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Hydrogen production by steam reforming of liquefied natural gas (LNG) over mesoporous nickel–alumina composite catalyst prepared by an anionic surfactant-templating method

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ABSTRACT

A mesoporous nickel–alumina composite catalyst (Ni–Al_2O_3) was prepared by an anionic surfactant-templating method, and was applied to hydrogen production by steam reforming of liquefied natural gas (LNG). For comparison, a nickel catalyst supported on mesoporous alumina (Ni/Al_2O_3) was prepared by an impregnation method. High surface area and well-developed mesopores of both Ni–Al_2O_3 and Ni/Al_2O_3 catalysts improved the dispersion of nickel species through the formation of nickel aluminate phase. In the Ni–Al_2O_3 catalyst, nickel species were homogeneously dispersed without significant pore blocking through the formation of Ni–O–Al composite structure. The Ni–Al_2O_3 catalyst was very efficient for suppressing the nickel sintering during the reduction process, resulting in enhanced nickel dispersion and active nickel surface area. Ni–Al_2O_3 catalyst showed a stable catalytic performance without significant catalyst deactivation during the reaction extending over 3000 min, while Ni/Al_2O_3 catalyst exhibited a stable catalytic performance at the initial stage but experienced a slight catalyst deactivation in the long run. The Ni–Al_2O_3 catalyst showed a better catalytic performance than the Ni/Al_2O_3 catalyst. High active nickel surface area and fine nickel dispersion of Ni–Al_2O_3 catalyst played an important role in enhancing the dehydrogenation reaction of hydrocarbon species and the gasification reaction of adsorbed carbon species in the steam reforming of LNG. Strong resistance of Ni–Al_2O_3 catalyst toward carbon deposition and nickel sintering was also responsible for its high catalytic performance.

1. Introduction

Development of new and clean energy has been widely studied because of the high price of fossil fuels and associated environmental problems [1]. In particular, hydrogen has attracted much attention as an alternative energy source due to its clean, renewable, and non-polluting nature [2]. Several catalytic processes for the production of hydrogen from hydrocarbons and alcohols have been investigated, including steam reforming [3–7], partial oxidation [8,9], auto-thermal reforming [10–12], and CO_2 reforming [13,14]. Among these catalytic reforming technologies, steam reforming has been recognized as the most feasible process for converting methane into hydrogen. Liquefied natural gas (LNG), which is abundant and mainly composed of methane, can serve as a promising source for hydrogen production by steam reforming reaction. LNG pipelines may become more widespread in the future, which will make LNG well suited as a hydrogen source for residential reformers in fuel cell applications. Sulfur-free nature of LNG also lessens the significant concern about environmental contamination and catalyst poisoning caused by sulfur compounds.

It is known that both palladium-based and nickel-based catalysts exhibit a high catalytic performance in the steam reforming reactions [15,16]. However, the palladium-based catalysts are disadvantageous in hydrogen production by steam reforming reaction due to their high price. Although the nickel-based catalysts have many advantages over the palladium-based catalysts in hydrogen production by steam reforming reactions due to their low cost and relatively high catalytic activity, the nickel-based catalysts require high reaction temperatures and excess amounts of steam to prevent nickel sintering and carbon deposition on the catalyst surface during the reactions [17–20].

Many efforts have been made to increase the stability of nickel-based catalysts in the steam reforming reactions [21–25]. In

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general, the catalytic performance of nickel-based catalysts strongly depends not only on the nature of active nickel, but also on the chemical and physical properties of supporting material. Therefore, modification of supporting material has been attempted as one of the promising approaches to achieve high catalytic performance of nickel-based catalysts. For example, it was reported that mesoporous alumina supports greatly enhanced the coking resistance of nickel-based catalysts in the reforming reactions by improving the active nickel surface area [4,14,26,27].

It has been reported that mesoporous aluminas with high surface area and narrow pore size distribution can be synthesized by a templating method using anionic [9,28–30], cationic [28,31,32], and non-ionic [33,34] surfactants. Among various surfactants, the anionic surfactant is known as a suitable template for the preparation of mesoporous metal–alumina composite catalyst, which can be obtained via the formation of (metal precursor)$^+$(anionic surfactant)$^-$(aluminum precursor)$^+$. However, the surfactant-templated mesoporous nickel–alumina composite has never been used as a catalyst for the reforming reactions. Therefore, developing an anionic surfactant-templated mesoporous nickel–alumina composite catalyst for hydrogen production by steam reforming of LNG would be of great interest.

In this work, a mesoporous nickel–alumina composite catalyst was prepared by an anionic surfactant-templating method, and was applied to hydrogen production by steam reforming of LNG. For comparison, a nickel catalyst supported on mesoporous alumina was prepared by an impregnation method. The effect of nickel dispersion and nickel surface area on the catalytic performance in the steam reforming of LNG was investigated. It is expected that pore blocking by nickel species, which is unavoidable in the preparation of nickel catalyst supported on mesoporous alumina by a conventional impregnation method, would be significantly suppressed in the mesoporous nickel–alumina composite catalyst.

2. Experimental

2.1. Preparation of mesoporous nickel–alumina composite catalyst

A mesoporous nickel–alumina composite catalyst was prepared by an anionic surfactant-templating method, according to the similar methods reported in literature [9,28]. 3 g of anionic surfactant (lauric acid, Sigma–Aldrich) was dissolved in 30 ml of 1-propanol (Sigma–Aldrich) at room temperature under constant stirring to yield a micelle solution (solution A). 17.4 g of aluminum precursor (aluminum *sec*-butoxide, Sigma–Aldrich) was then separately dissolved in 30 ml of 1-propanol at room temperature under constant stirring (solution B). After adding solution B to solution A, the resulting solution was stirred for 2 h to obtain a micelle-aluminum precursor complex (solution C). Another solution containing 3.6 g of nickel precursor (nickel nitrate hexahydrate, Sigma–Aldrich) and 2.75 ml of distilled water was diluted with 17.5 ml of 1-propanol (solution D). A semi-solid solution of nickel precursor–micelle–aluminum precursor complex was formed within a few seconds upon adding the solution D into the solution C. After stirring the semi-solid solution for 2 h, it was maintained at 100 °C for 24 h. The solid obtained by centrifugation was successively washed with ethanol and distilled water. The solid product was dried overnight at 100 °C, and then it was calcined at 700 °C for 5 h to yield the mesoporous nickel–alumina composite catalyst. The mesoporous nickel–alumina composite catalyst was denoted as Ni–Al_2O_3.

A mesoporous alumina was prepared according to the reported method [28] for use as a supporting material (simply denoted as Al_2O_3). A nickel catalyst supported on afore-mentioned mesoporous alumina (Al_2O_3) was then prepared by impregnating a known amount of nickel precursor (nickel nitrate hexahydrate, Sigma–Aldrich) on Al_2O_3 for comparison and reference. The nickel catalyst supported on mesoporous alumina was denoted as Ni/Al_2O_3.

2.2. Characterization

Nitrogen adsorption–desorption isotherms of support (Al_2O_3) and catalysts (Ni–Al_2O_3 and Ni/Al_2O_3) were obtained with an ASAP-2010 (Micromeritics) instrument, and pore size distributions of support (Al_2O_3) and catalysts (Ni–Al_2O_3 and Ni/Al_2O_3) were determined by the Barret–Joyner–Hallender (BJH) method applied to the desorption branches of nitrogen isotherms. Crystalline phases of support (Al_2O_3) and catalysts (Ni–Al_2O_3 and Ni/Al_2O_3) were investigated by XRD (D-Max2500-PC, Rigaku) measurements using Cu Kα radiation (λ = 1.541 Å) operated at 50 kV and 100 mA. In order to examine the reducibility of the 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 measurements, a mixed stream of H_2 (2 ml/min) and N_2 (20 ml/min) was used for 0.1 g of catalyst sample. Hydrogen chemisorption experiments (BELCAT-B, BEL Japan) were conducted to measure the nickel dispersion and nickel surface area of the catalysts. Prior to the chemisorption measurements, 50 mg of each catalyst was reduced with a mixed stream of hydrogen (2.5 ml/min) and argon (47.5 ml/min) at 700 °C for 3 h, and subsequently, it was purged with pure argon (50 ml/min) for 15 min at 700 °C. The sample was then cooled to 50 °C under a flow of argon (50 ml/min). The amount of hydrogen uptake was determined by periodically injecting diluted hydrogen (5% hydrogen and 95% argon) into the reduced catalyst using an on-line sampling valve. Nickel dispersion and nickel surface area were calculated by assuming that one hydrogen atom occupies one surface nickel atom and that cross-sectional area of atomic nickel is 6.49×10^{-20} m^2/Ni-atom. TEM analyses (JEM-2000EXII, JEOL) were conducted to examine the nickel dispersion on the reduced catalysts. Carbon deposition in the used catalysts was determined by CHNS elemental analyses (CHNS 932, Leco).

2.3. Steam reforming of LNG

Steam reforming of LNG was carried out in a continuous flow fixed-bed reactor at 600 °C under atmospheric pressure. Prior to the catalytic reaction, each catalyst (100 mg) was reduced with a mixed stream of H_2 (3 ml/min) and N_2 (30 ml/min) at 700 °C for 3 h. Feed composition was fixed at CH_4:C_2H_6:H_2O:N_2 = 4.6:0.4:10:30, and total feed rate with respect to catalyst weight was maintained at 27,000 ml/h g-catalyst. Reaction products were periodically sampled and analyzed using an on-line gas chromatograph (ACME 6000, Younglin) equipped with a TCD. LNG conversion and product composition in dry gas were calculated according to the following equations on the basis of carbon balance:

$$\textit{LNG conversion}\ (\%) = \left(1 - \frac{F_{CH_4,out} + F_{C_2H_6,out}}{F_{CH_4,in} + F_{C_2H_6,in}}\right) \times 100 \quad (1)$$

$$\textit{Product composition in dry gas}\ (\%) = \frac{F_{product,\,out}}{F_{H_2,\,out} + F_{CH_4,\,out} + F_{C_2H_6,\,out} + F_{CO,\,out} + F_{CO_2,\,out}} \times 100 \quad (2)$$

3. Results and discussion

3.1. Chemical and physical properties

Textural properties of support and catalysts were examined by nitrogen adsorption–desorption isotherm measurements. Fig. 1(a)