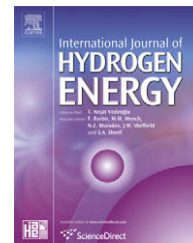


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Effect of calcination temperature of mesoporous alumina xerogel (AX) supports on hydrogen production by steam reforming of liquefied natural gas (LNG) over Ni/AX catalysts

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ABSTRACT

Mesoporous alumina xerogel (AX) supports prepared by a sol–gel method were calcined at various temperatures. Ni/mesoporous alumina xerogel (Ni/AX) catalysts were then prepared by an impregnation method, and were applied to the hydrogen production by steam reforming of liquefied natural gas (LNG). The effect of calcination temperature of AX supports on the catalytic performance of Ni/AX catalysts in the steam reforming of LNG was investigated. Physical and chemical properties of AX supports and Ni/AX catalysts were strongly influenced by the calcination temperature of AX supports. Crystalline structure of AX supports was transformed in the sequence of γ -alumina \rightarrow ($\gamma + \theta$)-alumina \rightarrow θ -alumina \rightarrow ($\theta + \alpha$)-alumina with increasing calcination temperature from 700 to 1000 °C. Nickel species were strongly bonded to the divalent vacancy of γ -alumina, ($\gamma + \theta$)-alumina, and θ -alumina through the formation of nickel aluminate phase. In the steam reforming of LNG, both LNG conversion and hydrogen composition in dry gas showed volcano-shaped curves with respect to calcination temperature of AX supports. Among the catalysts tested, Ni/AX-900 (nickel catalyst supported on AX that had been calcined at 900 °C) showed the best catalytic performance. The smallest nickel crystalline size and the strongest nickel–alumina interaction were responsible for high catalytic performance of Ni/AX-900 catalyst in the steam reforming of LNG.

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1. Introduction

Hydrogen has attracted much attention as an alternative energy source due to its clean, renewable, and non-polluting nature [1,2]. Especially, hydrogen has been widely used as a feed for PEMFC (polymer electrolyte membrane fuel cell) [3–5]. Several catalytic processes for the production of hydrogen from hydrocarbons have been investigated, including steam reforming [6–8], partial oxidation [9], auto-thermal reforming [10], and CO₂ reforming [11]. Among these reforming

reactions, steam reforming has been recognized as a promising process for converting methane into hydrogen because hydrogen-rich gas stream (H₂/CO = 3) can be obtained compared to the other reforming technologies.

Liquefied natural gas (LNG), which is abundant and mainly composed of methane, can serve as an alternate source for hydrogen production by steam reforming reaction. LNG infrastructure 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

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nature of LNG also lessens the significant concern about environmental contamination and catalyst poisoning caused by sulfur compound.

It is known that conventional nickel-based catalysts suffer from severe catalyst deactivation in the steam reforming reactions due to the carbon deposition and the nickel sintering [12–15]. Many attempts have been made to increase the stability of nickel-based catalysts in the steam reforming reactions [16–20]. For example, it has been reported that addition of small amount of alkali or alkali-earth metal enhanced the steam reforming performance of nickel-based catalysts [19–21]. On the other hand, modification of supporting material has also been attempted to achieve high catalytic performance of nickel-based catalysts. It was revealed that mesoporous alumina supports greatly enhanced the coking resistance of nickel-based catalysts, resulting in high catalytic performance in the reforming reactions [22,23]. In particular, mesoporous alumina xerogel was reported to be a promising supporting material for enhancing the catalytic performance of supported nickel catalysts in the steam reforming of LNG [24].

It is known that amorphous alumina is readily transformed into transition alumina (γ -alumina, δ -alumina, and θ -alumina), and finally, into crystalline alumina (α -alumina) with increasing calcination temperature. This means that physical and chemical properties of alumina are strongly influenced by the calcination temperature. It is expected that catalytic performance of nickel catalyst supported on mesoporous alumina xerogel in the steam reforming of LNG is also strongly affected by the calcination temperature of mesoporous alumina xerogel support.

In this work, mesoporous alumina xerogel (AX) supports prepared by a sol–gel method were calcined at various temperatures. Ni/mesoporous alumina xerogel (Ni/AX) catalysts were then prepared by an impregnation method, and were applied to the hydrogen production by steam reforming of LNG. The effect of calcination temperature of AX supports on the catalytic performance of Ni/AX catalysts in the steam reforming of LNG was investigated.

2. Experimental

2.1. Preparation of alumina xerogel support and supported nickel catalyst

Mesoporous alumina xerogel (AX) support was prepared by a sol–gel method, according to the similar method reported in the literature [22–24]. 7 g of aluminum precursor (aluminum *sec*-butoxide, Sigma–Aldrich) was dissolved in ethanol at 80 °C. Small amounts of nitric acid and distilled water that had been diluted with ethanol were then slowly added into the solution containing aluminum precursor. The resulting solution was maintained at 80 °C for a few minutes to obtain a clear sol. The sol was then cooled to room temperature. A

transparent monolithic gel was formed within a few minutes by adding an appropriate amount of water diluted with ethanol into the sol. After aging the alumina gel for 3 days, it was dried overnight at 120 °C. The resulting powder was calcined at various temperatures for 5 h to yield the alumina xerogel. The prepared alumina xerogel supports were denoted as AX-Y (Y = 700, 800, 900, and 1000), where Y represents the calcination temperature in Celsius degree.

Nickel catalysts supported on mesoporous alumina xerogel supports were prepared by impregnating a known amount of nickel precursor ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma–Aldrich) on the supports. The supported nickel catalysts were denoted as Ni/AX-Y (Y = 700, 800, 900, and 1000). The nickel loading was fixed at 20 wt% in all cases.

2.2. Characterization

Nitrogen adsorption–desorption isotherms of AX supports were obtained with an ASAP-2010 (Micromeritics) instrument, and pore size distributions of AX supports were determined by the Barret–Joyner–Hallender (BJH) method applied to the desorption branch of nitrogen isotherms. Crystalline phases of supports and supported catalysts were investigated by XRD (D-Max2500-PC, Rigaku) measurements using Cu-K α radiation ($\lambda = 1.541 \text{ \AA}$) operated at 50 kV and 100 mA. In order to examine the reducibility of supported nickel 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 H₂ (2 ml/min) and N₂ (20 ml/min) was used for 0.1 g of catalyst sample. 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 700 °C under atmospheric pressure. Prior to the catalytic reaction, each catalyst (100 mg) was reduced with a mixed stream of H₂ (3 ml/min) and N₂ (30 ml/min) at 700 °C for 3 h. Feed composition was fixed at CH₄:C₂H₆:H₂O:N₂ = 4.6:0.4:10:30, and total feed rate with respect to catalyst weight was maintained at 25,140 ml/h g. Reaction products were periodically sampled and analyzed using an on-line gas chromatograph (ACME 6000, Younglin) equipped with a thermal conductivity detector (TCD). LNG conversion and H₂ composition in dry gas were calculated according to the following equations on the basis of carbon balance:

$$\text{LNG conversion (\%)} = \left(1 - \frac{F_{\text{CH}_4,\text{out}} + F_{\text{C}_2\text{H}_6,\text{out}}}{F_{\text{CH}_4,\text{in}} + F_{\text{C}_2\text{H}_6,\text{in}}} \right) \times 100 \quad (1)$$

$$\text{H}_2 \text{ composition in dry gas (\%)} = \frac{F_{\text{H}_2,\text{out}}}{F_{\text{H}_2,\text{out}} + F_{\text{CH}_4,\text{out}} + F_{\text{C}_2\text{H}_6,\text{out}} + F_{\text{CO},\text{out}} + F_{\text{CO}_2,\text{out}}} \times 100 \quad (2)$$

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