperature and more coke depositions are observed.

Fig. 4. TEM images of fresh and used catalysts: (a) Ce-Co-H400 (b) Pr₅-Ce-Co-H400 (c) Pr₁₀-Ce-Co-H400 (The reaction time over ESR is 10 h).

Table 2. Quantitative analysis of deposited coke on the Pr-doped Ce_{0.5}Co_{0.5}O₂ catalysts after the ESR reaction under various pretreatments.

SR reaction under various pretreatments:					
Catalyst	Coke (%)		Time (h)	Deposition rte (%·h ⁻¹)	
	EA	TG		EA	TG
250 °C Reduction pretreatment					
Ce-Co	2.8	2.8	10	0.28	0.28
Pr ₅ -Ce-Co	1.3	1.2	10	0.13	0.12
Pr ₁₀ -Ce-Co	1.1	1.1	10	0.11	0.11
400 °C Reduction pretreatment					
Ce-Co	2.2	2.0	10	0.22	0.20
Pr ₅ -Ce-Co	1.1	1.0	10	0.11	0.10
Pr ₁₀ -Ce-Co	0.6	0.8	10	0.06	0.08

One of the main issues is to develop a stable catalyst in hydrogen production from the ESR reaction. We choose the active Pr₁₀-Ce-Co-H400 catalyst that has been evaluated. Fig. 5 compares the conversion and products distribution as a function of time-on-stream (TOS) during the ESR reaction over the Pr₁₀-Ce-Co-H400 catalyst under 400 °C. This catalyst displays highly stable and active on the ESR reaction. The complete conversion of ethanol maintains over 100 h, the hydrogen distribution approaches 73 % and only minor C₁ (< 1% of CO and CH₄) is detected. Comparison

with our other designed Ni-based catalyst, NiOMC [32], the catalyst has been proved highly stable and active on the ESR reaction. The activity maintained over 100 h at 450 °C, while, the hydrogen distribution only approached 65% and more CH₄ (~ 10%) was produced than the Pr₁₀-Ce-Co-H400 catalyst.

Fig. 5. Durability of ESR reaction over Pr₁₀-Ce-Co-H400 catalyst at 400 °C.

4. Conclusions

The doping of Pr into the ceria lattice not only enhanced the active and durability but also reduced the coke deposition. Moreover, the high reduction temperature pretreatment promoted the catalytic activity and products distribution on the ESR reaction. As a result, the Pr₁₀-Ce-Co-H400 catalyst was shown to be highly active and stable for ethanol steam reforming, where the hydrogen distribution approached 72% at 475 °C and only minor C₁ (< 2% of CO and CH₄) species was detected.

Acknowledgement

We are pleased to acknowledge the financial support for this study from the Ministry of Science and Technology of the Republic of China under contract number of MOST 104-2119-M-606-001.

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