

Steam Reforming of Ethanol over CeO₂–Co₃O₄ Composite Oxides

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Abstract

Hydrogen production via steam reforming of ethanol (SRE) on CeO₂-Co₃O₄ composite oxides has been investigated. The CeO₂-Co₃O₄ composite oxides are prepared by co-precipitation-oxidation method with different Ce/Co molar ratio of 1:1, 1:2 and 2:1, respectively (assigned as Ce₁Co₁, Ce₁Co₂ and Ce₂Co₁). The as-prepared samples are dried at 100 °C and calcined at 300 °C. The catalytic activities toward the SRE are tested in a fixed-bed reactor in the temperature range of 300 - 500 °C. Reaction condition is under 22,000 h⁻¹ GHSV and the H₂O/EtOH molar ratio of 13. Prior to the SRE reaction, the samples reduced under H₂ at 200 °C and 400 °C (assigned as H2 and H4). The samples were characterized by XRD, TEM, ICP, BET, EA and TPR. In the preliminary test, we found that the better activation pretreatment was H4. Under this condition, both the activity and selectivity of products can be improved. The Ce₁Co₂ sample possesses a preferential among these composite oxides. The ethanol can be converted completely under 325 °C. The distribution of H₂ exceeds 70%, both CO and CH₄ are lower than 4. According to the TEM and EA analysis, the coke deposition can be inhibited by increasing of ceria.

Keywords: Steam reforming of ethanol; Hydrogen production; Composite oxides.

1 Introduction

Hydrogen is a clean energy and it has nonpolluting, recyclability and high conversion efficiency. The primary hydrogen production routes include ethanol decomposition (ED), partial oxidation of ethanol (POE), steam reforming of ethanol (SRE) and oxidation steam reforming of ethanol (OSRE). The SRE reaction has good activity for hydrogen due to it can convert one mole of ethanol to six moles of hydrogen. Supported Ni [1] and Co [2, 3] catalysts have been shown to be active for the SRE reaction, but they may rapidly deactivate due to the deposited carbon on the surface of the catalysts. The ceria offers oxygen mobility that promotes the gasification and oxidation of deposited carbon on the surface, hence improving stability and resistance to coking [4]. Wang et al. [5] reported that Co₃O₄/CeO₂ catalyst prepared by co-precipitation method showed good activity and stability for the SRE reaction because of the incorporation of Co ions into CeO₂ crystal lattice beneficial for resistance the coke formation. There have been reported that some literatures showed good activity between cobalt incorporated with cerium because of interacting with the active metal [6, 7]. In this work, we aimed to prepare the different ratio of CeO₂-Co₃O₄ composite oxides by co-precipitation-oxidation method to compare the effect of cobalt ratio on the SRE reaction.

2 Experimental

2.1 Preparation of catalyst

The CeO₂-Co₃O₄ composite oxides were prepared by co-precipitation-oxidation method in an aqueous solution.

The solutions of cobalt nitrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and cerium nitrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were mixed at certain molar ratios and the Ce/Co molar ratio of 1:1, 1:2 and 2:1 were denoted as Ce_1Co_1 , Ce_1Co_2 and Ce_2Co_1 , respectively. The precipitation process was carried out by added 3.2 M NaOH solution drop-by-drop. Then, the H_2O_2 (35 wt%) was introduced dropwisely under constant stirring. The suspension was then settled, filtered, washed with deionized water, and dried in an oven at 110 °C for 24 h. The as-prepared sample was further calcined in the air at 300 °C for 3 h.

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).

2.3 Evaluation of catalysts

Catalytic activities of $\text{CeO}_2\text{-Co}_3\text{O}_4$ composite oxides toward the SRE reaction were performed at atmospheric pressure in a fixed-bed flow reactor. Approximately 100 mg catalyst was placed in a 4 mm i.d. quartz tubular reactor, held by glass-wool plugs. The feed of the reactants comprised a gaseous mixture of ethanol (EtOH), H_2O and Ar (purity 99.9995%, supplied by a mass flow controller). The composition of reactant mixture ($\text{H}_2\text{O}/\text{EtOH}/\text{Ar} = 37/3/60 \text{ vol.}\%$) was controlled by flow of an Ar stream (22 ml min^{-1}) through a 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 ($\text{H}_2\text{O}:\text{EtOH} = 80:20$ by volume). Prior to the reaction, the sample was activated by means of reduction with hydrogen at 200 and 400 °C (assigned as H2 and H4) for 3 h were compared. The SRE activity was tested from 200 to 500 °C. The analysis of the reactants and all reaction products were carried out online by gas chromatography, with columns of Porapak Q and Molecular Sieve 5A for separation.

3 Results and discussions

Fig. 1 shows the XRD patterns of series $\text{CeO}_2\text{-Co}_3\text{O}_4$ composite oxides. The perfect fluorite-type structure diffraction lines of CeO_2 appeared in all sample. While the diffraction peak of Co_3O_4 increases with the loading of cobalt. In order to calculate the particle size of ceria and cobaltic oxide, the (111) and (311) planes have been chosen separately to calculate by using the Scherrer equation. The calculated diameter of ceria and cobaltic oxide are 5.8, 5.1, 5.1 nm and 5.9, 11.8, 9.5 for Ce_2Co_1 , Ce_1Co_1 and Ce_1Co_2 , respectively. Among these composite oxides, the Ce_1Co_1 sample possesses higher surface area ($135 \text{ m}^2\cdot\text{g}^{-1}$) than others (118 and $116 \text{ m}^2\cdot\text{g}^{-1}$ for Ce_2Co_1 and Ce_1Co_2).

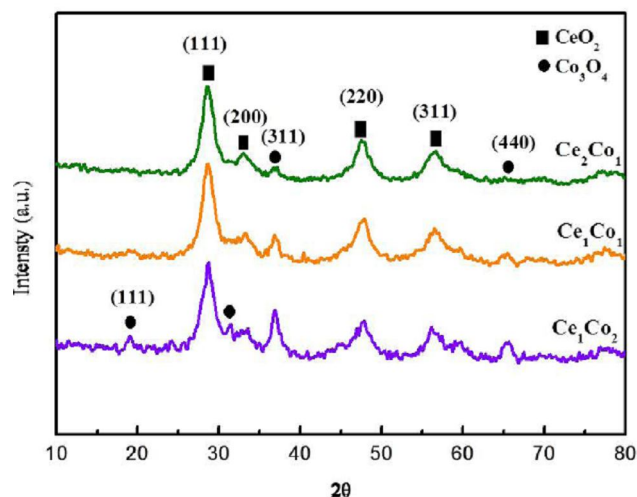


Figure 1 XRD patterns of $\text{CeO}_2\text{-Co}_3\text{O}_4$ composite oxides.

Fig. 2 shows the TPR profiles of series $\text{CeO}_2\text{-Co}_3\text{O}_4$ composite oxides. All of them exhibit four main hydrogen consumption peak around 250-260 (T_{r1}), 290-300 (T_{r2}), 350-370 (T_{r3}) and 500-700 °C (T_{r4}), respectively. Both the low-temperature peaks (T_{r1} and T_{r2}) are corresponding to the two steps reduction of cobaltic oxide: $\text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}$ [8]. The high-temperature peaks (T_{r3} and T_{r4}) are respectively attributed to the reduction of between cobalt and ceria interaction and the reduction of surface/subsurface CeO_2 . Notably, the TPR profiles indicate a gradual increase of the Co_3O_4 peak along with increase of cobalt ratio in the series composite oxides. Also, a higher hydrogen consumption of ceria can be observed with the increase loading of cobalt. This demonstrates that the dissociated hydrogen is able to spill over from the Co to the CeO_2 surface and further reduce it.

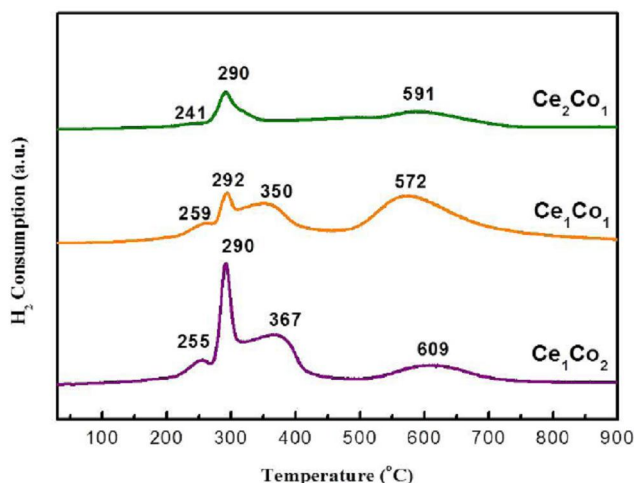


Figure 2 TPR profiles of $\text{CeO}_2\text{-Co}_3\text{O}_4$ composite oxides.

The catalytic performance of $\text{CeO}_2\text{-Co}_3\text{O}_4$ composite oxides in the steam reforming of ethanol under different temperature (T_R) are demonstrated in Figs. 3-4. Fig. 3 summarizes the effect reduction pretreatment on the conversion of ethanol over $\text{CeO}_2\text{-Co}_3\text{O}_4$ composite oxides. The results show that both the Ce/Co molar ratio and reduction pretreatment can influence the catalytic activity. Apparently, increase the molar ratio of cobalt and reduction temperature promotes the activity. For the low temperature reduction (H_2), only 20% ethanol converts under 300 °C. This can be attributed to the residue ions on the catalyst that inhibits the activity. Otherwise, the ions can be reduced under high temperature (H_4) that enhances the activity. The $\text{Ce}_1\text{Co}_2\text{-H}_4$ sample shows the best activity among composite oxides. Below 280 °C, above 90% ethanol can be converted and converts completely at 325 °C. Fig. 4 compares the H_2 and CO selectivity of $\text{CeO}_2\text{-Co}_3\text{O}_4$ composite oxides. The results indicate that high activity accompanies high selectivity of H_2 . Low CO selectivity (< 5%) for all samples below 350 °C demonstrates that the WGS reaction occurs, while the CO selectivity increases as the T_R exceeds 350 °C which might to be reverse water gas shift (RWGS) reaction. The $\text{Ce}_1\text{Co}_2\text{-H}_4$ sample shows the best activity and products selectivity. Under 325 °C, the H_2 selectivity exceeds 70 % and obtains less CO (0.8%) and CH_4 (3.3%). Fig. 5 shows the ethanol conversion and the distribution of products for the $\text{CeO}_2\text{-Co}_3\text{O}_4\text{-H}_4$ composite oxides. The ethanol can be converted completely for the $\text{Ce}_1\text{Co}_2\text{-H}_4$ sample at 325 °C [Fig. 5(C)], and the other two samples at 350 °C [Fig. 5(B), (C)]. According to the

products distribution, at low temperature (< 300 °C), the predominant reaction was the dehydrogenation of ethanol to acetaldehyde and acetyl intermediate. The acetyl intermediate cracks quickly into CO and methyl group. When $T_R = 250 - 350$ °C, the increase in CO_2 and H_2 is accompanied with a decrease in CO, which indicates that the water-gas shift (WGS) reaction occurs.

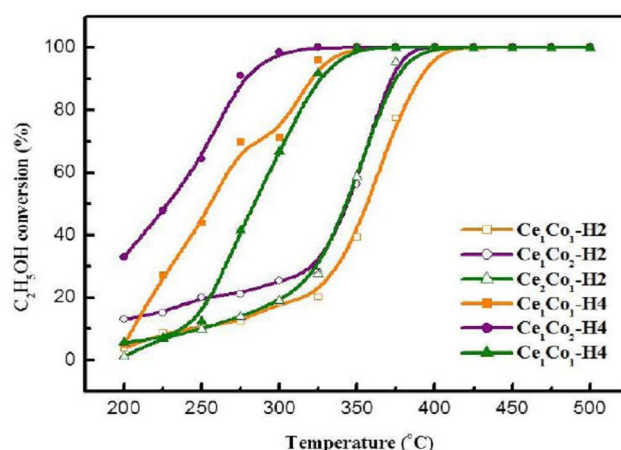


Figure 3 Effects of ethanol conversion toward the SRE reaction over $\text{CeO}_2\text{-Co}_3\text{O}_4$ composite oxides.

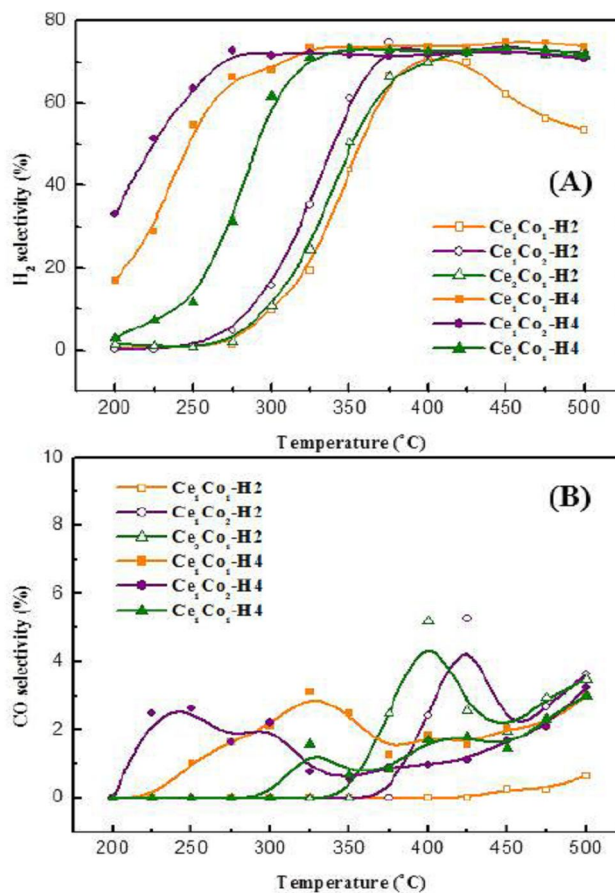


Figure 4 Products distribution on SRE reaction over $\text{CeO}_2\text{-Co}_3\text{O}_4$ composite oxides: (A) H_2 (B) CO.

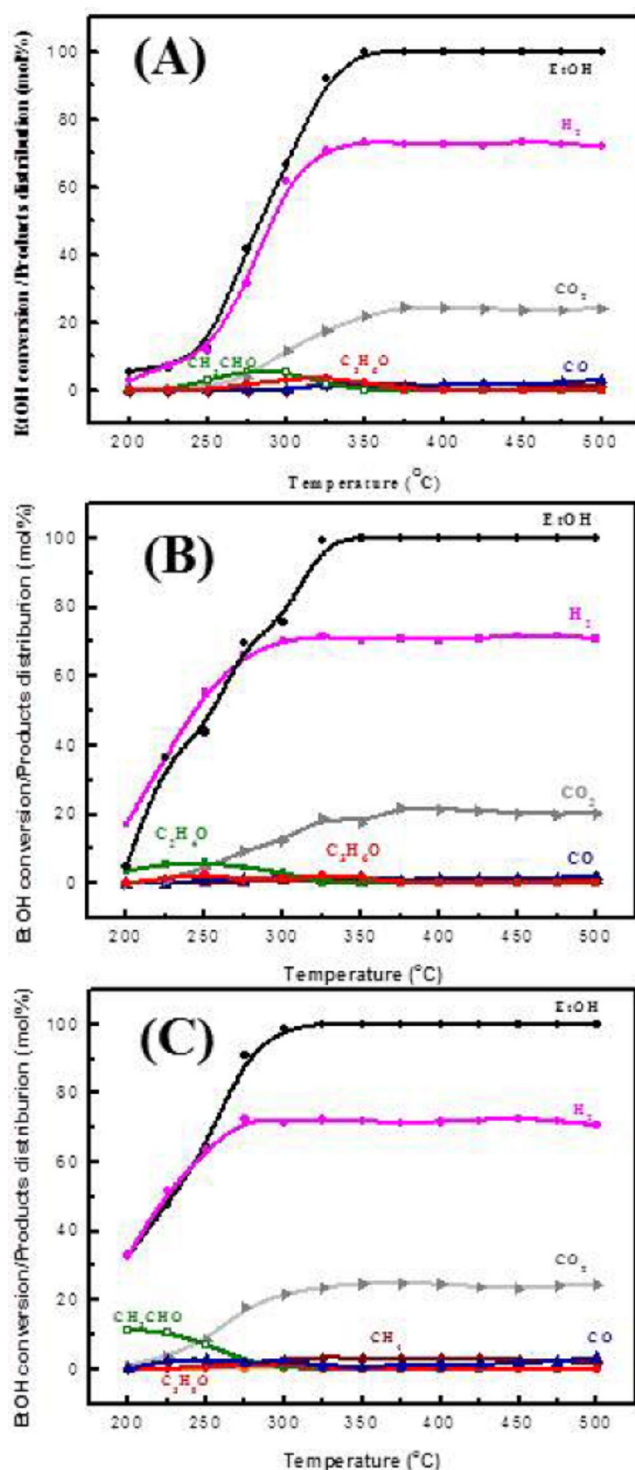


Figure 5 Ethanol conversion and products distribution for SRE reaction: (A) Ce_2Co_1 (B) Ce_1Co_1 (C) Ce_1Co_2 .

4 Conclusions

The CeO_2 - Co_3O_4 series composite oxides are significantly active on the steam reforming of ethanol. The Ce_1Co_2 -H4 catalyst shows the best activity among the CeO_2 - Co_3O_4 -H4 series catalysts. The ethanol can be

converted completely at 325 °C, H_2 selectivity exceeds 70 % and obtains less amounts of CO (0.8%) and CH_4 (3.3%).

Acknowledgments

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