Precipitation of Ni nanoparticle on Al₂O₃ powders by novel rotary chemical vapor deposition

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Ni nanoparticles were precipitated on Al₂O₃ support powder by rotary chemical vapor deposition (RCVD). The Ni nanoparticle size increased from 8 to 62 nm in diameter and the content of Ni decreased from 6.6 to 2.4 mass % with increasing Al₂O₃ powder diameter (D₁₉₋₅₀) from 80 nm to 150 μm. The catalytic activity of Ni precipitated Al₂O₃ (Ni/Al₂O₃) powder was evaluated by the hydrogen production rate (R₉₁₂) in a methanol-steam flow. The R₉₁₂ decreased with increasing D₁₉₋₅₀ and increased with increasing specific surface area of Ni/Al₂O₃ powder. The highest R₉₁₂ of Ni/Al₂O₃ powder was 709 × 10⁻³ mol kg⁻¹ s⁻¹ at 633 K, D₁₉ = 8 nm and D₁₉₋₅₀ = 80 nm.

Key-words : Ni nanoparticles, Rotary chemical vapor deposition, Alumina support, Catalytic activity

1. Introduction

Al₂O₃ powder is a candidate support material for catalysis due to its thermal/chemical inertness, and Ni nanoparticle-precipitated Al₂O₃ powder (hereafter Ni/Al₂O₃) has been found to exhibit good catalytic properties.¹ Many preparation methods have been used to precipitate Ni nanoparticles on Al₂O₃ powder. They can be classified into two types, i.e., wet and dry processes. Most of the wet processes such as heterogeneous precipitation,²¹ impregnation,³ solution-spraying plasma,⁴ sol–gel⁵ and electroless deposition,⁶ involve complex steps, including aqueous phase elimination and hydrogen reduction at high temperatures, leading to agglomeration or grain growth during the post-treatment. On the other hand, dry processes, such as mechanical alloying⁷ and chemical vapor deposition (CVD),⁸ are rather simple with no need for the post-treatment, mostly maintaining the as-prepared particle size.

We have developed rotary CVD (RCVD) to precipitate nanoparticles on support powder. In the present study, Ni nanoparticles were precipitated on various Al₂O₃ powders 80 nm to 150 μm in diameter. The effect of Al₂O₃ powder diameter (D₁₉₋₅₀) on the catalytic property of Ni nanoparticles was investigated by a methanol steam reforming reaction.

2. Experimental procedure

Ni nanoparticles were precipitated on Al₂O₃ powder by RCVD using nickelocene (NiCp₂) as a precursor. The details of the RCVD apparatus have been reported elsewhere.⁶ The NiCp₂ precursor was heated at 393 to 423 K and carried with H₂ at a flow rate of 1.67 × 10⁻³ m³ s⁻¹. The supply rate (Rs) of NiCp₂ was fixed at 0.56 × 10⁻⁵ kg s⁻¹. Al₂O₃ powder 80 nm to 150 μm in diameter and 4 g in weight was fed into the reactor and preheated at 823 K. The total pressure of the RCVD apparatus was kept at 800 Pa. The deposition time was fixed for 1.8 ks.

The crystal structure of Ni/Al₂O₃ was identified by X-ray diffraction (XRD; Geigerflex, Rigaku Corp.) with Cu Kα radiation. The microstructure was observed by field emission scanning electron microscopy (FESEM, JEOL, JSM-7500F) and transmission electron microscopy (TEM, JEOL; 2000EX). The average diameter of the Ni nanoparticles (D₉₅) was calculated from 50 particles in the TEM and FESEM images. The Ni content (C₅₃) in the Ni/Al₂O₃ powder was examined by energy-dispersive X-ray spectroscopy (EDS). The specific surface area of the Ni/Al₂O₃ was determined by BET surface area measurement (BEL Japan, Belsorp-mini II).

The catalytic property of Ni nanoparticles on Al₂O₃ powder was investigated by methanol-steam reforming (MSR) in a conventional flow catalytic reactor at 100 kPa. All samples were pretreated at 673 K for 1 h in a N₂ and H₂ mixture gas with flow rates of 0.17 and 0.5 × 10⁻⁶ m³ s⁻¹. The mixture of methanol and water 2 to 3 in molar ratio was introduced into the reactor at a flow rate of 2.7 × 10⁻⁶ m³ s⁻¹. N₂ gas at a flow rate of 0.5 × 10⁻⁶ m³ s⁻¹ was used as a diluter. The gas species produced by the MSR reaction were analyzed by an on-line gas chromatograph mass spectrometer (Shimadzu GC-14A). The SRM reaction was carried out at 513 to 633 K. The concentrations of H₂, CO, CO₂ and CH₄ were measured under a steady state for 1.8 ks.

3. Results and discussion

Figure 1 shows typical XRD patterns of the Ni/Al₂O₃ powders. The diameters of Al₂O₃ powder were 0.2, 1, 10 and 150 μm. The diffraction peaks of the Ni phase were identified at 2θ = 44.34° (111), 51.67° (200) and 76.09° (220). Figure 2 shows the effect of D₁₉₋₅₀ on the Ni content (C₅₃). At D₁₉₋₅₀ = 80 nm, C₅₃ was 6.6 mass %. The C₅₃ decreased with increasing D₁₉₋₅₀, and at D₁₉₋₅₀ = 150 μm, C₅₃ was 2.4 mass %.

Figure 3 shows TEM images of Ni nanoparticles precipitated on various Al₂O₃ powders 80 nm to 1 μm in diameter. Ni particles less than 10 nm in diameter were distributed on the Al₂O₃ powder [Fig. 3(a)]. Figure 4 shows FESEM images of Ni nanoparticle precipitated on Al₂O₃ powder at D₁₉₋₅₀ = 10 (a, b), 53 (c, d) and 150 μm (e, f). Table 1 shows the average diameter of Ni (D₉₅)
and Al2O3 (DAl2O3) of the Ni/Al2O3 powders reported in the literature and those of the present study. Wet processes required elimination of the aqueous phase and subsequent hydrogen reduction processes. It has been reported that NiO nanoparticles were precipitated on Al2O3 powder using nickel nitrate as a Ni precursor by heterogeneous precipitation, impregnation and solution-spraying plasma. The DAl2O3 was 10 to 55 nm in diameter after reduction of NiO to Ni at 973 K. Rodeghiero et al. fabricated Ni particles on Al2O3 powder using Ni(CH3CO2)2·2H2O as a Ni precursor and NiO was reduced to Ni at 1273 K. Due to the high reduction temperature, the DAl2O3 increased to about 1 μm. Dry processes, such as mechanical alloying and CVD, have also been employed. Li et al. synthesized Ni/Al2O3 powder via mechanical alloying of a mixture of Al and NiO raw powder. The DAl2O3 prepared by mechanical alloying was about 20 nm in diameter. However, a part of the Ni particles formed a solid solution with Fe contamination from the container and balls. The (Ni,Fe) alloy particles were about 250 nm in diameter and increased to around 1.5 μm after heat treatment at 1673 K. In the case of the fluidized bed CVD (FBCVD), Ni particles have been precipitated on coarse Al2O3 powder about 250 μm in diameter. Fine powder less than 40 μm in diameter is difficult to prepare by the FBCVD process due to powder agglomeration and difficulty in fluidization. In the present study, RCVD was employed to precipitate Ni nanoparticles on Al2O3 and the DAl2O3 was 8 nm at DAl2O3 = 80 nm. This size of Ni particles was lower than that reported in the literature.

Figure 5 summarizes the effect of DAl2O3 on the diameter of Ni nanoparticle (DNi). With decreasing DAl2O3 from 150 μm to 80 nm, the DNi decreased from 62 to 8 nm. The Ni nanoparticles on Al2O3 powder by rotary CVD also originated from nucleation and grain growth, which are typical steps of common CVD processes. When the powder size of Al2O3 is large, the specific surface area of Al2O3 will be small correspondingly. Thus Ni will grow from the former-precipitated Ni and the grain size of Ni will become large. Contrarily, when the powder size of Al2O3 is small, the specific surface area of Al2O3 is large. The possibility for the growth of Ni nanoparticles from the precipitated Ni will become low and the grain size of Ni will become small. Therefore, the size of Al2O3 will affect the Ni precipitation behavior naturally.

Table 2 shows the selectivity of CO, CO2 and CH4 using the Ni/Al2O3 powder. With decreasing DAl2O3 from 53 μm to 80 nm, the CO selectivity increased from 91.9% to 98.4%. In the methanol-steam reforming system, the possible reactions are shown by the following Eqs. (1) to (4). In the present study, CO selectivity was higher than 90%, indicating that H2 formed mainly from Eq. (1). The small amount of CO2 indicated that water might have participated in the reactions as shown in Eqs. (2) and (3). Although a trace of CH4 was detected at DAl2O3 = 80 nm, the reaction of Eq. (4) was minimal.

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\begin{align*}
\text{CH}_3\text{OH} & \rightarrow 2\text{H}_2 + \text{CO} \\
\text{CO} + \text{H}_2\text{O} & \rightarrow 2\text{H}_2 + \text{CO}_2 \\
\text{CH}_3\text{OH} + \text{H}_2\text{O} & \rightarrow 3\text{H}_2 + \text{CO}_2 \\
3\text{H}_2 + \text{CO} & \rightarrow \text{CH}_4 + \text{H}_2\text{O}
\end{align*}
\]

Figure 6 shows the H2 production rate (R_{H2}) at 513 to 633 K and the specific surface area \(S_w\) of the Ni/Al2O3 powder as a function of DAl2O3. The \(S_w\) was 0.02 m² g⁻¹ at DAl2O3 = 53 μm. With decreasing DAl2O3 from 200 to 80 nm, the \(S_w\) of the Ni/Al2O3 increased from 9.6 to 21.4 m² g⁻¹. At 633 K, \(R_{H2}\) was 10 × 10⁻² mol kg⁻¹ s⁻¹ at DAl2O3 = 53 μm and increased to
The $R_{H_2}$ increased to $709 \times 10^{-3} \text{mol kg}^{-1} \text{s}^{-1}$ at $D_{\text{Al}_2\text{O}_3} = 80 \text{ nm}$, implying that the catalytic properties significantly increased at a nanometer size level.\(^{10}\) Figure 7 shows a comparison of the $R_{H_2}$ of Ni/Al$_2$O$_3$ in the present study with that of Ni-containing catalysts reported in the literature as a function of reaction temperature. The $R_{H_2}$ in the present study was much higher than those of most of the Ni-containing catalysts. The $R_{H_2}$ has been reported to be $56.2$ to $200 \times 10^{-3} \text{mol kg}^{-1} \text{s}^{-1}$ using Raney Ni, Ni$_3$Al,\(^{12}\) layered (Ni, Al) catalysts,\(^{13}\) layered (Ni, Al) promoted by Ga(Na),\(^{14}\) and NiSn/MgO–Al$_2$O$_3$ catalysts.\(^{15}\) The $R_{H_2}$ in the present study using the Ni/Al$_2$O$_3$ was $709 \times 10^{-3} \text{mol kg}^{-1} \text{s}^{-1}$ at $D_{\text{Al}_2\text{O}_3} = 80$ nm.

Table 1. A list of the previous investigations on Ni/Al$_2$O$_3$ powders

| Fabrication method          | $D_{\text{Al}_2\text{O}_3}$ (μm) | $D_{\text{Ni}}$ (nm) | Ni precursors | Temperature (K) | Reference |
|-----------------------------|----------------------------------|----------------------|---------------|-----------------|-----------|
| Rotary CVD                 | 0.08                              | 8                    | NiCp$_2$      | 823             | Present study |
| Heterogeneous precipitation method followed by hydrogen reduction | 0.35                              | 10–55               | Ni(NO$_3$)$_2$·6H$_2$O | Reduction: 973 K | 2)        |
| Impregnation followed by hydrogen reduction | Spheres of 3 μm with pores of 4.5 nm | <2 nm               | Ni(NO$_3$)$_2$·H$_2$O | Impregnation: 353 K | 3)        |
| Solution-spraying plasma followed by hydrogen reduction | Hollow balls, <3 μm | ~10 nm               | Nickel nitrate | Reduction: 973 K | 4)        |
| Sol-gel followed by hydrogen reduction | N/A                               | ~1 μm               | Ni(CHO$_2$)$_2$·2H$_2$O | Sol-gel: 333 K | 5)        |
| Electroless deposition followed by heat treatment | 17–74 μm | ~1 μm (amorphous Ni-P) | NiCl$_2$·6H$_2$O | Reduction: 1273 K | 6)        |
| Ball milling followed by heat treatment | 1–3 μm                            | ~20 nm              | NiO and Al powder | Heat treatment: 1673 K | 7)        |
| FBCVD                       | 250 μm                            | N/A                 | NiCl$_2$      | Preheated at 523 K | 8)        |

Fig. 4. FESEM images of Ni nanoparticles precipitated on Al$_2$O$_3$ powders at $D_{\text{Al}_2\text{O}_3} = 10$ (a, b), 53 (c, d) and 150 μm (e, f).
 nm and 633 K, about three times as great as the reported value ($256 \times 10^{-3}$ mol kg$^{-1}$ s$^{-1}$) for the Ni$_3$Al catalysts at about 627 K$^{12}$. The specific surface area of Ni/Al$_2$O$_3$ (8 nm, 80 nm) is only 21.4 m$^2$ g$^{-1}$, lower than that of other catalyst, e.g., NiSn/MgO–Al$_2$O$_3$ catalysts (52–138 m$^2$ g$^{-1}$), indicating that the high catalytic activity of Ni/Al$_2$O$_3$ does not arise from the specific surface area. Thus, the nanosized effect of Ni nanoparticle is the possible reason because when metal atoms are in a nanoscale space, large fractions of metal electrons will be located on the surface and accelerate the catalytic process.

4. Conclusions

Ni nano-particles 8 to 62 nm in diameter were uniformly precipitated on Al$_2$O$_3$ support powders ranging from 80 nm to 150 μm in diameter. With the increase of Al$_2$O$_3$ powder size, the average size of the precipitated Ni nanoparticles increased from 8 to 62 nm, while the content decreased from 6.6 to 2.4 mass %. The Ni/Al$_2$O$_3$ showed high catalytic activity for H$_2$ formation from CH$_3$OH and H$_2$O. The catalytic activities increased with increasing specific surface area and with decreasing diameter of Al$_2$O$_3$ powders. The highest H$_2$ production rate of Ni/Al$_2$O$_3$ was $709 \times 10^{-3}$ mol kg$^{-1}$ s$^{-1}$ at 633 K and $D_{Ni} = 8$ nm and $D_{Al_2O_3} = 80$ nm.

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