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Methanation of carbon dioxide over mesoporous Ni–Fe–Al_2O_3 catalysts prepared by a coprecipitation method: Effect of precipitation agent

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ABSTRACT

Mesoporous nickel (30 wt%)–iron (5 wt%)–alumina (denoted as NiFeAl–X) catalysts were prepared by a coprecipitation method with a variation of precipitation agent ($X = (NH_4)_2CO_3$, Na_2CO_3, NH_4OH, and NaOH), and they were applied to the methane production from CO_2 and H_2. Metal particle size of reduced NiFeAl–X catalysts decreased in the order of NiFeAl–NaOH > NiFeAl–NH_4OH > NiFeAl–Na_2CO_3 > NiFeAl–$(NH_4)_2CO_3$. In the methanation of CO_2, yield for CH_4 increased in the order of NiFeAl–NaOH < NiFeAl–NH_4OH < NiFeAl–Na_2CO_3 < NiFeAl–$(NH_4)_2CO_3$. This indicates that the catalytic performance in the methanation of CO_2 was strongly influenced by the identity of precipitation agent.

1. Introduction

Synthetic natural gas (SNG) has attracted much attention with increasing demand for natural gas which is considered as a green and eco-friendly energy [1–3]. Among various chemical processes for the production of SNG, coal-to-SNG is known to be a promising process for producing SNG [4–6]. However, this process inevitably releases carbon dioxide into the atmosphere. Because carbon dioxide is known to be one of the greenhouse gases, various strategies such as separation, storage, and utilization of carbon dioxide are necessary to reduce the concentration of carbon dioxide in the SNG process [7–9]. Among these strategies, methanation of carbon dioxide, which produces methane from carbon dioxide and hydrogen, not only reduces carbon dioxide but also increases yield for SNG. In other words, methanation of carbon dioxide has many benefits from environmental and economical viewpoints. Therefore, developing an efficient catalyst for carbon dioxide methanation would be of great interest.

Methanation of carbon dioxide has been investigated over a number of metal catalysts (Ni, Fe, Co, Cu, Ru, Rh, and Rh) supported on various metal oxides (SiO_2, Al_2O_3, ZrO_2, TiO_2, and CeO_2) [10–12]. Among these catalysts, Ni-based catalysts have been widely employed for carbon dioxide methanation due to their high catalytic activity and high selectivity for methane. Recently, it has been reported that addition of iron significantly improved the stability and activity of mesoporous nickel-alumina catalyst in the methanation of carbon dioxide [13]. On the other hand, the coprecipitation method has been considered as the most conventional method for the preparation of mesoporous nickel–alumina catalysts due to its high reproducibility [14,15]. The coprecipitation method also has advantages of high metal loading and high metal dispersion compared to the impregnation method [16]. However, any studies on the methanation of carbon dioxide over mesoporous nickel–iron–alumina catalysts prepared by a coprecipitation method have not been attempted yet. It is expected that physicochemical properties and catalytic activities of mesoporous nickel–iron–alumina catalysts in the methanation of carbon dioxide would be influenced by the identity of precipitation agent.

In this work, a series of mesoporous nickel–iron–alumina catalysts were prepared by a coprecipitation method with a

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variation of precipitation agent ($(NH_4)_2CO_3$, Na_2CO_3, NH_4OH, and NaOH), and they were applied to the methane production from carbon dioxide and hydrogen. The effect of precipitation agent on the physicochemical properties and catalytic activities of mesoporous nickel–iron–alumina catalysts in the methanation reaction was investigated. The nickel–iron–alumina catalysts were characterized by ICP-AES, N_2 adsorption–desorption, XRD, TPR, and TEM analyses.

2. Experimental

2.1. Preparation of mesoporous nickel–iron–alumina catalysts

A series of mesoporous nickel (30 wt%)–iron (5 wt%)–alumina (denoted as NiFeAl–X) catalysts were prepared by a coprecipitation method with a variation of precipitation agent (X = $(NH_4)_2CO_3$, Na_2CO_3, NH_4OH, and NaOH) according to the similar method reported in the literatures [17,18]. For example, typical procedures for the preparation of NiFeAl–$(NH_4)_2CO_3$ are as follows. 13.5 g of aluminum precursor (aluminum nitrate nonahydrate, Junsei), 5.3 g of nickel precursor (nickel nitrate hexahydrate, Sigma–Aldrich), and 1.1 g of iron precursor (iron nitrate nonahydrate, Sigma–Aldrich) were dissolved in 26 ml of distilled water. 24 g of $(NH_4)_2CO_3$ was separated dissolved in 84 ml of distilled water. These two solutions were then slowly added into 74 ml of distilled water to form a mixed solution. pH of the mixed solution was kept at 7. The mixed solution was stirred for 1 h. After aging the resulting product at room temperature for 24 h, a solid was recovered from the mixture by filtration. The solid was washed with distilled water several times. The solid product was then dried at 100 °C for 20 h, and subsequently, it was calcined at 700 °C for 5 h to yield the mesoporous NiFeAl–$(NH_4)_2CO_3$ catalyst. Mesoporous NiFeAl–Na_2CO_3, NiFeAl–NH_4OH, and NiFeAl–Na_2OH catalysts were prepared with the same produces described above, except that Na_2CO_3, NH_4OH, and NaOH were employed as a precipitation agent to form the corresponding catalyst.

2.2. Characterization

Chemical compositions of NiFeAl–X (X = $(NH_4)_2CO_3$, Na_2CO_3, NH_4OH, and NaOH) catalysts were determined by ICP-AES (Shimadz, ICP-1000IV) analyses. Physical properties (surface area, pore volume, and average pore size) of the catalysts were measured using an ASAP-2010 (Micromeritics) instrument. Crystalline phases of the catalysts were investigated by XRD (Rigaku, D-MAX2500-PC) measurements using Cu-Kα radiation (λ = 1.54056 Å) operated at 50 kV and 100 mA. TEM (JEOL, JEM-2100) analyses were conducted to examine the morphology of the reduced catalysts. In order to examine the metal–support interaction of NiFeAl–X (X = $(NH_4)_2CO_3$, Na_2CO_3, NH_4OH, and NaOH) catalysts, temperature-programmed reduction (TPR) measurements were carried out in a conventional flow system with a moisture trap connected to a thermal conductivity detector (TCD) at temperatures ranging from room temperature to 1000 °C with a ramping rate of 5 °C/min. For the TPR measurement, a mixed stream of hydrogen (2 ml/min) and nitrogen (20 ml/min) was used for 50 mg of catalyst sample.

2.3. Methane production from carbon dioxide and hydrogen

Methane production from carbon dioxide and hydrogen over NiFeAl–X (X = $(NH_4)_2CO_3$, Na_2CO_3, NH_4OH, and NaOH) catalysts was carried out in a continuous flow fixed-bed reactor. Prior to the catalytic reaction, each catalyst (50 mg) was reduced with a mixed stream of hydrogen (3 ml/min) and nitrogen (30 ml/min) at 700 °C for 5 h. Carbon dioxide and hydrogen were continuously fed into the reactor together with nitrogen carrier. Feed composition was fixed at $CO_2:H_2:N_2$ = 1.0:4.0:1.7 (volume ratio). Total feed rate with respect to catalyst weight was maintained at 9600 ml/h g. Reactor was then pressurized to 10 bar with the feed. Catalytic reaction was carried out at 220 °C and 10 bar. Reaction products were analyzed with gas chromatographs (Younglin 600D and Younglin ACME 6000). Conversion of CO_2, conversion of H_2, and product selectivity were calculated according to Eqs. (1)–(4). Yield for CH_4 was calculated by multiplying conversion of CO_2 and selectivity for CH_4.

$$\text{Conversion of } CO_2\,(\%) = \frac{\text{moles of } CO_2 \text{ reacted}}{\text{moles of } CO_2 \text{ supplied}} \times 100 \tag{1}$$

$$\text{Conversion of } H_2\,(\%) = \frac{\text{moles of } H_2 \text{ reacted}}{\text{moles of } H_2 \text{ supplied}} \times 100 \tag{2}$$

$$\text{Selectivity for hydrocarbon } (C_n)\,(\%) = \frac{\text{moles of } C_n \text{ formed}}{\text{moles of } CO_2 \text{ reacted}} \times 100 \tag{3}$$

$$\text{Selectivity for CO}\,(\%) = \frac{\text{moles of CO formed}}{\text{moles of } CO_2 \text{ reacted}} \times 100 \tag{4}$$

3. Results and discussion

3.1. Physicochemical properties of NiFeAl–X catalysts

Physical properties of NiFeAl–X (X = $(NH_4)_2CO_3$, Na_2CO_3, NH_4OH, and NaOH) catalysts calcined at 700 °C were examined by nitrogen adsorption–desorption isotherm measurements. Fig. 1(a) shows the nitrogen adsorption–desorption isotherms of NiFeAl–X catalysts calcined at 700 °C. All the catalysts exhibited IV-type isotherms with H2-type hysteresis loops, indicating the existence of well-developed mesopores [19]. However, the hysteresis loops of NiFeAl–$(NH_4)_2CO_3$ and NiFeAl–Na_2CO_3 catalysts prepared using carbonate ion-containing precipitation agent appeared at higher relative pressure than those of NiFeAl–NH_4OH and NiFeAl–NaOH catalysts prepared using hydroxide ion-containing precipitation agent. Pore size distributions of NiFeAl–X catalysts were within the mesopore range, as shown in Fig. 1(b). However, NiFeAl–$(NH_4)_2CO_3$ and NiFeAl–Na_2CO_3 catalysts prepared using carbonate ion-containing precipitation agent showed larger average pore size than NiFeAl–NH_4OH and NiFeAl–NaOH catalysts prepared using hydroxide ion-containing precipitation agent.

Detailed physicochemical properties of NiFeAl–X catalysts are summarized in Table 1. Nickel and iron contents in the NiFeAl–X catalysts determined by ICP-AES analyses were in good agreement with the designed values. NiFeAl–NH_4OH and NiFeAl–NaOH catalysts prepared using hydroxide ion-containing precipitation agent showed higher surface area than NiFeAl–$(NH_4)_2CO_3$ and NiFeAl–Na_2CO_3 catalysts prepared using carbonate ion-containing precipitation agent. Pore volume and average pore size of NiFeAl–$(NH_4)_2CO_3$ and NiFeAl–Na_2CO_3 catalysts were larger than those of NiFeAl–NH_4OH and NiFeAl–NaOH catalysts. The above results indicate that physical properties of NiFeAl–X catalysts were strongly affected by the identity of precipitation agent. Carbonate ions in the precipitation agent react with nickel, iron, and aluminum species, and in turn, they may form a layered double hydroxide structure (LDH), while hydroxide ions in the precipitation agent may form a metal hydroxide ($M(OH)_n$) structure [18,20]. The formation of LDH structure of NiFeAl–$(NH_4)_2CO_3$ and NiFeAl–Na_2CO_3 catalysts during the preparation step can be understood by their high porosity. Carbonate ions in the LDH structure are