1. Introduction

Hydrogen can be produced using renewable energy (e.g., biomass and solar energy) so is considered to be a future energy carrier and feedstock for CO2 hydrogenation. However, storage of H2 is challenging because of its flammability. Methanation is a potentially promising approach for converting H2 and CO2 to CH4, which is less flammable than H2. During the reduction, the growth of Ni particles was hindered by CeO2 particles. Consequently, the Ni size was relatively small (20 nm) despite the extremely high Ni content (80 wt%), as observed by scanning transmission electron microscopy. In contrast, incorporation of Ni using nickel acetate tetrahydrate into the CeO2 support resulted in formation of inhomogeneous Ni particles (20-100 nm) after H2 reduction. H2 chemisorption measurement showed the surface area of Ni particles in the former catalyst was 13.7 m2 g−1, which was 2.4 times larger than that in the latter catalyst. The former catalyst exhibited remarkable performance for CO2 methanation (47% CO2 conversion at 250 °C), 2 times higher than in the latter catalyst.

Keywords
Flame spray pyrolysis, Methanation, Carbon dioxide, Nickel catalyst, Nickel support, Ceria

NiO and CeO2 were prepared via flame spray pyrolysis. The specific surface area and total pore volume were 251 m2 g−1 and 2.3 cm3 g−1 for NiO and 338 m2 g−1 and 3.3 cm3 g−1 for CeO2, respectively. The high porosity and surface area of the NiO allowed deposition of small CeO2 particles (~5 nm) by the impregnation of cerium acetate monohydrate. The particles were reduced using 5% H2 at 500 °C for 1 h which converted NiO to metallic Ni. During the reduction, the growth of Ni particles was hindered by CeO2 particles. Consequently, the Ni size was relatively small (~20 nm) despite the extremely high Ni content (80 wt%), as observed by scanning transmission electron microscopy. In contrast, incorporation of Ni using nickel acetate tetrahydrate into the CeO2 support resulted in formation of inhomogeneous Ni particles (20-100 nm) after H2 reduction. H2 chemisorption measurement showed the surface area of Ni particles in the former catalyst was 13.7 m2 g−1, which was 2.4 times larger than that in the latter catalyst. The former catalyst exhibited remarkable performance for CO2 methanation (47% CO2 conversion at 250 °C), 2 times higher than in the latter catalyst.

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Higher Ni loading is a straightforward strategy for increasing the Ni surface area and Ni-CeO2 interface. However, the optimal loading is essential, because excessive loading induces the growth of Ni particles. The upper limit for Ni loading is 15-30 wt% for CO2 methanation via Ni supported on TiO2 and Ce0.5Zr0.5O2. Recently, Ni-Al hydrotalcite usually exhibit superior performance compared to Ni7,14–16 and Co17 catalysts. However, noble metal catalysts are expensive, so we sought to improve the catalytic performance of Ni and Co catalysts. Catalyst support is extremely important in the catalytic activity and selectivity. Ni catalysts with CeO2 supports are more suitable than those using other metal oxide supports, such as Al2O3, TiO2, SiO2, and MnO2, because of the moderate CO2 adsorption and high reducibility, which are favorable for CO2 activation. Furthermore, CeO2 strongly interacts with Ni, which promotes the dispersion of metallic Ni and increases thermal stability. CO2 methanation via Ni/Al2O3 requires high Ni surface area and high Ni dispersion on CeO2, because the Ni surface is the active site for H2 activation and the activated H2 reacts with CO2 near the Ni-CeO2 interface.

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(78 wt% of Ni) and commercial sponge Ni26) (Ni > 92.5 wt%, Al > 6.5 wt% with impurities) were proposed as more active compared to 20-78 wt% Ni/Al2O325) and Ni/CeO226) catalysts prepared through conventional impregnation. In these catalysts, Al is the second compound, as the Al acts as a dopant or Al2O3 as support, but Al2O3 is not the best-suited catalyst for CO2 methanation. Indeed, Ni/Al2O321), Ni-Al hydrottalcite25), and sponge Ni26) suffer from minor formation of CO by-product (₂ 2 %). Moreover, approximately 50 wt% of small Ni particles were deposited on CeO2 via La2O3 doping27) and formation of a mesoporous structure using an SiO2 template28). In this study, CeO2 was deposited on metallic Ni nanoparticles through a simple impregnation method using a porous nano-NiO. The nano-NiO was prepared by flame spray pyrolysis (FSP)29), which can be scaled up to commercial production rates of kg h–1. FSP-fabricated particles have a fractal structure31) and agglomeration of these fractal-like particles form a porous structure, as observed in several metal oxides (TiO232), SnO233), and CeCe₃(ZrO2)241,30)). Moreover, FSP enables the formation of small particles (<10 nm) and less thermally stable materials (e.g., CuO26)). This type of structure and size is beneficial for support materials.

The porosity and specific surface area of the catalysts were evaluated using N2 adsorption-desorption isotherms at 77 K. The CO2 methanation activity of the catalysts, pre-reduced in 5 % H2 at 500 °C, was evaluated in a fixed bed reactor. The characteristics of the catalysts before and after H2 reduction, were investigated with X-ray diffraction (XRD), electron microscopy, H2 pulse titration, and temperature-programmed reduction by H2.

2. Experimental

2.1. Preparation of Metal Oxide Supports

Metal oxide supports (CeO2 and NiO) were produced using an FSP reactor29). Cerium(III) 2-ethylhexanoate, 49 % in 2-ethylhexanoic acid (Alfa Aesar, Ce: 12 %) and nickel(II) acetate tetrahydrate (FUJIFILM Wako Pure Chemical Corp., purity > 98.0 %) as the precursors of CeO2 and NiO, respectively, were added to a mixture (1 : 1 in volume) of 2-ethylhexanoic acid (Sigma-Aldrich, purity > 99 %) and methanol (FUJIFILM Wako Pure Chemical Corp., Guaranteed Reagent Grade), to obtain a Ni or Ce concentration of 0.2 M.

As illustrated in Fig. 1, the prepared precursor solution was fed to the two-fluid spray nozzle at 3 mL min–1, and dispersed into a fine spray by 5 LSTP min–1 of O2 dispersant (technical grade). The spray was evaporated and combusted by a premixed CH4/O2 pilot flame (1.5 LSTP min–1/3.2 LSTP min–1) to form particles. The particles were collected on a glass-fiber filter (Albet LabScience, GF6, 257 mm in diameter) that was located 65 cm above the FSP nozzle using a vacuum pump (Busch Seco SV1040C).

2.2. Deposition of Ni on CeO2 and CeO2 on NiO

Ni was impregnated into CeO2 prepared via FSP, to form the composition NiCe-x (where x is the nominal mass fraction of Ni). Subsequently, 1 g of FSP-fabricated CeO2 was dispersed in 50 mL of DI-water through sonication for 5 min, and stirred using a magnetic stirrer for 2.5 h. The suspension was then mixed with DI-water, containing an appropriate amount of nickel(II) acetate tetrahydrate (FUJIFILM Wako Pure Chemical Corp., purity > 98.0 %), using magnetic stirrer for 20 h. The mixture was dried at 60 °C for 2 h under continuous evacuation (0.08-0.085 bar) using a rotary evaporator. The dried powder was collected and calcined in air at 450 °C for 3 h, and the calcined powder was gently ground in a mortar.

CeO2 was then impregnated into NiO prepared via FSP, to form the composition CeNi-x (where x is the nominal mass fraction of Ni). The preparation procedure was the same as that for NiCe-x, with 0.5 g of FSP-fabricated NiO and cerium(III) acetate monohydrate (FUJIFILM Wako Pure Chemical Corp., purity > 90.0 %) used as the support and precursor of Ce, respectively, for the impregnation.

If required, NiCe-x and CeNi-x were reduced at 500 °C in 5 % H2-Ar (100 mL min–1) for 1 h. The reduced powder was cooled to room temperature in Ar (100 mL min–1), then the surface of only the metallic Ni was oxidized by 1 % O2-4 % N2-Ar (100 mL min–1), thus avoiding complete oxidation of Ni.
2.3 Evaluation of Catalytic Performance for CO2 Methanation

Catalytic activity was evaluated using a fixed bed tubular reactor. The catalyst (100 mg) and SiC powder (FUJIFILM Wako Pure Chemical Corp., 400 mg) were mixed in a mortar, and filled into a quartz tube (inner/outer diameters of Φ6 mm/Φ8 mm). The catalyst was reduced at 500 °C for 1 h in 5 % H2-Ar (100 mL/min), and cooled to 25 °C. Subsequently, the reactant gas (CO2/H2/N2 = 1/4/1) was fed to the catalyst at 60 mL/min. The temperature of the catalyst bed was measured using a K-type thermocouple (Φ1 mm). The temperature ramping rates below and above 250 °C was measured using a K-type thermocouple (Φ1 mm). CO2 hydrogenation was CH4 and CO was not detected under any conditions examined in this study. Thus, CO2 conversion was evaluated by Eq. (1),

\[
\text{CO2 conversion [%]} = 100 \times \frac{(C_{\text{CO2,in}} - C_{\text{CO2,out}})}{C_{\text{CO2,in}}} \tag{1}
\]

Prior to the measurement, the sample was heated at 300 °C for 1 h, and cooled to 45 °C under an Ar flow. The sample was heated from 45 to 700 °C at a ramping rate of 5 °C min⁻¹ in a 5 % H2-Ar flow (100 mL min⁻¹). The product gas was introduced into a molecular sieve trap (Shinwa Chemical Industries Ltd., 3A), and then to the TCD. To calculate the H2 consumption from the sample, commercial CuO powder (FUJIFILM Wako Pure Chemical Corp., purity > 99.9 %) was used as the reference material.

2.4 Particle Characterization

2.4.1 Powder X-ray Diffraction (PXRD)

PXRD patterns of the catalysts were obtained using a diffractometer (Rigaku Ultima IV, Cu Kα, 40 kV, 40 mA). Crystallite size was calculated using Scherrer’s equation, as follows.

\[
\text{Crystallite size [nm]} = \frac{K \lambda}{\beta \cos \theta} \tag{2}
\]

where K (0.89) is the shape factor, λ (0.154 nm) is the X-ray wavelength, β is the line broadening at half the maximum intensity in radians, and θ is the Bragg angle.

2.4.2 X-ray Fluorescence (XRF) Analysis

Ni content of the samples was measured using an energy-dispersive XRF meter (Rigaku EDXL 300).

2.4.3 N2 Adsorption

Specific surface area (SSA) was determined from the amount of adsorbed N2 on the particle surface at 77 K using the Brunauer-Emmett-Teller (BET) method. Additionally, the pore volume and size were calculated using the Barrett-Joyner-Halenda (BJH) method. N2 adsorption of the powders was measured using a BELSORP-mini II (MicrotracBEL Corp.). Prior to the measurement, the samples were degassed at 150 °C under a vacuum at 1 Pa for 1 h.

2.4.4 Temperature-programmed Reduction by H2 (H2-TPR)

Reducibility of the samples was evaluated via H2-TPR using a BELCAT II (MicrotracBEL Corp.) using a sample of approximately 20 mg placed in a quartz tube. The temperature ramping rates below and above 250 °C was measured using a K-type thermocouple (Φ1 mm). The composition of the product gas was measured using an online gas chromatograph (Shimadzu Corp., GC-2014) equipped with a thermal conductivity detector (TCD) with an He carrier (for N2, CO, CO2, and CH4). The major product of CH4 and CO was not detected under any conditions examined in this study. Thus, CO2 conversion was evaluated by Eq. (1), assuming that every Ni atom on the catalyst surface adsorbs one hydrogen atom.

\[
\text{SSA [m2 gcat⁻¹]} = \frac{2 \times M_{\text{H2}} \times N_{\text{av}}}{A_{\text{Ni}}} \tag{3}
\]

where \(M_{\text{H2}}\), \(N_{\text{av}}\), and \(A_{\text{Ni}}\) are the amount of H2 molecules adsorbed on the catalyst (mol gcat⁻¹), Avogadro’s number (6.02 × 10²³ atom mol⁻¹) and the number of Ni surface atoms per unit area (15.4 × 10¹⁸ atom m⁻²), respectively.

2.4.6 Scanning Transmission Electron Microscopy (STEM)

Samples for STEM were prepared by ultrasonically dispersing suspensions of each FSP-fabricated particle in ethanol (FUJIFILM Wako Pure Chemical Corp., purity > 99.5 %) and placing onto a molybdenum grid (Okenshoji Co., Ltd., UHR-M10 STEM Mo100P). STEM used an atomic resolution analytical STEM (Thermo Fisher Scientific K.K., Titan G2 60-300 Cubed, and JEOL Ltd., JEM-ARM200F) equipped with spherical probe aberration correctors. High-angle annular dark-field (HAADF)-STEM images of the FSP-fabricated catalyst particles were obtained with a HAADF detector, and elemental maps of the Ni K-line and Ce L-line were recorded using an energy-dispersive X-ray (EDX) detector in STEM mode.

3. Results and Discussion

Figure 2 depicts the catalytic activity of Ni supported on CeO2 (NiCe-x) and CeO2 supported on Ni (CeNi-x) for CO2 methanation. For all catalysts, the product of CO2 hydrogenation below 400 °C was only CH4 and CO was not detected by the TCD with a He carrier, as reported previously. Ni deposited on CeO2 (NiCe-x)
showed higher activity with lower Ni content (20 wt%) because excess Ni loading resulted in the formation of large Ni particles, as discussed below. For conventional Ni/CeO$_2$ catalysts, it has been reported that the optimal Ni loading is 20-30 wt%$^{24}$. Remarkably, the activity of CeO$_2$ impregnated with the Ni catalyst (CeNi-80) was double that of NiCe-80, regardless of the same nominal Ni content (80 wt%). Furthermore, the activity of CeNi-80 exceeded that of NiCe-20. CO$_2$ conversion by 100 mg of CeNi-80 at a relatively high space velocity (10$^5$ h$^{-1}$) was 47% at 250°C, which is superior to that of Ni/CeO$_2$ as reported$^{14}$. Interestingly, the light-off temperature of CeNi-80 (175-200 °C) was similar to that reported$^{26}$. Therefore, the active sites of conventional Ni/CeO$_2$ were similar to those of CeNi-80, but the number of sites in CeNi-80 was significantly larger than that in conventional Ni/CeO$_2$, as discussed below.

To investigate the durability of CeNi-80, after the reaction at 400 °C, the temperature was decreased to 300 °C for a holding time of 10 h. Subsequently, the CO$_2$ conversion of CeNi-80 at 300 °C had slightly decreased from 80 to 83 % (conversion at the initial temperature ramp). Therefore, CeNi-80 exhibited remarkable stability even with a high Ni content. Reducibility of NiCe-80 and CeNi-80 was investigated in 5 % H$_2$Ar, as depicted in Fig. 3. Ni/CeO$_2$ is reported to have three types of reduction peaks at low (α), moderate (β), and high (γ) temperatures$^{37}$, as observed in NiO/CeO$_2$ prepared via impregnation$^{14}$, hydrolysis$^{24}$ and solution combustion$^{38}$ methods. The α peak arises from the reduction of Ni$^{2+}$ substituted into the CeO$_2$ lattice and Ni-O-Ce interface. This α peak was assigned to the gradual rise of the signal at 150-250 °C for NiCe-80 and CeNi-80. The β and γ peaks were assigned to the reduction at 250-500 °C, which predominantly corresponded to the reduction of particulate NiO to metallic Ni$^{37}$. The β and γ peaks reflected the strength of the interaction between NiO and CeO$_2$. If the interaction was weak, NiO was reduced at a moderate (β) temperature. Indeed, the reduction temperature of NiO/CeO$_2$ was higher than that of pure NiO because of the interaction between NiO and CeO$_2$. If NiO was highly dispersed on CeO$_2$, a γ peak occurred. Therefore, the higher reduction temperature of CeNi-80 compared to NiCe-80 suggests a stronger interaction between NiO and CeO$_2$ and the presence of smaller NiO particles.

The reducibility of the catalysts depended on the preparation route, but NiO in the catalysts was completely reduced to metallic Ni below 500 °C. The H$_2$ consumption by the catalysts was evaluated from the peak area below 500 °C. Furthermore, the expected H$_2$ consumption was calculated assuming that the Ni content was consistent with the nominal values (20 wt% or 80 wt%), all Ni species in the samples were NiO, and the entire H$_2$ consumption was derived from the reduction of NiO.

Table 1 presents the measured and expected H$_2$ consumptions of the FSP-fabricated NiO and catalysts NiCe-x and CeNi-x. For NiO, the measured and expected H$_2$ consumptions were identical, suggesting that the nickel oxide was present predominantly as NiO. The measured H$_2$ consumption of NiCe-20 was higher than the expected value, because some of the CeO$_2$ was reduced below 500 °C$^{14}$. In contrast, the measured consumption of NiCe-80 was approximately 20 % lower than the expected value. According to the XRF.
In analysis, the Ni content of NiCe-80 was 31% lower than the nominal value. Therefore, 80 wt% of Ni was difficult to incorporate onto CeO₂, and some Ni precursors were lost during the impregnation (Ni acetate remained on the walls of the flask and calcining dishes). However, impregnating CeO₂ with NiO (CeNi-80) resulted in the Ni content determined using the XRF in agreement with the nominal value. The measured H₂ consumption of CeNi-80 was higher than the expected consumption. Consequently, the additional H₂ uptake resulted from reduction of CeO₂.

The porosities of the FSP-fabricated NiO, CeO₂, and impregnated catalysts were investigated using N₂ adsorption-desorption isotherms, as depicted in Fig. 4. The isotherms of the FSP-fabricated NiO and CeO₂ (Fig. 4a) were classified as type IV with a large hysteresis above $p/p₀ = 0.8$. After impregnation of Ni into CeO₂ (NiCe-80) and CeO₂ into Ni (CeNi-80), the isotherms (Fig. 4b) remained as type IV, indicating the presence of mesoporous structures.

The BJH pore size distributions of the catalysts (NiCe-80 and CeNi-80) and the FSP-fabricated NiO and CeO₂ were also obtained, as depicted in Fig. 4c. The pore sizes were 10-50 nm for the FSP-fabricated NiO and CeO₂, and total pore volumes were 2.3 cm³ g⁻¹ and 3.3 cm³ g⁻¹, respectively. Typically, ceramic particles fabricated via FSP have a fractal structure, and agglomeration of these types of particles form a high porosity structure (>90%) [39,40]. Moreover, the SSAs of NiO and CeO₂ were 251 cm² g⁻¹ and 338 cm² g⁻¹, respectively. These high porosity and SSA values are desirable for support materials.

The pore volumes of NiCe-80 and CeNi-80 decreased to 0.31 cm³ g⁻¹ and 0.19 cm³ g⁻¹, respectively, after impregnation with Ni or CeO₂, because the Ni (or CeO₂) was impregnated into the pores of NiO and CeO₂. CeO₂ impregnation (CeNi-80) caused formation of a new pore structure with an average pore diameter of 2.8 nm. These small pores were attributed to the spaces between the neighboring particles. CeNi-80 had a narrow pore size distribution, so CeO₂ was uniformly dispersed on NiO.

Figure 5 depicts the PXRD patterns of the FSP-fabricated NiO and CeO₂ and impregnated catalysts (NiCe-20, NiCe-80, and CeNi-80) before and after reduction in 5% H₂ at 500 °C for 1 h. The peaks of bunsenite NiO (37° and 43°) and fluorite CeO₂ (28°, 33°, and 47°) were observed for NiO and CeO₂, consistent with other FSP-fabricated NiO [41,42] and CeO₂ [43] reported. NiO
peaks appeared after impregnation of Ni with CeO$_2$ (NiCe-x), but the broadness of the CeO$_2$ peaks remained the same. Alternatively, CeO$_2$ was formed by impregnation of CeO$_2$ into NiO (CeNi-80). Cerium acetate is oxidized into CeO$_2$ via calcination in air at 400 °C for 2 h$^{44)}$. Thus, the calcination condition in this study (450 °C, 3 h) was observed adequate to form CeO$_2$. The peak of CeO$_2$ in CeNi-80 was exceedingly broad, indicating that CeO$_2$ was present as small particles or an amorphous state. H$_2$ reduction at 500 °C converted NiO to metallic Ni (44° and 52°)$^{37)}$ but rarely affected the crystallinity of CeO$_2$. The peaks of metallic Ni in NiCe-80 were significantly sharper than those in CeNi-80, indicating considerable growth of Ni in NiCe-80 compared to CeNi-80.

Table 2 summarizes the crystallite size and SSA of the FSP-fabricated NiO, CeO$_2$, and impregnated catalysts (NiCe-80 and CeNi-80) before and after reduction in 5 % H$_2$ at 500 °C for 1 h. For comparison, the crystallite size and SSA of NiCe-20 are presented. The expected particle sizes are 4 nm and 3 nm based on the SSA of NiO and CeO$_2$, respectively, assuming spherical particles. Their sizes are smaller than the crystallite size, suggesting the presence of an amorphous phase in the as-prepared FSP particles$^{45,46)}$.

The Ni crystallite size was significantly larger for NiCe-80 than for NiO. The crystallite size of CeO$_2$ in NiCe-80 was rarely affected by the impregnation and reduction processes, so the growth of Ni particles can be attributed to the decreased contact between Ni and CeO$_2$. Most of the Ni surface was not bonded with the CeO$_2$ surface at excess Ni content, resulting in low thermal stability of the Ni particles. In contrast, growth of the Ni crystallite size in CeNi-80 was less than in NiCe-80. Furthermore, the CeO$_2$ crystallite size remained exceedingly small (4 nm), even after H$_2$ reduction at 500 °C. Such limited particle growth indicates stronger contact between Ni and CeO$_2$ particles in CeNi-80 compared to NiCe-80. This difference in Ni-CeO$_2$ contact is consistent with the reduction temperature of NiCe-80 and CeNi-80. H$_2$-TPR (Fig. 3) showed that the presence of CeO$_2$ increased the reduction temperature of NiO because of the Ni-CeO$_2$ interaction. The higher reduction temperature of CeNi-80 than NiCe-80 indicated better contact between Ni and CeO$_2$.

Deposition of 20 wt% of CeO$_2$ onto NiO provided a significant surface area to bond the CeO$_2$ particles, thus limiting the growth of Ni particles. The preparation route did not affect the bonding strength between Ni and CeO$_2$ particles, because the growth of NiO to Ni through H$_2$ reduction process in NiCe-20 was comparable to that of CeNi-80.

The surface area of Ni in the catalysts was evaluated based on the amount of H$_2$ adsorbed on the Ni surface. More Ni incorporated onto CeO$_2$ (NiCe-20 and NiCe-80) resulted in lower surface area of Ni in the catalyst, because excess Ni loading formed large Ni particles, as expected. Notably, the surface area of Ni was 1.5 and 2.4 times larger in CeNi-80 than in NiCe-20 and NiCe-80, respectively. The surface area of FSP-fabricated pure NiO was fairly small (<0.1 m$^2$/g$_{cat}$), so the impregnated CeO$_2$ hindered the growth of Ni particles. The large Ni surface area in CeNi-80 was important for its superior catalytic performance.

The SSAs of NiCe-80 and CeNi-80 were approxi-
mately equal, unlike the surface areas of Ni, because of the differences in the actual Ni contents of NiCe-80 and CeNi-80. **Table 1** shows the actual Ni content in CeNi-80 was consistent with the nominal value, whereas that in NiCe-80 was approximately 30% lower than the nominal value. Thus, the fraction of CeO$_2$ with higher SSA than Ni particles was larger for NiCe-80 than for CeNi-80, resulting in similar SSA. After subtracting the Ni surface area from the SSA, the expected surface areas of CeO$_2$ in NiCe-80 and CeNi-80 were 54.3 m$^2$/g$_{cat}$ and 43.3 m$^2$/g$_{cat}$, respectively. The actual fraction of CeO$_2$ in NiCe-80 was almost double that of CeNi-80 based on the XRF analysis, so the size of CeO$_2$ was smaller in CeNi-80 than in NiCe-80, and consistent with the crystallite size.

Electron microscopy was used to investigate the morphology and Ni size of the catalysts after H$_2$ reduction. **Figure 6** shows (a) STEM and EDX mapping images of (b) Ni and (c) Ce species in NiCe-20 reduced in 5% H$_2$-Ar at 500 °C for 1 h. The STEM image indicates the aggregated particles, and the locations matched with the distribution of the Ce species, but not with the Ni species. Thus, the Ni particles were deposited on CeO$_2$, and not all CeO$_2$ particles interacted with Ni particles. The size of the Ni particles was 5-15 nm, comparable to the crystallite size (**Table 2**).

Inhomogeneous Ni size distribution is often observed at high Ni content (80 wt%)$^{21}$. Therefore, TEM images of NiCe-80 and CeNi-80 at low magnification were obtained to evaluate the homogeneity of the Ni particles. Some large Ni particles (~10 nm) (**Fig. 7a**, arrows) were observed in NiCe-80 after H$_2$ reduction. In contrast, small Ni and CeO$_2$ particles were homogeneously distributed, and large Ni particles could not be observed in reduced CeNi-80 (**Fig. 7b**).

STEM imaging and EDX mapping were performed to further investigate the size of Ni and CeO$_2$ particles. The STEM image of H$_2$ reduced NiCe-80 (**Figs. 8a, 8d**) showed particles of a few nanometers and large particles (~100 nm in **Fig. 8a** and ~20 nm in **Fig. 8d**). EDX mapping (**Figs. 8b-8c, 8e-8f**) indicated the small and large particles were CeO$_2$ and Ni, respectively, and the presence of both large (~100 nm) and small (~20 nm) Ni particles was confirmed. This inhomogeneous particle morphology is attributed to the excess Ni loading$^{21,22}$.

The STEM image of the reduced CeNi-80 (**Fig. 9a**) showed particles of few nanometers deposited on large particles of 10-20 nm. EDX mapping indicated these small and large particles corresponded to the CeO$_2$ and
These particle sizes are comparable with the crystallite sizes of CeO\textsubscript{2} (3 nm) and Ni (13 nm) in CeNi-80 reduced in H\textsubscript{2} at 500 °C. The agreement between the particle and crystalline sizes indicates relatively homogeneous size distribution, as confirmed by TEM at low magnification (Fig. 7b). Therefore, impregnation of 20 wt% CeO\textsubscript{2} into porous NiO nanoparticles, prepared via FSP, enables the formation of CeO\textsubscript{2} containing 80 wt% of Ni nanoparticles with high uniformity.

4. Conclusions

FSP-fabricated NiO with high porosity (2.3 cm\textsuperscript{3} g\textsuperscript{-1}) and high SSA (251 m\textsuperscript{2} g\textsuperscript{-1}) enabled the deposition of CeO\textsubscript{2} particles of a few nanometers on NiO. Reduction of the catalyst in 5 % H\textsubscript{2} at 500 °C for 1 h converted NiO to metallic Ni but growth of Ni particles was prevented by the CeO\textsubscript{2}. Consequently, the STEM image showed that the Ni size was relatively small (~20 nm), despite the extremely high Ni content (80 wt%). These small Ni particles at high Ni contents achieved superior catalytic performance for CO\textsubscript{2} methanation compared to catalysts prepared through impregnation of Ni (20 wt% and 80 wt%) into CeO\textsubscript{2} support.

Despite the high porosity (3.3 cm\textsuperscript{3} g\textsuperscript{-1}) and SSA (338 m\textsuperscript{2} g\textsuperscript{-1}) of the CeO\textsubscript{2} support, some large Ni particles (~100 nm) were formed after reduction, and the actual Ni content (55 %) was lower than the nominal value (80 wt%). However, 20 wt% of Ni incorporated...
into the CeO₂ support using the same procedure resulted in no formation of large Ni particles (∼100 nm), and the actual Ni content was consistent with the nominal value. Thus, excess Ni incorporation oversaturated the CeO₂ surface, resulting in lower Ni content and inhomogeneous Ni size distribution. These problems can be solved by incorporating CeO₂ with NiO fabricated by FSP.

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要旨

火炎噴霧熱分解法により合成した多孔質ナノ NiO を用いた
80 wt% Ni–CeO₂触媒の調製とその CO₂メタン化反応活性

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火炎噴霧熱分解法によりCeO₂およびNiOを調製した。比表面積と縫孔体積は、それぞれNiOが251 m² g⁻¹と2.3 cm³ g⁻¹, CeO₂が338 m² g⁻¹と3.3 cm³ g⁻¹であった。酸酸セリウム水和物をNiOに含浸し、5% H₂-Ar雑雰気下において500 ℃で1時間還元処理することで、80 wt% Ni–CeO₂触媒（以下、CeNi-80）を得た。電子顕微鏡観察により、この触媒のNi粒子サイズは10～20 nm程度であることが分かった。一方、酢酸ニッケル四水和物をCeO₂に含浸した触媒（以下、NiCe-80）では、20～100 nmの不均一なNi粒子が確認された。また、H₂化学吸着法により測定したCeNi-80のNi表面積は13.7 m² g⁻¹であり、NiCe-80より2.4倍大きい値であった。両触媒のCO₂メタン化活性を比較すると、250 ℃におけるCO₂転化率はCeNi-80が47%であり、NiCe-80の約2倍であった。