

Steam Reforming of Ethanol over Ni-Rh/Ce_{0.5}Zr_{0.5}O₂ Catalysts : Influence of Preparation of Support

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NSC Project no.: 99-2113-M-606-001-MY3

Abstract

The Ce_{0.5}Zr_{0.5}O₂ composited oxide was prepared by co-precipitation method and the NiRh/Ce_{0.5}Zr_{0.5}O₂ bimetallic catalysts were prepared by incipient wetness impregnation (IWI) for hydrogen production by steam reforming of ethanol (SRE) has been studied. Three kinds of aqueous solution of Na₂CO₃, NaOH and KOH were added slowly into the stoichiometric quantities of ZrCl₂O·8H₂O and Ce(NO₃)₃·6H₂O mixed solution (Zr/Ce molar ratio was 1) at 80 °C and stirred for 2 h, respectively. Then, the as-prepared composited oxides calcined at 400 °C in air for 3 h. Subsequently, loaded the Ni(NO₃)₂·6H₂O (5 wt%) and RhCl₃·3H₂O (1 wt%) by IWI method, and calcined at 400 °C in air for 3 h which assigned as NiRh/CeZr(C), NiRh/CeZr(N) and NiRh/CeZr(K), respectively. All samples were characterized by using TG、XRD、TPR and BET. The catalytic activity of SRE reaction was evaluated in a fixed-bed reactor under H₂O/EtOH molar ratio of 13 and 22,000 h⁻¹ GHSV. Preliminary results show that the ethanol can be converted completely at 325 °C. The cracking of CH₃CHO into CO and CH₄ increased with the temperature. The formation of CO can proceed the water gas shift (WGS) reaction to get H₂ and CO₂. The NiRh/CeZr(C) catalyst has the lowest temperature (< 250 °C) of WGS reaction. Also, the selectivity of CH₄ has the least. When the temperature achieved 400 °C, the products distribution of the selectivity of H₂, CO₂ and CH₄ were 72%, 0.4% and 7%, respectively.

Keywords: Steam reforming of ethanol; Hydrogen production; Nickel oxide; Rhodium oxide.

1 Introduction

Hydrogen is a potential and attractive source of energy since its combustion to provide energy only water product. The major advantages are system efficiency and environmental benefits in conjunction with fuel cells [1]. Several catalytic processes for hydrogen production from ethanol have been investigated, including steam reforming (SR), partial oxidation, and auto-thermal reforming [2]. Steam reforming of ethanol for the production of hydrogen is very attractive among the various processes, because ethanol is abundantly available from bio-fuel that easy to store and is nontoxic. Another advantage of using ethanol is that the CO₂ produced during steam reforming of ethanol is equal to the CO₂ required for biomass growth and thus provides a closed cycle for CO₂ consumption.

Nickel-based catalysts are widely used in commercial reforming process and recognized as appropriate catalyst in SRE for their low cost, relatively high activity towards C-C bond cleavage and hydrogenation/dehydrogenation reactions [3, 4]. However, the major problem for nickel catalysts in this reaction is the deactivation by sintering and carbon deposition, which is greatly affected by the reaction conditions and kinds of catalyst. Kugai et al [5] had shown that ethanol is adsorbed on Rh and Ni surface as ethoxide species, which formed an oxametallacycle intermediate and favored C-C bond rupture. Ni possesses

high activity for C–C bond and O–H bond breaking, and also has high activity for hydrogenation, facilitating H atoms to form molecular H_2 [6].

2 Experimental

2.1 Preparation of catalyst

The ceria-zirconia composite oxide with 1:1 molar ratio was prepared by co-precipitation-oxidation (CPO) method. Initially, a stoichiometric aqueous solution of cerium nitrate [$Ce(NO_3)_2 \cdot 6H_2O$, 99.5%, Acros] and zirconium oxychloride [$ZrOCl_2 \cdot 8H_2O$, 99%, Showa] was added slowly with three kinds of aqueous solution of 3.2 M Na_2CO_3 , NaOH and KOH at 80 °C for 2 h, respectively. 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 400 °C in air for 3 h which assigned as CeZr(C), CeZr(N) and CeZr(K), respectively. The NiRh/Ce_{0.5}Zr_{0.5}O₂ catalysts were prepared by IWI method. First, an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (5 wt%) was loaded on the support. The obtained samples were dried at 110 °C for overnight and calcined at 400 °C in air for 3 h. Second, an aqueous solution of $RhCl_3 \cdot 6H_2O$ (1 wt%) was further loaded and calcined at 400 °C in air for 3 h. The obtained catalysts were named as NiRh/CeZr(C), NiRh/CeZr(N) and NiRh/CeZr(K), respectively.

2.2 Characterization of catalysts

The BET surface area of the samples was measured using a Micromeritics ASAP 2010 analyzer by nitrogen adsorption at the boiling temperature of liquid nitrogen. XRD measurement was performed using a MAC Science MXP18 diffractometer with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) at 40 kV and 30 mA. The reduction behavior of the NiRh/CeZr 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 ml·min⁻¹. During TPR, the temperature increased at a rate of 7 °C·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 ($H_2O/EtOH/Ar = 37/3/60$ 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 h⁻¹ and the $H_2O/EtOH$ molar ratio was 13. Prior to the reaction, the sample was activated by reduction with hydrogen at 400 °C for 3 h (assigned H400). The SRE activity was tested stepwise by increasing the temperature from 200 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 XRD patterns of NiRh/CeZr catalysts. Diffraction peaks of 29.1, 48.4 and 57.5° were ascribed to face center cubic structure (JCPDS 38-1439) for all catalysts. The signal of NiO and Rh_2O_3 does not observe in NiRh/CeZr samples. This indicates that the doped Ni and Rh incorporates into the ceria lattice. The intensity of diffraction patterns of CeZrO₂ decreases with Ni and Rh loading. The calculated particle size (from 5.8 nm to 4.5 nm) indicates that the doped Ni and Rh can be well-dispersed.

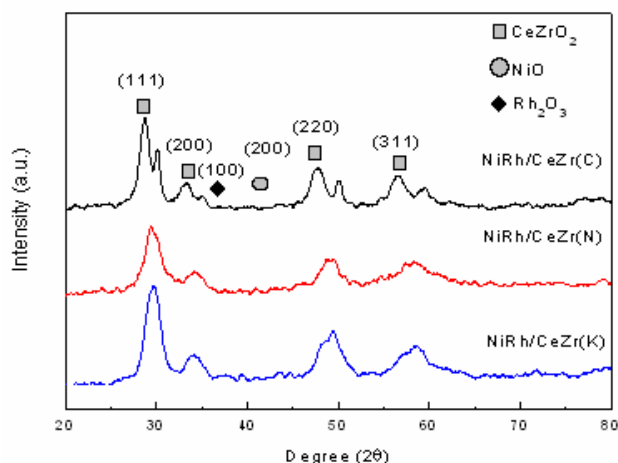


Figure 1 XRD patterns of NiRh/CeZr catalysts.

Fig. 2 shows the TPR profiles of NiRh/CeZr catalysts. All of them exhibit four main hydrogen consumption peak around 120-137 (T_{r1}), 290-310 (T_{r2}), 529 (T_{r3}) and 703 (T_{r2}), respectively. The low temperature peak (T_{r1}) is responding

to the reduction of rodium oxide: $\text{Rh}_2\text{O}_3 \rightarrow \text{Rh}$ [5]. The second low temperature peak (T_{r2}) is attributed to the reduction of nickel oxide: $\text{NiO} \rightarrow \text{Ni}$ [5, 7]. The T_{r3} is the reduction of surface/subsurface CeO_2 and T_{r4} is due to the reduction of the material in the bulk [8]. The ZrO_2 reduction peak at higher temperature was not observed.

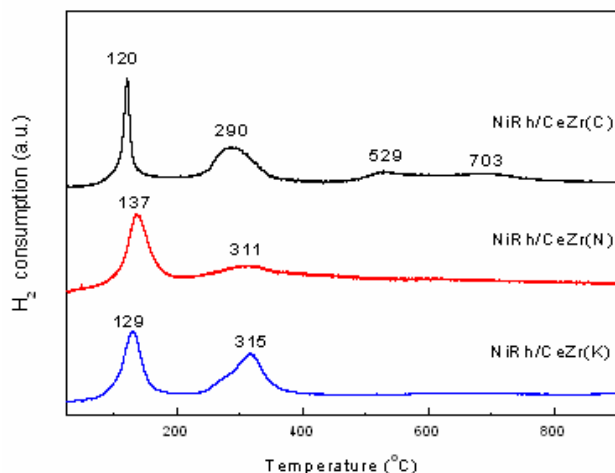


Figure 2 TPR profiles of NiRh/CeZr catalysts.

The catalytic performance of NiRh/CeZr catalysts in the steam reforming of ethanol under different precipitants is demonstrated in Figs. 3-4. Fig. 3 summarizes the effect of precipitants on the conversion of ethanol over NiRh/CeZr catalysts. Preliminary results showed that the ethanol can be converted completely at 325 °C for all catalysts. Apparently, the weak base of precipitant in the preparation can promote the activity. Fig. 4 compares the CH_4 and CO selectivity of NiRh/CeZr catalysts. The results indicate that the temperature of WGS is lowest for NiRh/CeZr(C) among the three catalysts (< 250 °C), and the selectivity of CH_4 has the least before 350 °C. Fig. 5 shows the ethanol conversion and the distribution of products for the NiRh/CeZr catalysts. The acetaldehyde intermediate followed decomposition into methane and CO with the reaction temperature. As the temperature exceeds 275 °C, with increasing temperature, selectivity of CH_4 decreases due to its reformation with H_2O , which becomes thermodynamically favorable at higher temperature. In the same, the CO can be transferred rapidly into CO_2 and H_2 by the WGS reaction. When temperature increases, methane and water are consumed resulting in increase in the selectivity of H_2 and CO_2 . The H_2 , CO and CH_4 products distribution at 400 °C were 72%, 0.4% and 7%,

respectively over the NiRh/CeZr(C) catalyst. Furthermore, this catalyst possesses the capacity of re-dispersion that can avoid the sintering and depress the carbon deposition.

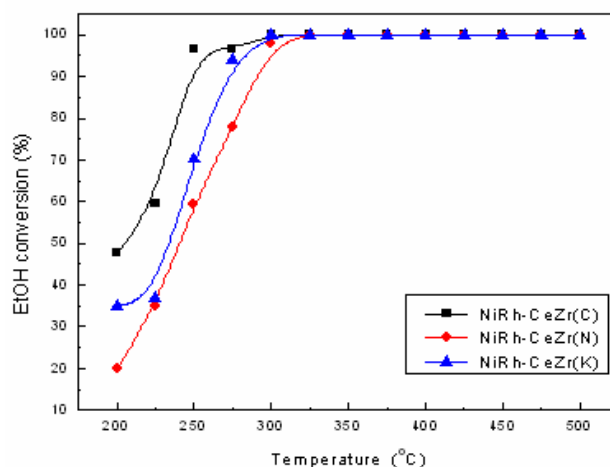


Figure 3 Effects of ethanol conversion toward the SRE reaction over NiRh/CeZr catalysts.

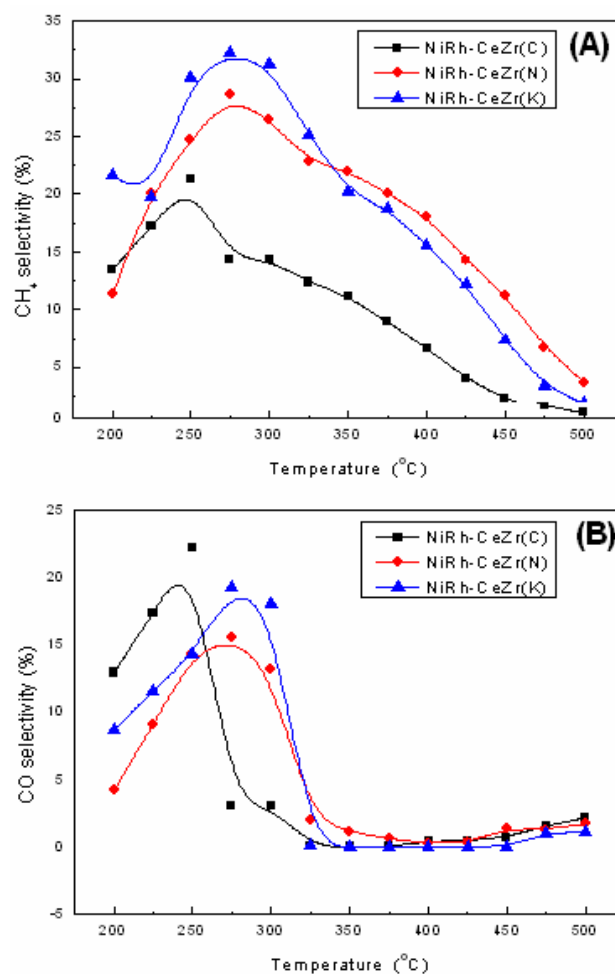


Figure 4 Products distribution on SRE reaction over NiRh/CeZr catalysts: (A) CH_4 (B) CO.

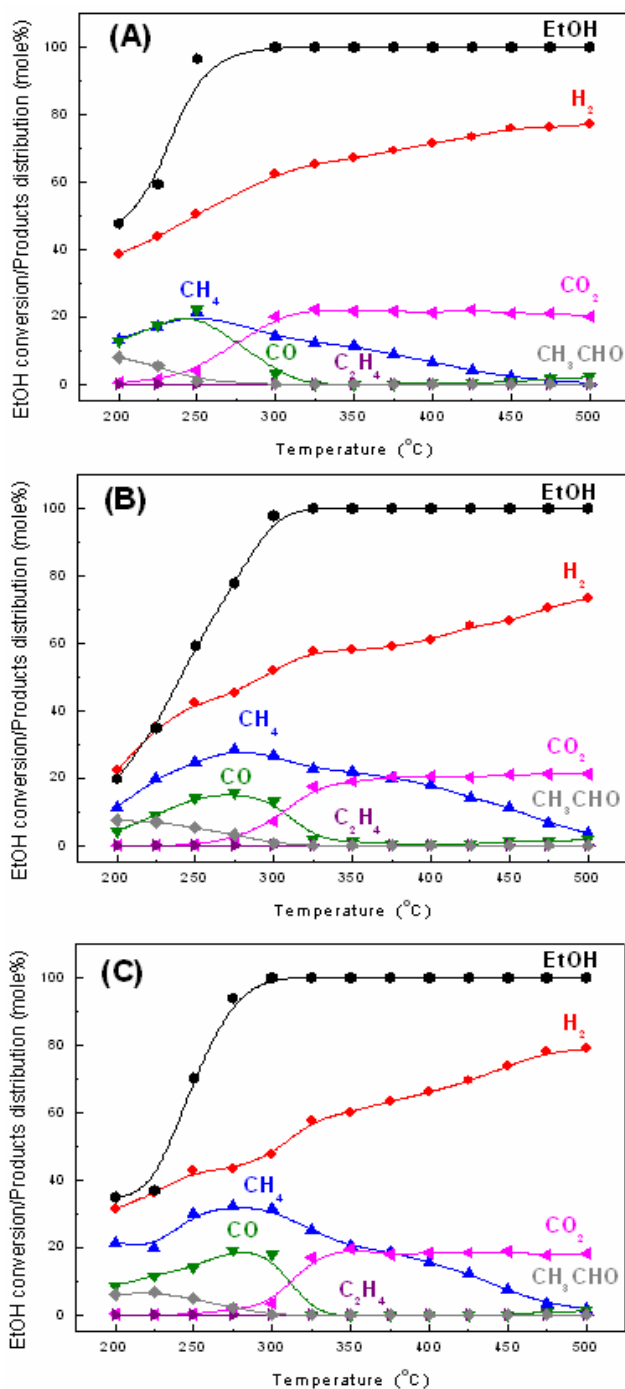


Figure 5 Ethanol conversion and products distribution for SRE reaction: (A) NiRh/CeZr(C) (B) NiRh/CeZr(N) (C) NiRh/CeZr(K).

4 Conclusions

We have investigated the different precipitants to prepare support can affect the catalytic activity on the SRE reaction over the NiRh/CeZr catalysts. The conversion and hydrogen selectivity increase with weak base of precipitan. The NiRh/CeZr(C) catalyst shows the best catalytic

performance with the less selectivity of CH₄ and CO can be transferred rapidly into CO₂ at the low temperature.

Acknowledgments

We are pleased to acknowledge the financial support for this study by the National Science Council of the Republic of China under contract numbers of NSC 99-2113-M-606-001-MY3.

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