Precipitation of Ni nanoparticle on Al_2O_3 powders by novel rotary chemical vapor deposition

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Ni nanoparticles were precipitated on Al_2O_3 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 Al_2O_3 powder diameter ($D_{\text{Al}_2\text{O}_3}$) from 80 nm to 150 μm . The catalytic activity of Ni precipitated Al_2O_3 (Ni/ Al_2O_3) powder was evaluated by the hydrogen production rate (R_{H_2}) in a methanol-steam flow. The R_{H_2} decreased with increasing $D_{\text{Al}_2\text{O}_3}$ and increased with increasing specific surface area of Ni/ Al_2O_3 powder. The highest R_{H_2} of Ni/ Al_2O_3 powder was $709 \times 10^{-3} \text{ mol kg}^{-1} \text{ s}^{-1}$ at 633 K, $D_{\text{Ni}} = 8 \text{ nm}$ and $D_{\text{Al}_2\text{O}_3} = 80 \text{ nm}$.

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1. Introduction

Al_2O_3 powder is a candidate support material for catalysis due to its thermal/chemical inertness, and Ni nanoparticle-precipitated Al_2O_3 powder (hereafter Ni/ Al_2O_3) has been found to exhibit good catalytic properties.¹⁾ Many preparation methods have been used to precipitate Ni nanoparticles on Al_2O_3 powder. They can be classified into two types, i.e., wet and dry processes. Most of the wet processes such as heterogeneous precipitation,²⁾ 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 Al_2O_3 powders 80 nm to 150 μm in diameter. The effect of Al_2O_3 powder diameter ($D_{\text{Al}_2\text{O}_3}$) on the catalytic property of Ni nanoparticles was investigated by a methanol steam reforming reaction.

2. Experimental procedure

Ni nanoparticles were precipitated on Al_2O_3 powder by RCVD using nickelocene (NiCp_2) as a precursor. The details of the RCVD apparatus have been reported elsewhere.⁹⁾ The NiCp_2 precursor was heated at 393 to 423 K and carried with H_2 at a flow rate of $1.67 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$. The supply rate (R_s) of NiCp_2 was fixed at $0.56 \times 10^{-6} \text{ kg s}^{-1}$. Al_2O_3 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/ Al_2O_3 was identified by X-ray

diffraction (XRD; Geigerflex, Rigaku Corp.) with $\text{CuK}\alpha$ 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 (D_{Ni}) was calculated from 50 particles in the TEM and FESEM images. The Ni content (C_{Ni}) in the Ni/ Al_2O_3 powder was examined by energy-dispersive X-ray spectroscopy (EDS). The specific surface area of the Ni/ Al_2O_3 was determined by BET surface area measurement (BEL Japan, Belsopr-mini II).

The catalytic property of Ni nanoparticles on Al_2O_3 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 N_2 and H_2 mixture gas with flow rates of 0.17 and $0.5 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$. The mixture of methanol and water 2 to 3 in molar ratio was introduced into the reactor at a flow rate of $2.7 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$. N_2 gas at a flow rate of $0.5 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ 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 H_2 , CO , CO_2 and CH_4 were measured under a steady state for 1.8 ks.

3. Results and discussion

Figure 1 shows typical XRD patterns of the Ni/ Al_2O_3 powders. The diameters of Al_2O_3 powder were 0.2, 1, 10 and 150 μm . The diffraction peaks of the Ni phase was identified at $2\theta = 44.347^\circ$ (111), 51.673° (200) and 76.095° (220). **Figure 2** shows the effect of $D_{\text{Al}_2\text{O}_3}$ on the Ni content (C_{Ni}). At $D_{\text{Al}_2\text{O}_3} = 80 \text{ nm}$, C_{Ni} was 6.6 mass %. The C_{Ni} decreased with increasing $D_{\text{Al}_2\text{O}_3}$, and at $D_{\text{Al}_2\text{O}_3} = 150 \mu\text{m}$, C_{Ni} was 2.4 mass %.

Figure 3 shows TEM images of Ni nanoparticles precipitated on various Al_2O_3 powders 80 nm to 1 μm in diameter. Ni particles less than 10 nm in diameter were distributed on the Al_2O_3 powder [Fig. 3(a)]. **Figure 4** shows FESEM images of Ni nanoparticle precipitated on Al_2O_3 powder at $D_{\text{Al}_2\text{O}_3} = 10$ (a, b), 53 (c, d) and 150 μm (e, f). **Table 1** shows the average diameter of Ni (D_{Ni})

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Fig. 1. XRD patterns of Ni/Al₂O₃ powder at $D_{\text{Al}_2\text{O}_3}$ = (a) 0.2, (b) 1, (c) 10 and (d) 150 μm .

Fig. 2. Effect of $D_{\text{Al}_2\text{O}_3}$ on C_{Ni} of Ni/Al₂O₃ powder.

and Al₂O₃ ($D_{\text{Al}_2\text{O}_3}$) 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,²⁾ impregnation³⁾ and solution-spraying plasma.⁴⁾ The D_{Ni} was 10 to 55 nm in diameter after reduction of NiO to Ni at 973 K. Rodeghiero et al.⁵⁾ fabricated Ni particles on Al₂O₃ powder using Ni(CHO₂)₂·2H₂O as a Ni precursor and NiO was reduced to Ni at 1273 K. Due to the high reduction temperature, the D_{Ni} 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.⁷⁾ The D_{Ni} 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.⁸⁾ Fine powder less than 40 μm in diameter is difficult to prepare by the FBCVD process due to powder agglomeration and difficulty

Fig. 3. TEM images of Ni nanoparticles precipitated on Al₂O₃ powders at $D_{\text{Al}_2\text{O}_3}$ = (a) 0.08, (b) 0.2, (c) and (d) 1 μm .

in fluidization.^{10),11)} In the present study, RCVD was employed to precipitate Ni nanoparticles on Al₂O₃ and the D_{Ni} was 8 nm at $D_{\text{Al}_2\text{O}_3}$ = 80 nm. This size of Ni particles was lower than that reported in the literature.

Figure 5 summarizes the effect of $D_{\text{Al}_2\text{O}_3}$ on the diameter of Ni nanoparticle (D_{Ni}). With decreasing $D_{\text{Al}_2\text{O}_3}$ from 150 μm to 80 nm, the D_{Ni} decreased from 62 to 8 nm. The Ni nanoparticle 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 $D_{\text{Al}_2\text{O}_3}$ 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 $D_{\text{Al}_2\text{O}_3}$ = 80 nm, the reaction of Eq. (4) was minimal.

Figure 6 shows the H₂ production rate (R_{H_2}) at 513 to 633 K and the specific surface area (S_w) of the Ni/Al₂O₃ powder as a function of $D_{\text{Al}_2\text{O}_3}$. The S_w was 0.02 m² g⁻¹ at $D_{\text{Al}_2\text{O}_3}$ = 53 μm . With decreasing $D_{\text{Al}_2\text{O}_3}$ 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_{H_2} was 10×10^{-3} mol kg⁻¹ s⁻¹ at $D_{\text{Al}_2\text{O}_3}$ = 53 μm and increased to

Fig. 4. FESEM images of Ni nanoparticles precipitated on Al₂O₃ powders at $D_{\text{Al}_2\text{O}_3} = 10$ (a, b), 53 (c, d) and 150 μm (e, f).

Table 1. A list of the previous investigations on Ni/Al₂O₃ powders

Fabrication method	$D_{\text{Al}_2\text{O}_3}$	D_{Ni}	Ni precursors	Temperature	Reference
Rotary CVD	0.08 μm	8 nm	NiCp ₂	823 K	Present study
Heterogeneous precipitation method followed by hydrogen reduction	0.35 μm	10–55 nm	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	<20 nm	Ni(NO ₃) ₂ ·6H ₂ O	Impregnation: 353 K Reduction: 973 K	3)
Solution-spraying plasma followed by hydrogen reduction ⁴⁾	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 Reduction: 1273 K	5)
Electroless deposition followed by heat treatment	17–74 μm	~1 μm (amorphous Ni-P)	NiCl ₂ ·6H ₂ O	358–363 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 Precipitated at 773–1073 K	8)

$34 \times 10^{-3} \text{ mol kg}^{-1} \text{ s}^{-1}$ at $D_{\text{Al}_2\text{O}_3} = 200 \text{ nm}$. 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/Al₂O₃ 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, Ni₃Al,¹²⁾ layered (Ni, Al) catalysts,¹³⁾ layered (Ni, Al) promoted by Ga(Na)¹⁴⁾ and NiSn/MgO–Al₂O₃ catalysts.¹⁵⁾ The R_{H_2} in the present study using the Ni/Al₂O₃ was $709 \times 10^{-3} \text{ mol kg}^{-1} \text{ s}^{-1}$ at $D_{\text{Al}_2\text{O}_3} = 80$

Fig. 5. Effect of $D_{\text{Al}_2\text{O}_3}$ on D_{Ni} of Ni/ Al_2O_3 powder.Table 2. Selectivity of CO, CO₂ and CH₄ in methanol-steam reforming using Ni/ Al_2O_3 catalyst at 633 K

$D_{\text{Al}_2\text{O}_3} / \mu\text{m}$	$D_{\text{Ni}} / \text{nm}$	Selectivity/%		
		CO	CO ₂	CH ₄
0.08	8	98.4	1.2	0.4
1	19	94.5	5.5	—
53	48	91.9	8.1	—

Fig. 6. (Color online) Effect of $D_{\text{Al}_2\text{O}_3}$ on S_w and R_{H_2} of Ni/ Al_2O_3 catalysts.

nm and 633 K, about three times as great as the reported value ($256 \times 10^{-3} \text{ mol kg}^{-1} \text{ s}^{-1}$ for the Ni₃Al catalysts at about 627 K¹²). The specific surface area of Ni/ Al_2O_3 (8 nm, 80 nm) is only $21.4 \text{ m}^2 \text{ g}^{-1}$, lower than that of other catalyst, e.g., NiSn/MgO- Al_2O_3 ($52\text{--}138 \text{ m}^2 \text{ g}^{-1}$), indicating that the high catalytic activity of Ni/ Al_2O_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_2O_3 support powders ranging from 80 nm to $150 \mu\text{m}$ in diameter. With the increase of Al_2O_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_2O_3 showed high catalytic activity for H_2 formation from CH_3OH and H_2O . The catalytic activities increased with

Fig. 7. (Color online) Temperature dependence of R_{H_2} in the present study compared with that of Ni-containing catalysts.

increasing specific surface area and with decreasing diameter of Al_2O_3 powders. The highest H_2 production rate of Ni/ Al_2O_3 was $709 \times 10^{-3} \text{ mol kg}^{-1} \text{ s}^{-1}$ at 633 K and $D_{\text{Ni}} = 8 \text{ nm}$ and $D_{\text{Al}_2\text{O}_3} = 80 \text{ nm}$.

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