Precipitation of Ni and NiO nanoparticle catalysts on zeolite and mesoporous silica by rotary chemical vapor deposition

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Ni and NiO catalytic nanoparticles were precipitated onto mesoporous silica and zeolite by rotary chemical vapor deposition (RCVD) using NiCp2 as a precursor. The diameter of the nanoparticles precipitated onto zeolite increased from 5 to 50 nm when the oxygen flow rate (R_o2) increased from 0 to 0.33 × 10⁻⁶ m³ s⁻¹, whereas that of the nanoparticles precipitated onto mesoporous silica was 5 nm, independent of R_o2. The nanoparticles could be precipitated inside of the mesoporous silica pores but outside the zeolite pores. The highest H₂ production rate in the methanol–steam reforming reaction was 1150 × 10⁻³ mol kg⁻¹ s⁻¹ at 633 K, which was achieved with a Ni/NiO catalyst on mesoporous silica, and this H₂ production rate is almost six times greater than that of the best Ni catalysts reported in literature.

Key-words : Ni/NiO nanoparticle, Rotary chemical vapor deposition, Zeolite, Mesoporous silica

1. Introduction

Because of recent demands triggered by a global energy deficiency and more severe emission regulations, hydrogen needs to be produced by highly active and economical catalysts, e.g., Ni and Ni₃Al, through catalytic reactions such as methanol steam reforming.¹⁻⁴ To improve the performance of such catalysts, Ni or Au catalysts have been adsorbed onto high-specific-surface-area supports, e.g., mesoporous silica, and zeolite.⁵⁻⁶ In particular, mesoporous silica and zeolite with nanoscaled catalysts have attracted considerable attention.⁶⁻⁸ However, only a few studies have reported the precipitation of nanoparticle catalysts into the channels of mesoporous supports.

The most widely used methods for the preparation of these catalysts include sol–gel and incipient wetness impregnation processes.⁹⁻¹¹ The main drawbacks of these methods are the difficulties in controlling the particle size and surface morphology as well as the weak binding force between the catalysts and supports.¹² Because the nanoparticles are usually physically adsorbed onto the support surface, they tend to agglomerate during the catalytic reaction at high temperatures, which results in a decrease in the specific surface area and in the catalytic activity. In contrast, chemical vapor deposition (CVD) is a useful method for dispersing nanoparticle catalysts on powder supports.¹³ In the CVD process, the nanoparticles are formed by the nucleation of precursor gases, which leads to high dispersion and strong bonding of the nanoparticles to the support surface by chemical reaction. The catalytic nanoparticles may exhibit high thermal stability because they are prepared at high temperatures close to that of the catalytic reaction. Fluidized-bed CVD (FBVD) is a common method for the deposition of nanoparticles on floating powders, which ensures reactive gas–powder contact.¹⁴⁻¹⁶ However, the powder size used in FBVD is limited to the range of 40–500 μm.¹⁷

We have developed rotary CVD (RCVD) to precipitate nanoparticles onto powder in a rotating CVD chamber. The powder is floated in the CVD chamber, into which reactive gases are introduced; this method thereby allows sufficient contact between the powder and reactant gases. The advantages of RCVD include a uniform temperature distribution and the flexibility to use powders with different sizes and densities.¹⁸⁻¹⁹

In the present study, Ni and NiO nanoparticles were precipitated onto mesoporous silica and zeolite powders by RCVD. The effect of CVD parameters on the morphology, specific surface area, deposition features, and catalytic activities of the nanoparticles were investigated.

2. Experimental procedure

Ni and NiO nanoparticles were precipitated onto zeolite (HS-320, CAS No. 308081-00-7, Wako, Japan; 0.8 nm in pore size, Y-type) and mesoporous silica (MSU-H, CAS No. 7631-86-9, Sigma-Aldrich, USA; 7.1 nm in pore size) powders by RCVD using nickelocene [Ni(C₅H₅)₂; NiCp₂, CAS No. 1271-28-9, Wako, Japan] as a precursor. The details of the RCVD apparatus have been reported elsewhere.¹⁹ The NiCp₂ precursor was heated at 393–423 K and was carried into the reactor by Ar at a flow rate of 1.67 × 10⁻⁶ m³ s⁻¹. Oxygen at a flow rate (R_o2) of 0 to 0.83 × 10⁻⁶ m³ s⁻¹ was supplied to eliminate the carbon impurity that originated from the decomposition of C₅H₅ moieties in NiCp₂. The supply rate (R_c) of NiCp₂ was fixed at 0.56 × 10⁻⁶ kg s⁻¹. The total pressure of the RCVD apparatus was maintained at 800 Pa, and the deposition time was fixed at 1.8 ks.

The crystal structure was investigated by low angle X-ray diffraction (LAXRD, Rigaku, SmartLab, Cu Kα, 2θ = 0 to 5°) and wide angle X-ray diffraction (XRD, Rigaku, RAD-C, 2θ = 10 to 70°). The microstructure was observed by field-emission scanning electron microscopy (FESEM, JEOL, JSM-7500F, Japan) and transmission electron microscopy (TEM, JEOL: JEM-2000EX, Japan). The Ni content (C_Ni) was examined by energy-dispersive X-ray spectroscopy (EDS). The specific surface area was calculated from the BET Eq. (1):²⁰

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where $P$ and $P_0$ are the equilibrium and saturation pressure, respectively, of adsorbates at the temperature of adsorption; $V$ is the volume of the adsorbed gas; $V_m$ is the quantity of monolayer-adsorbed gas; and $C$ is the BET constant. The BET specific surface area ($a_{\text{BET}}$) can be calculated from the following equation:

$$a_{\text{BET}} = \frac{V_m L a_m}{V_L}$$

where $a_m$ is the area occupied by a molecule of the adsorbate, $L$ is Avogadro’s number, and $V_L$ is the molar volume of the analysis gas at standard temperature and pressure (STP).

The catalytic properties were investigated by methanol–steam reforming (MSR) in a conventional flow catalytic reactor at 100 kPa. All specimens were pretreated at 673 K for 1 h in a mixture of N$_2$ and H$_2$ gases at flow rates of $0.17 \times 10^{-6}$ and $0.5 \times 10^{-6}$ m$^3$s$^{-1}$, respectively. The mixture of methanol and water in a 2:3 molar ratio was introduced into the reactor at a flow rate of $2.7 \times 10^{-6}$ m$^3$s$^{-1}$. Nitrogen gas at a flow rate of $0.5 \times 10^{-6}$ m$^3$s$^{-1}$ was used as a diluent. The gases produced by the MSR reaction were analyzed by an online gas chromatograph–mass spectrometer (Shimadzu GC-14A) equipped with a ShinCarbon column; Ar was used as the carrier gas. The MSR reaction was performed at 513–633 K. The H$_2$ concentration was measured under a steady state for 1.8 ks. The H$_2$ production rate can be calculated from Eq. (3):

$$R_{\text{H}_2} = \frac{n_{\text{H}_2}}{m_{\text{cat}}}$$

where $n_{\text{H}_2}$ is the molar flow rate of H$_2$ produced by the MSR reaction, and $m_{\text{cat}}$ is the weight of the catalyst used.

**3. Results and discussion**

**Figure 1(a)** shows the XRD patterns of the Ni- and NiO-precipitated zeolites prepared at oxygen flow rates of 0 to 0.33 × 10$^{-6}$ m$^3$s$^{-1}$. Only Ni peaks were identified in the pattern of the sample prepared at $R_{\text{O}_2} = 0$, while both Ni and NiO peaks were observed in the patterns of the sample prepared at $R_{\text{O}_2} = 0.08 \times 10^{-6}$ m$^3$s$^{-1}$. Only NiO peaks were identified in the pattern of the sample prepared at $R_{\text{O}_2} = 0.33 \times 10^{-6}$ m$^3$s$^{-1}$, which indicates that Ni was oxidized by oxygen gas.

**Figure 1(b)** shows the XRD patterns of the Ni-precipitated mesoporous silica prepared under oxygen flow rates of 0 to 0.83 × 10$^{-6}$ m$^3$s$^{-1}$. Only Ni peaks were observed in the pattern of the sample prepared at $R_{\text{O}_2} = 0$; both Ni and NiO peaks were observed in the pattern of the sample prepared at $R_{\text{O}_2} = 0.17 \times 10^{-6}$ m$^3$s$^{-1}$. Only NiO peaks were identified in the pattern of the sample prepared at $R_{\text{O}_2} = 0.34$ to 0.83 × 10$^{-6}$ m$^3$s$^{-1}$.

**Figure 2** shows the TEM images of the zeolite (a, b) and the Ni and NiO nanoparticle precipitated zeolite powders at $R_{\text{O}_2} = 0$ (c), 0.08 × 10$^{-6}$ m$^3$s$^{-1}$ (d), 0.17 × 10$^{-6}$ m$^3$s$^{-1}$ (e) and 0.33 × 10$^{-6}$ m$^3$s$^{-1}$ (f).
Nanoparticles approximately 5 nm in diameter were uniformly distributed on the mesoporous silica in the sample prepared at $R_{O2} = 0$. The nanoparticles maintained almost the same diameter as $R_{O2}$ was increased to 0.83 $\times$ $10^{-6}$ m$^3$/s$^1$. The increased oxygen flow significantly promoted the grain growth of nanoparticles on the zeolite, whereas almost no effect of oxygen was observed in case of the mesoporous silica powder. The pore size of the zeolite was 0.8 nm, whereas the grain size of the Ni nanoparticles was approximately a few nanometers. Therefore, the Ni and NiO nanoparticles could not be impregnated inside the zeolite powder, and Ni and NiO nanoparticles grew on the powder’s outside surface. However, the average pore size of the mesoporous silica was 7.1 nm. The Ni precursor gas can easily access the interior of the pores, whereas the Ni nanoparticles could not grow in the pore to a size greater than the pore size.

Figure 4 shows the LAXRD patterns of mesoporous silica (a) and Ni and NiO nanoparticle precipitated mesoporous silica at $R_{O2} = 0$ (b) and 0.33 $\times$ $10^{-6}$ m$^3$/s$^1$ (c). The Ni nanoparticles caused the significant decrease in (100) peak, indicating that a long-range structure was diminished due to Ni nanoparticles in the pore channel. The (100) peak shifted from $2\theta = 0.94$ to 0.88° and the $d_{100}$ increased from about 94 to 100 nm. This implies that the framework of mesoporous silica expanded by the precipitated Ni nanoparticles inside the pore channel.

Figure 5 shows the BET plots for zeolite (a) and mesoporous silica (b). The specific surface areas of the zeolite and mesoporous silica were 322 and 702 m$^2$/g, respectively. After the precipitation of the nanoparticles, the specific surface area ($a_{BET}$) of the zeolite and mesoporous silica decreased. The $a_{BET}$ of the Ni-precipitated zeolite prepared at $R_{O2} = 0.33$ $\times$ $10^{-6}$ m$^3$/s$^1$ was 209 m$^2$/g, which is approximately 20% lower than that of the sample prepared at $R_{O2} = 0$. In contrast, the $a_{BET}$ of the Ni-precipitated mesoporous silica prepared at $R_{O2} = 0.33$ $\times$ $10^{-6}$ m$^3$/s$^1$ was 369 m$^2$/g, which is only approximately 6% lower than that of the sample prepared at $R_{O2} = 0$. The Ni and NiO nanoparticles may have precipitated on the zeolite surface, and the pores on the zeolite surface would have decreased as the grain size of the nanoparticles increased. However, the nanoparticles showed no grain growth in the mesoporous silica, and no decrease in $a_{BET}$ was observed as $R_{O2}$ was increased.

Figure 6 shows the hydrogen production rate ($R_{H2}$) of the zeolite catalysts prepared at $R_{O2} = 0$ and 0.33 $\times$ $10^{-6}$ m$^3$/s$^1$ and the mesoporous silica catalysts prepared at $R_{O2} = 0$ and 0.33 $\times$ $10^{-6}$ m$^3$/s$^1$.
\(10^{-6} \text{m}^3 \text{s}^{-1}\). The \(R_{H2}\) of Ni-containing catalysts reported in the literature are included for comparison. The \(R_{H2}\) at 633 K for the mesoporous silica catalysts prepared at \(R_{O2} = 0\) and \(0.33 \times 10^{-6} \text{m}^3 \text{s}^{-1}\) was \(1150 \times 10^{-3} \text{mol kg}^{-1} \text{s}^{-1}\). The \(R_{H2}\) of the zeolite catalyst prepared at \(R_{O2} = 0.33 \times 10^{-6} \text{m}^3 \text{s}^{-1}\) was \(254 \text{mol kg}^{-1} \text{s}^{-1}\), which is approximately 20\% lower than that of the catalyst prepared at \(R_{O2} = 0\). This result implies that Ni and NiO nanoparticles both exhibit high catalytic activity, which is mainly determined by the size of the nanoparticles. The \(R_{H2}\) values in the cases of Ni-Sn/MgO-Al\(_2\)O\(_3\) catalysts\(^{11}\) and layered (Ni,Al) catalysts\(^{21}\) have been reported to be \(56.2 \times 10^{-1}\) to \(200 \times 10^{-3} \text{mol kg}^{-1} \text{s}^{-1}\). The highest \(R_{H2}\) achieved in the present study with the mesoporous silica was \(1150 \times 10^{-3} \text{mol kg}^{-1} \text{s}^{-1}\), which is approximately six times greater than that of the layered (Ni,Al) catalysts.

4. Conclusions

Ni and NiO nanoparticles were precipitated onto zeolite and mesoporous silica by RCVD using NiCp\(_2\) as a precursor. The diameter of the nanoparticles precipitated onto zeolite increased from 5 to 50 nm when \(R_{O2}\) was increased from 0 to \(0.33 \times 10^{-6} \text{m}^3 \text{s}^{-1}\), whereas that of the nanoparticles precipitated on mesoporous silica remained 5 nm when \(R_{O2}\) was increased from 0 to \(0.83 \times 10^{-4} \text{m}^3 \text{s}^{-1}\). The Ni and NiO nanoparticles were precipitated on the zeolite surface, whereas they could be precipitated inside the pores of mesoporous silica. The highest \(H_2\) production rate was \(1150 \times 10^{-3} \text{mol kg}^{-1} \text{s}^{-1}\) at 633 K by Ni- and NiO-nanoparticle-precipitated mesoporous silica.

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