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Effect of Co, Fe and Rh addition on coke deposition over Ni/Ce_{0.5}Zr_{0.5}O₂ catalysts for steam reforming of ethanol

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ABSTRACT

Ni-based monometallic and bimetallic catalysts (Ni, NiRh, NiCo and NiFe) supported on Ce_{0.5}Zr_{0.5}O₂ support were evaluated on the steam reforming of ethanol (SRE) performance. The supports of Ce_{0.5}Zr_{0.5}O₂ composite oxide was prepared by co-precipitation method with Na₂CO₃ precipitant and assigned as CeZr(N). The monometallic catalyst was prepared by incipient wetness impregnation method and assigned as Ni/CeZr(N). The bimetallic catalysts were prepared by co-impregnation method to disperse the metals on the CeZr(N) support and assigned as NiM/CeZr(N). All samples were characterized by using XRD, TPR, BET, EA and TEM techniques at various stages of the catalyst. The results indicated that the facile reduction and smaller particle size of Ni/CeZr(N) ($T_{99} = 300$ °C) and NiRh/CeZr(N) ($T_{99} = 250$ °C) catalysts were preferential than the NiFe/CeZr(N) ($T_{99} = 325$ °C) and NiCo/CeZr(N) ($T_{99} = 375$ °C) catalysts. Also, both the Ni/CeZr(N) and NiRh/CeZr(N) catalysts displayed better durability among these catalysts over 100 h and 400 h, respectively. Since the serious coke formation for the NiCo/CeZr(N) catalyst, the activity only maintained around 6 h, the durability on the NiFe/CeZr(N) catalyst approached 50 h.

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Introduction

Hydrogen is a potential and attractive source of energy since its combustion provides energy only water product. The major advantages are system efficiency and environmental benefits in conjunction with fuel cells [1,2]. Several catalytic processes for hydrogen production from ethanol have been investigated, including steam reforming, partial oxidation, and auto-thermal reforming. Steam reforming of ethanol (SRE) for the production of hydrogen is very attractive among the various

processes, because ethanol is abundantly available from bio-fuel that can be stored easily and is nontoxic [3–6]. Its application to industrial scale needs to overcome catalyst deactivation by coke deposition on active phase. Development of effective, cheap and durable catalysts for the reaction is essential for the green energy source industry. Several papers have evaluated the nature of metal and support, metal loading and their effect on the reforming reactions.

The nature of the supports is great importance for the catalytic performance of supported catalysts on the SRE in the presence of water at high temperature [7]. Acidic supports,

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such as Al_2O_3 are known preferentially dehydrate, while basic supports such as MgO favor dehydrogenation and condensation [8,9]. Reducible oxides, such as ZrO_2 and CeO_2 are expected to offer improved catalytic performance with high selectivity to H_2 and low selectivity to the undesirable byproducts. CeO_2 – ZrO_2 mixed oxide possesses potential applications as catalyst support due to its high surface area, thermal stability, and oxygen storage/release capacity (OSC) [10,11]. In addition, the strong metal-support interaction (SMSI) prevents metal particle sintering, which also contributes to catalyst deactivation [12]. The capacity of oxygen mobility and surface adsorption over CeO_2 – ZrO_2 strongly depends on the texture and structure, which is affected greatly by the preparation method [13–17]. Jilei et al. [18] investigated the $\text{NiO}/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ catalyst that exhibited highly active and selective for hydrogen production on the SRE reaction. Especially, the prepared catalysts were very active at low temperature and sustained stability for both carbon resistance and anti-sintering. So, the $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ support is a promising candidate for SRE and its catalytic performance will be influenced by the preparation method markedly.

Various base metals (Ni, Co, Cu, Fe) [8,11,19–24] and noble metals (Pd, Pt, Rh, Ru, Ir) [9,25–29] had been evaluated for the steam reforming of ethanol. Among these catalysts, noble metal catalysts were more active and stable than base metal catalysts in the SRE reaction. Because the price of noble metal catalysts is a serious drawback to the use in the industrial applications, Nickel and/or cobalt-based catalysts are widely used in commercial reforming process and recognized as appropriate catalyst in SRE due to their low cost, relatively high activity towards C–C bond cleavage and hydrogenation/dehydrogenation reactions [19,20]. However, the main challenge in the SRE reaction is the formation of carbonaceous species [30,31]. To overcome the problem, the monometallic Ni catalysts can be improved by doping another metal, i.e., addition of Cr, Fe, Zn and Cu to modify the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst [32], modified Ni/CeO_2 catalyst with Rh [33], or mixed oxides of CoNiZnAl [34] and NiMgAl [35] catalysts. Apparently, with or without combination of Ni and Rh, Co, Fe-based catalysts exhibited favor toward the SRE reaction [8,9,11,21–24,32–34]. These bimetallic and/or alloy catalysts were known to be highly active in the production of hydrogen, and low formation of carbonaceous species over the monometallic Ni catalysts.

In the present research, the effect of Rh, Co, or Fe-doped on the $\text{Ni}/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ catalyst has been investigated for high hydrogen production to solve the deactivation by the carbonaceous species from the SRE process. A comparative study on the performance and durability of the respective monometallic and bimetallic catalysts, and different S/C ($\text{H}_2\text{O}/\text{EtOH}$) ratios is also evaluated.

Experimental

Preparation of catalysts

The $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ composite oxide with 1:1 M ratio was prepared by co-precipitation method. Initially, a stoichiometric aqueous solution of cerium nitrate and zirconium oxychloride

was added slowly with aqueous solution of 2 M Na_2CO_3 at 80 °C for 2 h, respectively. The obtained suspension was filtered and washed with DI water. Finally, it was dried at 110 °C overnight and further calcined at 400 °C in air for 3 h which assigned as CeZr(N) . The pure CeO_2 and ZrO_2 were prepared by precipitation method under similar synthesis conditions (precursor, precipitating agent, calcined temperature) to compare with the mixed oxide. Then, the monometallic ($\text{Ni}/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$) and bimetallic ($\text{NiM}/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$, M = Rh, Co, Fe) catalysts were prepared by incipient wetness impregnation and co-impregnation methods, respectively. The precursors were $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5 wt%), $\text{RhCl}_3 \cdot 6\text{H}_2\text{O}$ (1 wt%), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5 wt%) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (5 wt%). The obtained samples were dried at 110 °C for overnight and calcined at 400 °C in air for 3 h which assigned as $\text{Ni}/\text{CeZr(N)}$, $\text{NiRh}/\text{CeZr(N)}$, $\text{NiCo}/\text{CeZr(N)}$ and $\text{NiFe}/\text{CeZr(N)}$, respectively.

Characterization of catalysts

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 Siemens D5000 diffractometer with $\text{Cu K}_{\alpha 1}$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 30 mA. The microstructure and particle size of the samples were observed by using transmission electron microscopy (TEM) with a JEOL JEM-2010 microscope equipped with a field emission electron source and operated at 200 kV. The reduction/oxidation behaviors of catalysts were studied by temperature-programmed reduction (TPR) and temperature-programmed oxidation (TPO). About 50 mg of the sample was heated in a flow of 10% H_2/N_2 gas with the increment of 7 °C min^{-1} from room temperature to 900 °C, and then cooled to room temperature with N_2 gas. Further, the reactant gas was switched to 5% O_2/N_2 at the same procedure for TPO analysis from room temperature to 200 °C and maintained 1 h. All used (post-reaction) catalysts were characterized with TEM, elemental analysis (EA) and thermogravimetry (TG). The EA of the carbon was determined by a HERAEUS VarioEL-III analyzer.

Evaluation of catalytic activity

Catalytic activity of $\text{NiM}/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ and $\text{NiM}/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ catalysts in an SRE reaction was determined at atmospheric pressure in a fixed-bed flow reactor. 100 mg of the catalyst were placed in a 4 mm i.d. quartz tubular reactor and held by glass-wool plug. The temperature of the reactor was controlled by heating tape and measured by a thermo-couple (1.2 mm i.d.) at the center of the reactor bed. The feed of the reactants was comprised of a gaseous mixture of EtOH , H_2O and Ar (purity 99.9995%, supplied by a mass flow controller). The composition of the reactant mixture ($\text{H}_2\text{O}/\text{EtOH}/\text{Ar} = 37/3/60 \text{ vol\%}$) was controlled by the Ar flow stream (22 mL/min) through a 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 $\text{H}_2\text{O}/\text{EtOH}$ molar ratio was 13 ($\text{H}_2\text{O}:\text{EtOH} = 80:20$ by volume). Prior to reactivity measurement, all samples were subjected to the reduction pretreatment at 400 °C with 10% H_2/N_2 gas for 3 h. The SRE activity was tested stepwise, increasing the temperature from 200 to

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