# Catalytic Performance of Metal Nanoparticles Supported by Ceramic Composite Produced by Partial Reduction of Solid Solution with Dopant

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A composite with well-dispersed metal nanoparticles at a ceramic surface was produced by partial reduction of solid solution. It was found that a small amount of dopant, such as  $Al_2O_3$ ,  $Cr_2O_3$ , or  $Sc_2O_3$ , accelerated the precipitation of the metal nanoparticles during the reduction. Catalytic performance of the composite for methanol reforming was evaluated. In the Nibased catalysts, the dopant decreased the CO production by promoting a methanation reaction, while in the Co-based catalysts, the dopant did it by inducing a water–gas shift reaction. Co/MgO with  $Sc_2O_3$  doping showed the most preferable reforming performance, high H<sub>2</sub> production, and CO<sub>2</sub> selectivity.

## I. Introduction

COMPOSITE with nanosized metal particles on the ceramic A surface is useful for the applications to catalysts and functional devices.<sup>1,2</sup> As the properties of the composite are influenced by dispersion morphology of the metal particles, such as the particle size, the number density, and homogeneity, it is important to control it. In general, an impregnation method is used to prepare fine catalysts on the ceramic substrate. However, using the conventional method, it is difficult to control the dispersion and aggregation of the metal particles. The partial reduction method makes it possible to provide composite homogeneously dispersed metal nanoparticles at the ceramic surface.<sup>3,4</sup> In this method, an oxide solid solution, composed of reducible oxide and irreducible oxide, is used as a precursor. By heating the precursor in a reductive atmosphere, only unstable oxide is reduced, producing metal nanoparticles in situ. This method is effective in making a homogeneous texture without aggregation for the samples in any form. The composite has several features, notably fine and well-dispersed metal nanoparticles and strong bonding with ceramic substrate. Dispersion morphology of the metal particles is controllable by changing the composition and reduction conditions. Furthermore, it is thermally stable because it is produced at a temperature higher than that of use. In our previous paper, we studied Ni/MgO catalysts fabricated by partial reduction of NiO-MgO solid solution.<sup>5,6</sup> We found that a small amount of Al<sub>2</sub>O<sub>3</sub> contained in the MgO raw powder drastically changed the dispersion morphology of the Ni nanoparticles.<sup>6</sup> It is considered that the Al<sup>3+</sup> doped into MgO created lattice defects and promoted an increase in the diffusion rate of the Ni ions to the ceramic surface during the reduction.<sup>7</sup>

Other dopants that have the same effects as  $Al_2O_3$  were investigated. As a result, it was found that  $Cr_2O_3$  and  $Sc_2O_3$  were also effective in enhancing the metal nanoparticle precipitation.

It is known that the nanosized Ni- and Co-supported materials have high potential for the reforming catalysts of methane and ethanol.<sup>8,9</sup> These materials are expected to be stable and inexpensive catalysts. In this paper, the composites produced by partial reduction of solid solution with dopant were prepared and a steam-reforming test for methanol was performed. The effects of the doping materials on reforming performance are discussed.

#### II. Experimental Procedure

MgO powder (1 µm, 4Nup, Kojundo Chemical Lab. Co. Ltd., Saitama, Japan), NiO powder (1 µm, >99%, FP-NiO, Sumitomo Metal Mining Co. Ltd., Tokyo, Japan), and CoO powder (1 µm, 3Nup, Kojundo Chemical Lab. Co. Ltd.) were used as raw powders. Mixed powders of NiO-MgO and CoO-MgO were prepared. The molar ratios of NiO:MgO and CoO:MgO were fixed at 1:2. 0.1 mol% of Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, or Sc<sub>2</sub>O<sub>3</sub> was added to the mixed powder. The mixture was cold pressed into a compact and sintered at 1300°C for 5 h. Solid solution (Ni, Mg)O and (Co, Mg)O with dopant were obtained. The sample density was calculated from the mass and dimensions of the sample. The solid solution was reduced at 1000°C for 10 min under a hydrogen flow, and the Ni and the Co particles were precipitated at the ceramic surface. The weight loss of the sample was measured during the reduction using a TG machine (TGD-9600, ULVAC-Riko Inc., Yokohama, Japan). To characterize the composite, the phase composition was analyzed by an X-ray diffractometer (XRD, Rigaku Corp., Tokyo, Japan). The physical surface area and the active metal surface area were measured by the gas absorption method (AUTOSORB-1C, Quantachrome Instruments Corp., Boynton Beach, FL), using nitrogen and hydrogen, respectively. The reduction samples were directly observed using a scanning electron microscopy (SEM; Model JSM-840F, JEOL Co. Ltd., Tokyo, Japan). Although some samples were coated with a gold by a sputtering device to impart more electroconduction, it is not considered to influence the observation. The acceleration voltage was 5 kV.

The steam reforming test of methanol was performed using the reduced sample. Before reduction, the solid solution was crushed into pieces and sieved at over 200  $\mu$ m through a mesh. About 2 g of the sample (including ceramic support) was fixed by glass wool in a stainless-steel tube of 10 mm i.d. as shown in Fig. 1. A liquid mixture of CH<sub>3</sub>OH and H<sub>2</sub>O was fed at a speed of 0.15 cc/min using an automated syringe and vaporized at 150°C. A molar ratio of H<sub>2</sub>O:CH<sub>3</sub>OH = 4:1 was used (gaseous flow rates of 120 cc/min H<sub>2</sub>O and 30 cc/min CH<sub>3</sub>OH). The temperature of the reactor was controlled by a thermocouple

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Fig. 1. Schematic of the methanol reforming test.

located in the catalyst bed. The reactor was heated by an electric furnace. Vapors (unreacted CH<sub>3</sub>OH and H<sub>2</sub>O) were trapped using a cooling condenser. The gas lines were heated at about  $150^{\circ}$ C by heating tapes. 50 cc/min N<sub>2</sub> was used as both the carrier gas and the reference gas for the gas analyzer. Gas analysis was performed using a gas chromatography (micro-GC; CP400, Varian Inc., Palo Alto, CA), equipped with a thermal conductivity detector. CP-Cox column (Ar carrier) was used for the separation of H<sub>2</sub> and CO<sub>2</sub>, while Molsieve5Å column (He carrier) was used for the separation of CO, CH<sub>4</sub>, and N<sub>2</sub>.

The methanol conversion  $X_{CH_3OH}$  is assumed by Eq. (1), considering that CH<sub>3</sub>OH was converted to carbon-containing products (CO, CO<sub>2</sub>, and CH<sub>4</sub>). And the selectivity of the carbon-containing products,  $S_{CO}$ ,  $S_{CO_2}$ , and  $S_{CH_4}$ , is given by Eqs. (2)–(4).

$$X_{\rm CH_3OH} = (F_{\rm CO} + F_{\rm CO_2} + F_{\rm CH_4}) / F_{\rm CH_3OH} \times 100$$
(1)

$$S_{\rm CO} = F_{\rm CO} / (F_{\rm CO} + F_{\rm CO_2} + F_{\rm CH_4}) \times 100$$
(2)

 $S_{\rm CO_2} = F_{\rm CO_2} / (F_{\rm CO} + F_{\rm CO_2} + F_{\rm CH_4}) \times 100$ (3)

$$S_{\rm CH_4} = F_{\rm CH_4} / (F_{\rm CO} + F_{\rm CO_2} + F_{\rm CH_4}) \times 100$$
 (4)

where F represents the molar flow rates of the gas products.

Every reforming test was performed under the condition of  $W/F = 4 \text{ g}_{\text{cat}} \cdot \mathbf{h} \cdot \text{mol}^{-1}$  (W is the catalyst weight and F the total flow rate of feed gas), and the gas hourly space velocity was about 7000 h<sup>-1</sup>.

#### III. Results and Discussion

The weight loss of the NiO-MgO solid solution with no doping was 0.4% at 1000°C during the reduction. Various oxide dopants were examined before this study. Among them, it was found that three dopants containing trivalent cation, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, and Sc<sub>2</sub>O<sub>3</sub>, showed incomparable weight loss during the reduction, promoting the precipitation of the Ni particles. Existence of the nickel was confirmed by XRD. The material properties used in this study are shown in Table I. The weight loss is the total amount after the reduction at 1000°C for 10 min. The precipitation of the metal particles started from about 700°C for all the samples. It was confirmed by weight loss in TG measurement. It suggests that the materials should be steadily used at a temperature lower than that. The active metal surface area for the materials with dopant, which is related to catalytic activity, increased remarkably. Figure 2 shows the microstructures of the Ni/MgO composites with each dopant, comparing them with doping-free material. It was difficult to catch the Ni particles in the dopant-free material because they were very fine in spite of reducing at 1000°C. On the other hand, the addition of a small

Table I. Material Properties Used in This Study

| Dopant    | Doping amount<br>(mol%) | Density<br>(g/cm <sup>3</sup> ) | Weight loss during<br>reduction (%) | Active metal surface area $(m^2/g)$ |
|-----------|-------------------------|---------------------------------|-------------------------------------|-------------------------------------|
| Non       | 0                       | 3.75                            | -0.4                                | 0.20                                |
| $Al_2O_3$ | 0.1                     | 3.34                            | -6.3                                | —                                   |
| $Cr_2O_3$ | 0.1                     | 2.94                            | -10.3                               | 1.45                                |
| $Sc_2O_3$ | 0.1                     | 3.73                            | -10.1                               | 1.47                                |



**Fig. 2.** Scanning electron microscopy micrographs of Ni/MgO composites after the reduction. (a) No doping, (b)  $Al_2O_3$  doping, (c)  $Cr_2O_3$  doping, (d)  $Sc_2O_3$  doping.

amount of Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, or Sc<sub>2</sub>O<sub>3</sub> drastically changed the dispersion morphology of the Ni nanoparticles. These dopants can be dissolved into MgO substrate and they create the lattice defects (Shottky defects), replacing  $Mg^{2+}$  to  $Me^{3+}$  (Me: Al, Cr, Sc). Therefore, it is thought that the defects made the diffusion rate of the Ni ions to the ceramic surface (or grain boundary) increase during the reduction process. Henriksen reported that the solid solubility of Cr<sub>2</sub>O<sub>3</sub> and Sc<sub>2</sub>O<sub>3</sub> into MgO was much larger than that of Al<sub>2</sub>O<sub>3</sub>.<sup>10</sup> This suggests that more defects were formed for the materials with Cr<sub>2</sub>O<sub>3</sub> and Sc<sub>2</sub>O<sub>3</sub> than those with Al<sub>2</sub>O<sub>3</sub>, and it promoted the production of more Ni particles.

Furthermore, the matrix grain size of the composite was smaller than that of the material without doping. This is considered to be because the dopant that exceeded the solution limit remained at the grain boundary of the matrix and prevented the grain growth of the MgO.

The amount of precipitation and the size of metal particle are controllable by changing the material composition and reduction conditions. In this study, the materials reduced at  $1000^{\circ}$ C were used for methanol reforming test to clarify the effect of doping materials.

Table II shows the reforming performance at 350° and 400°C for the Ni-based catalysts. Methanol was completely converted at these temperatures. The CO production rapidly decreased at a certain temperature. The temperature was shifted to a lower

Table II. Methanol Conversion and Product Composition on the Ni-Based Catalysts Produced by Partial Reduction Reaction

| Keaction                    |           |                                       |                                       |                                       |  |  |  |
|-----------------------------|-----------|---------------------------------------|---------------------------------------|---------------------------------------|--|--|--|
|                             | Ni        |                                       |                                       |                                       |  |  |  |
| Product composition         | No doping | Al <sub>2</sub> O <sub>3</sub> doping | Cr <sub>2</sub> O <sub>3</sub> doping | Sc <sub>2</sub> O <sub>3</sub> doping |  |  |  |
| 350°C                       |           |                                       |                                       |                                       |  |  |  |
| Conversion (%)              | 100       | 100                                   | 100                                   | 100                                   |  |  |  |
| H <sub>2</sub> (%)          | 64.9      | 63.0                                  | 65.0                                  | 63.6                                  |  |  |  |
| CO (%)                      | 28.7      | 2.2                                   | 5.4                                   | 0.5                                   |  |  |  |
| $CO_2(\%)$                  | 4.6       | 23.2                                  | 21.2                                  | 24.3                                  |  |  |  |
| $CH_4(\%)$                  | 1.9       | 11.6                                  | 8.4                                   | 11.7                                  |  |  |  |
| CO <sub>2</sub> selectivity | 13.1      | 62.7                                  | 60.6                                  | 66.5                                  |  |  |  |
| 400°C                       |           |                                       |                                       |                                       |  |  |  |
| Conversion (%)              | 100       | 100                                   | 100                                   | 100                                   |  |  |  |
| $H_2$ (%)                   | 68.7      | 60.0                                  | 59.9                                  | 59.3                                  |  |  |  |
| CO (%)                      | 1.4       | 0.6                                   | 0.9                                   | 0.7                                   |  |  |  |
| $CO_2(\%)$                  | 23.8      | 24.3                                  | 24.2                                  | 24.0                                  |  |  |  |
| $CH_4$ (%)                  | 6.1       | 15.1                                  | 15.0                                  | 16.0                                  |  |  |  |
| CO <sub>2</sub> selectivity | 76.0      | 60.8                                  | 60.3                                  | 59.0                                  |  |  |  |



Fig. 3. Selectivity of the carbon-containing products for the reforming on the Ni-based catalysts with the  $Sc_2O_3$  dopant.

temperature by the dopant. In particular, the Sc<sub>2</sub>O<sub>3</sub> doping material showed the lowest CO production at 350°C. However, it seemed that the enhanced Ni particles also caused the increase of the CH<sub>4</sub> production. This is not preferable because it leads to the decrease of the H<sub>2</sub> production as follows (Eq. (5)):

$$CO + 3H_2 \Leftrightarrow CH_4 + H_2O$$
 (5)

The selectivity of the carbon-containing products for the material with  $Sc_2O_3$  dopant is shown in Fig. 3. The  $CH_4$  production increased with the reforming temperature.

On the other hand, these dopants were applied to the Cobased catalysts. Figure 4 shows the microstructure of the Co/ MgO with Sc<sub>2</sub>O<sub>3</sub> dopant. Enhanced Co precipitation was observed at the CoO–MgO solid solution surface as well as in the Ni-based materials. The product composition of methanol reforming is shown in Table III, compared with that of the material without doping. It was observed that the Sc<sub>2</sub>O<sub>3</sub> doping material was active at 350°C, indicating 100% methanol conversion. And the CO production decreased, maintaining low CH<sub>4</sub> production. This is thought to be because the water–gas shift (WGS) reaction occurred simultaneously with the reforming reaction.

$$CO + H_2O \Leftrightarrow H_2 + CO_2 \tag{6}$$

The WGS reaction takes advantage of the extra  $H_2$  production. Consequently, high  $CO_2$  and  $H_2$  selectivity were achieved.



**Fig.4.** Scanning electron microscopy micrographs of Co/MgO composites with Sc<sub>2</sub>O<sub>3</sub> doping after reducing at 1000°C.

Table III.Methanol Conversion and Product Composition<br/>on the Co-Based Catalysts Produced by Partial Reduction<br/>Reaction

|                             |        | Со             |      |  |  |  |
|-----------------------------|--------|----------------|------|--|--|--|
|                             | No dop | No doping (°C) |      | Sc <sub>2</sub> O <sub>3</sub> doping (°C) |  |  |
| Product composition         | 350    | 400            | 350  | 400  |  |  |
| Conversion (%)              | 100    | 100            | 100  | 100  |  |  |
| $H_2(\%)$                   | 69.7   | 72.6           | 73.3 | 71.9                                       |  |  |
| CO (%)                      | 16.2   | 6.8            | 1.2  | 1.6  |  |  |
| $CO_{2}(\%)$                | 13.6   | 20.4           | 23.9 | 23.6                                       |  |  |
| $CH_{4}(\%)$                | 0.5    | 0.3            | 1.7  | 2.8  |  |  |
| CO <sub>2</sub> selectivity | 44.9   | 74.2           | 89.4 | 84.1                                       |  |  |



Fig. 5. Selectivity of the carbon-containing products for reforming on the Co-based catalysts with the  $Sc_2O_3$  dopant.

The selectivity of the carbon-containing products for the Cobased catalysts with  $Sc_2O_3$  dopant is shown in Fig. 5. As for this material, no change in performance and no significant deactivation were observed in experiments repeated many times. At present, it is well known that the Cu-based catalyst is the most effective for methanol reforming. However, it has low thermal stability, and significant deactivation occurs after the oxidization. So, the developed material deserves attention as a nonprecious-metal catalyst with outstanding reforming performance. Although the specific surface area of the material is as small as about 1 m<sup>2</sup>/g, the dispersion morphology of the metal nanoparticles makes high catalytic activity possible. Optimization of the dispersion morphology of the metal particles is necessary to further improve performance. This will be clarified in the next paper.

The Ni/MgO and Co/MgO systems are also among the promising candidates for methane and ethanol-reforming catalyst. Regarding the material we developed, applications to these various fuels are expected.

We developed a new composite material having a high catalytic performance for methanol reforming. This technology is not limited to methanol reforming. We expected it to lead to development of other new functional materials.

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