



Hydrogen production by steam reforming of acetic acid over Ni-based catalysts

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ABSTRACT

The Ni metallic phase supported metal oxides such as α -Al₂O₃, Ce_{0.75}Zr_{0.25}O₂, and MgO were tested under the steam reforming of acetic acid selected as a representative compound for the aqueous phase of the bio-oil derived from biomass pyrolysis. It was found that the catalytic activity and carbon formation for the catalysts studied were significantly dependent on the Ni content and the nature of support. The 15%Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst exhibited the highest catalytic performance in terms of C–C breakage conversion and hydrogen yield. In addition, the redox property of Ce_{0.75}Zr_{0.25}O₂ provided higher stability than the MgO and α -Al₂O₃ due to its less carbon deposition even at low steam-to-carbon ratios.

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1. Introduction

Hydrogen is being considered as an environmentally friendly source of energy for power generation with fuel cells. Currently, hydrogen is produced from fossil fuels such as natural gas, naphtha and coal [1]. However, these resources utilized result in a large quantity of greenhouse gas emission. For this reason, a renewable energy source such as biomass may be used as an alternative feedstock because it appears to have formidably positive environmental properties resulting from no net releases of carbon dioxide (CO₂) and very low sulfur content [2]. Biomass can be converted to bio-oils by fast pyrolysis and then the bio-oils can be converted to hydrogen (H₂) by catalytic steam reforming [3–5].

Bio-oils produced from biomass pyrolysis are virtually separated into the oil and water-rich phases. The oil phase contains lignin-derived materials that can be used for the production of more valuable products while the water-rich phase contains mostly carbohydrate-derived compounds that can be catalytically reformed with steam [6–8]. Since acetic acid is one of the major components of the water-rich phase of bio-oil [5,9], therefore, steam reforming (SR) of acetic acid has been extensively investigated as a model reaction in order to understand the integrity required for designing the efficient catalysts for use in the SR of the bio-oil water-rich phase.

Ni based catalysts are intensively used for steam reforming of hydrocarbons including oxygenate hydrocarbons [10–12]. It was reported the major problem of a Ni-based catalyst is its fast deactivation due to carbon deposition and/or metal sintering [13,14].

Alternative supports such as dolomite, olivine, MgO and MgO–CaO were reported to improve the catalytic stability [15–17]. Recently, it has been reported that Ce_{1-x}Zr_xO₂ mixed oxides exhibited a superior resistance to carbon formation on the partial oxidation and steam reforming of hydrocarbons [18,19], due to the high oxygen vacancy and oxygen mobility. In our early study, we have also found that Ce_{0.75}Zr_{0.25}O₂ solid solution exhibited the highest reducibility and activity for oxidation reactions [18–20]. In this study, we investigate the effect of the supports on the steam reforming catalytic activity and stability of acetic acid as a biomass-derived oxygenate compound model over Ni/Ce_{0.75}Zr_{0.25}O₂, Ni/ α -Al₂O₃ and Ni/MgO catalysts.

2. Experimental

2.1. Catalyst preparation and characterizations

Ce_{0.75}Zr_{0.25}O₂ and MgO were prepared via urea hydrolysis and precipitation method, respectively, whereas α -Al₂O₃ was obtained from a company. Ni(NO₃)₂ aqueous solution as Ni precursors was incorporated into the supports by the impregnation method. The desired amounts of Ni loading were 5–25 wt% for Ce_{0.75}Zr_{0.25}O₂, and 15 wt% for both MgO and α -Al₂O₃. The catalysts were characterized by BET, XRD, TPR, TPO, and TEM techniques. The detailed synthesis procedure and characteristics of catalysts were reported elsewhere [19].

2.2. Catalytic activity testing

To compare the catalytic activity and stability of the catalysts on the steam reforming of acetic acid, the reaction was carried out at 650 °C with steam-to-carbon (S/C) ratios ranging from 1 to 6.

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Typically, 0.1 g of catalyst was packed between the layers of quartz wool in a quartz tube microreactor (i.d. 10 mm) placed in an electric furnace equipped with K-type thermocouples. The temperature of catalyst bed was monitored and controlled using Shinko temperature controllers. A liquid mixture feed consisting of a known composition of acetic acid aqueous solution was introduced into an evaporator at ca. 140 °C to vaporize and mix with a gas stream prior to entering the reactor set at a desired temperature. Gaseous products were analyzed using on-line gas chromatographs in series equipped with TCD and FID detectors. Prior to running the reaction, the catalyst was reduced *in situ* with a flow of 50% H₂ in N₂ gas at 600 °C for 2 h. The C–C breakage conversion of acetic acid was defined as a molar ratio of the gaseous single carbon compounds (CH₄, CO and CO₂) in the product steam to the acetic acid reactant and the product yield was defined as a molar ratio of the product to the theoretical amount of product produced from steam reforming of acetic acid. The C–C breakage conversion and product yield reported in this work were calculated as follows:

C – C breakage conversion (%)

$$= \frac{\text{mol}_{\text{CH}_4, \text{out}} + \text{mol}_{\text{CO}, \text{out}} + \text{mol}_{\text{CO}_2, \text{out}}}{2 \times \text{mol}_{\text{AcOH}, \text{in}}} \times 100 \quad (1)$$

$$\% \text{ yield}_{\text{H}_2} = \frac{\text{mol}_{\text{H}_2, \text{out}}}{4 \times \text{mol}_{\text{AcOH}, \text{in}}} \times 100 \quad (2)$$

$$\% \text{ yield}_{\text{CO}} = \frac{\text{mol}_{\text{CO}, \text{out}}}{2 \times \text{mol}_{\text{AcOH}, \text{in}}} \times 100 \quad (3)$$

$$\% \text{ yield}_{\text{CO}_2} = \frac{\text{mol}_{\text{CO}_2, \text{out}}}{2 \times \text{mol}_{\text{AcOH}, \text{in}}} \times 100 \quad (4)$$

$$\% \text{ yield}_{\text{CH}_4} = \frac{\text{mol}_{\text{CH}_4, \text{out}}}{2 \times \text{mol}_{\text{AcOH}, \text{in}}} \times 100 \quad (5)$$

3. Results and discussion

3.1. Catalyst characterization

The BET surface areas, degrees of metal dispersion, and mean size diameters of the catalysts are shown in Table 1. As for the Ni/Ce_{0.75}Zr_{0.25}O₂ catalysts, their surface areas are in the range of 58–78 m²/g and decreased with increasing Ni loading. At a given support, the degree of metal dispersion is decreased and the mean size diameter is increased as the Ni loading is increased. This is due to the formation of NiO bulk particles [19]. However, at a given Ni loading (15 wt%), the Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst possesses the highest metal dispersion degree with the smallest mean size diameter. The low metal dispersion degree of 15%Ni/α-Al₂O₃ is due to the low surface area of the support while that of 15%Ni/MgO is owed to the formation of NiO–MgO solid solution.

The XRD patterns of the Ni/Ce_{0.75}Zr_{0.25}O₂ catalysts indicate a typical cubic fluorite structure of ceria with the presence of NiO phase (37°, 43°, and 62° (2θ)) as shown in Fig. 1. However, the Ni or NiO phase was absent in the case of low Ni loading (5 wt%). Since

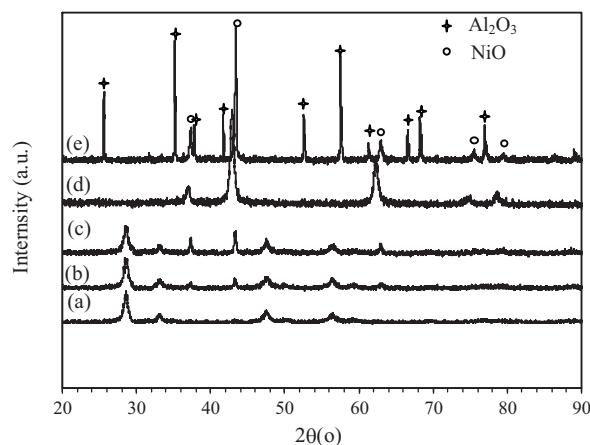


Fig. 1. XRD patterns for the catalysts investigated (a) 5%Ni/Ce_{0.75}Zr_{0.25}O₂, (b) 15%Ni/Ce_{0.75}Zr_{0.25}O₂, (c) 25%Ni/Ce_{0.75}Zr_{0.25}O₂, (d) 15%Ni/MgO, and (e) 15%Ni/α-Al₂O₃.

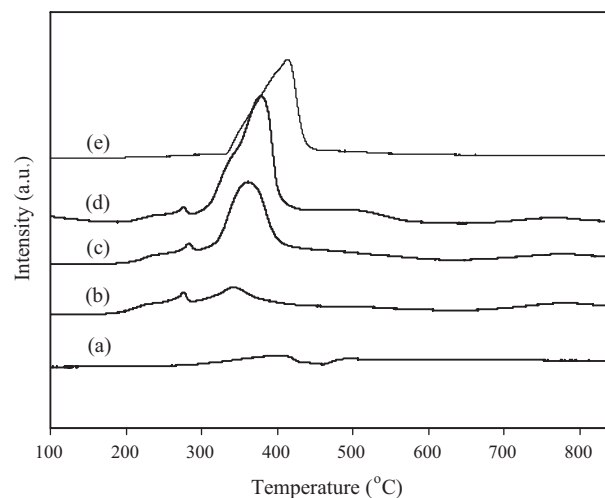


Fig. 2. H₂-TPR profiles for the catalysts with a heating rate of 10 °C/min, a reducing gas containing 5% H₂ in N₂ with a flow rate of 30 ml/min: (a) 15%Ni/MgO, (b) 5%Ni/Ce_{0.75}Zr_{0.25}O₂, (c) 15%Ni/Ce_{0.75}Zr_{0.25}O₂, (d) 25%Ni/Ce_{0.75}Zr_{0.25}O₂, and (e) 15%Ni/α-Al₂O₃.

the peak intensity was amplified with increasing Ni loading, it was suggested that NiO species is present in the forms of nano-particles and bulk agglomerated particles at a low- and a high-Ni content, respectively [19]. This result appears to be in good agreement with the data on degree of metal dispersion. Furthermore, the XRD pattern of the 15%Ni/α-Al₂O₃ catalyst reveals the separate phases of NiO and α-Al₂O₃, yet the absence of Ni–Al alloy phase. However, that of the 15%Ni/MgO catalyst indicates a NiO–MgO solid solution as similar to what reported elsewhere [21].

Fig. 2 depicts the H₂-TPR profiles for Ni/Ce_{0.75}Zr_{0.25}O₂, Ni/α-Al₂O₃ and Ni/MgO. The results showed that the reducibility

Table 1
BET surface area, degree of metal dispersion and mean size diameter of the catalysts.

Catalyst	BET surface area (m ² /g)	Degree of metal dispersion (%)	Mean size diameter ^a (nm)	Mean size diameter ^b (nm)
5%Ni/Ce _{0.75} Zr _{0.25} O ₂	78	8.29	–	12.2
15%Ni/Ce _{0.75} Zr _{0.25} O ₂	68	3.06	29.5	33.0
25%Ni/Ce _{0.75} Zr _{0.25} O ₂	58	2.15	44.7	47.0
15%Ni/Al ₂ O ₃	4	1.98	47.6	51.0
15%Ni/MgO	50	2.11	–	47.8

^a Calculated from XRD.

^b Calculated from H₂-chemisorption.

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