

Preparation of Ni-ZrO₂ composites via mechanochemistry processes and their catalytic properties

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Ni-ZrO₂ catalytic materials were prepared by the selective oxidation of Ni-ZrH₂ composite and amorphous Ni-Zr alloy powders synthesized by means of ball milling of NiZr₂ alloys under pressurized H₂ and Ar atmospheres, respectively. Structural characterization was performed using X-ray diffraction and transmission electron microscopy. Ni-ZrH₂ composite and amorphous Ni-Zr alloy powders were oxidized at 550 °C and 800 °C, respectively. The size of Ni particles in Ni-ZrO₂-h ranged from 5 to 20 nm while that of Ni-ZrO₂-a were not separated obviously as fine particles. The mean sizes of the Ni particles in Ni-ZrO₂-h and Ni-ZrO₂-a obtained by XRD were about 16.9 nm and 28.4 nm, respectively. The methanol conversion ratio of Ni-ZrO₂-h was higher than that of the Ni-ZrO₂-a catalysts at all temperatures. Furthermore, it was found that Ni-ZrO₂-h has a highly endurable structure. It is believed that the enhanced catalytic properties of Ni-ZrO₂-h are due to its high surface area and separately dispersed Ni nanoparticles.

Key words: Mechanical hydrogenation, Nano-composite catalysts, Steam reforming of methanol, Gas-solid reaction.

Introduction

Ni-based catalysts are widely used for steam reforming of organics to produce hydrogen [1-2]. However, Ni-based catalysts are subject to coking, which leads to fast deactivation during steam reforming [3-4]. It is known that the coke formation is related to the structure of the catalyst, requiring sintering of the metallic particles under a thermal atmosphere [5-6].

In general, nickel-based catalysts are prepared by wet chemical processes of loading metallic Ni onto various supports such as Al₂O₃, ZrO₂, SiO₂, and mixed oxides or co-precipitation [1-2]. This method generally requires multiple steps and excessive handling, which produce waste in the intermediate synthesis steps [7-9]. The mechanochemistry process is another promising synthesis route capable of synthesizing nanostructured materials. This process allows for the preparation of desired materials at room temperature, a reduction of the number of handling/processing steps, resulting in less waste from intermediate synthesis steps, and a reduction of the loss of material through handling [10-11]. When a gas-solid reaction is induced, it is possible to dissociate or reform phases by means of mechanical impact during a room-temperature mechanochemical process [12-14]. This process is promising for the

synthesis of materials with desired microstructures, such as composite materials which contain dispersed nanoparticles. Using this process, a Ni-ZrO₂ composite was prepared to form catalytic materials with a structure which includes fine particles of metallic Ni.

In this study, Ni-ZrH₂ composite and amorphous Ni-Zr alloy powders, a precursor of Ni-ZrO₂ catalysts, were synthesized by means of ball milling of NiZr₂ alloys under pressurized H₂ and Ar atmospheres, respectively. These Ni-ZrO₂ catalysts were prepared by a selective oxidation process of the Ni-ZrH₂ and amorphous Ni-Zr alloy powders, and their catalytic properties were investigated.

Experimental Procedure

Button-type ingots of NiZr₂ alloys with diameters of about 50 mm weighing around 50 g were prepared via arc melting in an Ar gas atmosphere. The ingots were crushed to form a powder and sieved to a particle size of less than 113 μm by using a 120 mesh. Ni-ZrH₂ and amorphous powders were prepared in a planetary high-energy ball mill under pressurized H₂ and Ar atmospheres, respectively. The ball : powder weight ratio was 10 : 1. To prepare the powder for milling, about 20 g of the powder were added to a stainless steel vial together with stainless balls (10 mm diameter). The disc and vial rotating speeds were 600 and 320 rpm, respectively. The crystal structures of the samples were analyzed via X-ray diffraction (XRD) using a CuKα source (Rigaku, D-Max 2500). The grain sizes of Ni in the samples were

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calculated from the full width at half-maximum (FWHM) of the diffraction peak using C. Suryanarayana and M. Grant Norton's formula [15] as follows:

$$B_r(B_{\text{crystalline}} + B_{\text{strain}}) \cos\theta = k \lambda / L + \eta \sin\theta \quad (1)$$

where B_r is the FWHM of the diffraction peak after instrument correction, $B_{\text{crystalline}}$ and B_{strain} are the FWHM values caused by the small grain size and internal stress, respectively, k is a constant (value of 0.9), λ is the wavelength of the X-ray radiation, L and η are the grain size and internal strain, respectively, and θ is the Bragg angle. The parameters B and B_r follow Cauchy's form with the relationship of $B = B_r + B_s$, where B and B_s are the FWHM values of the broadened Bragg peaks and the standard sample's Bragg peaks, respectively.

The thermal behavior was studied using a differential scanning calorimeter (DSC, Shimadzu 60 plus) at a heating rate of 40 K/min in air. The reduction behaviors of the NiO-ZrO₂ powders were examined by using a temperature programmed reduction (TPR) instrument (BEL-CAT, BEL). The Brunauer-Emmett-Teller (BET) surface area was measured by nitrogen adsorption using a surface area analyzer (Micromeritics TRI-3000). The microstructures of the samples were observed by field emission transmission electron microscopy (TEM; JEM-2010, Jeol).

Catalytic experiments of the production of hydrogen from methanol were performed using a conventional gas flow system with a fixed catalyst bed. 0.2 g of the Ni-ZrO₂ powders was placed in a stainless steel tube with an internal diameter of 8 mm in the reactor. The reactants were introduced into the reactor at a water:methanol molar ratio of 1.5 : 1.0 at a liquid hourly space velocity of 15 h⁻¹ (defined as the volume of methanol that has passed over the unit volume of catalyst per hour). The reaction temperature was increased stepwise from 200 to 500 °C at an interval of 25 °C. The outlet composition of the gas products was analyzed after 25 min at each temperature using gas chromatography (Shimadzu, GC-2010).

Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of the (a) NiZr₂ alloy powder used as the raw material, (b) amorphous Ni-Zr prepared by milling in Ar gas, and (c) Ni-ZrH₂ prepared by milling under pressured H₂ gas. When raw powder of the NiZr₂ single phase was milled under an Ar atmosphere for 20 hrs, it was converted to an amorphous phase. However, after milling under a pressurized H₂ atmosphere for 20 hrs, a ZrH₂ phase clearly appeared, indicating that the NiZr₂ phase was resolved into ZrH₂ and Ni phases [16]. The H₂ content of the powder milled for 20 hrs was about 40 at%. This value corresponds to about 80% of its

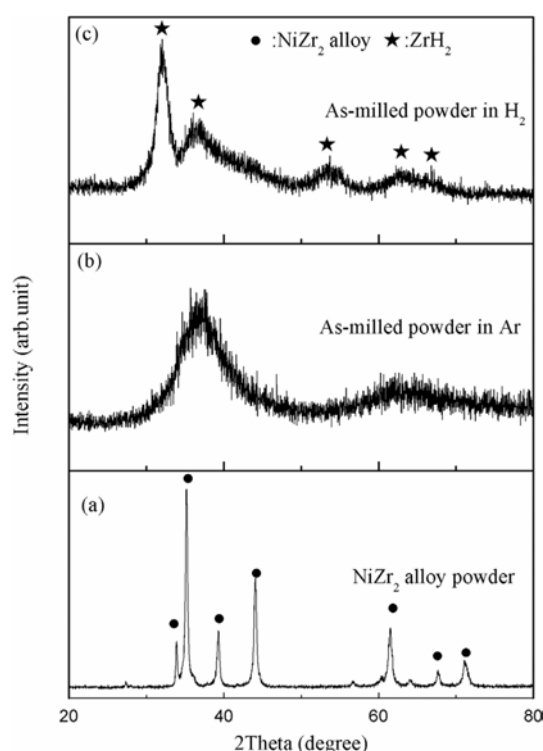


Fig. 1. XRD patterns of (a) raw and milled powders under (b) N₂ and (c) H₂ atmospheres for 25 hrs.

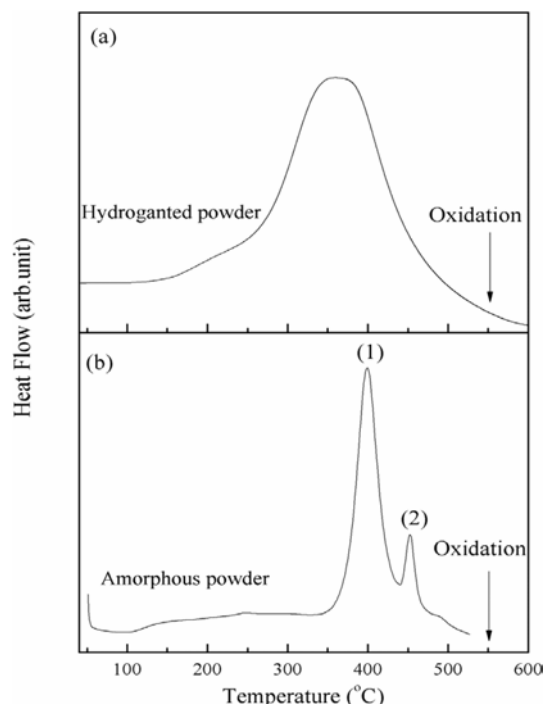


Fig. 2. DTA of powders milled under (a) N₂ and (b) H₂ atmospheres for 25 hrs.

stoichiometry. EDS measurements indicated that Ni-ZrH₂ and amorphous Ni-Zr contained less than 1.0 wt% and less than 0.9 wt% Fe and oxygen impurities, respectively.

Fig. 2 shows the DSC curves for the (a) Ni-ZrH₂ and amorphous (b) Ni-Zr phases prepared by mechanical

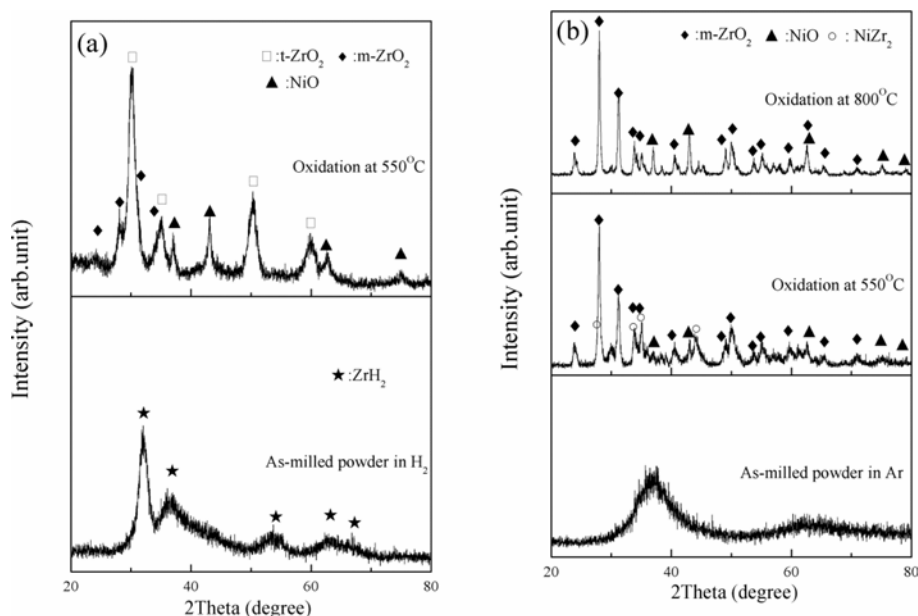


Fig. 3. XRD patterns of (a) Ni-ZrH₂ and (b) amo.-NiZr₂ powders after oxidation.

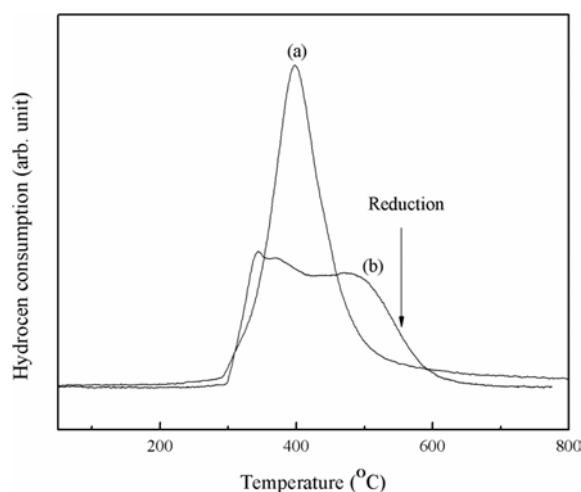


Fig. 4. Reduction behaviors of (a) NiO-ZrO₂-h and (b) NiO-ZrO₂-a powders obtained via TPR analysis.

milling for 20 hrs. The Ni-ZrH₂ phase shows one exothermic peak, while the amorphous Ni-Zr phase has two peaks. The peaks correspond to oxidation and crystallization reactions. Therefore, the oxidation of the samples was conducted at 550 °C for 1 hr in air, at which point the reactions were completely finished. When they were oxidized at 550 °C, the Ni-ZrH₂ powder was converted to NiO + ZrO₂ (mixture of tetragonal and monoclinic), that was designated as NiO-ZrO₂-h, as shown in Fig. 3(a). Meanwhile, the amorphous powder was not oxidized completely and remained a metallic phase formed by crystallization which consisted of three phases of NiO, ZrO₂ (monoclinic), and NiZr₂. This indicated that the oxidation temperature was insufficient. Therefore, further oxidation was carried out at 800 °C, where it was oxidized to NiO-ZrO₂ completely. This sample is designated as NiO-ZrO₂-a, as shown in Fig.

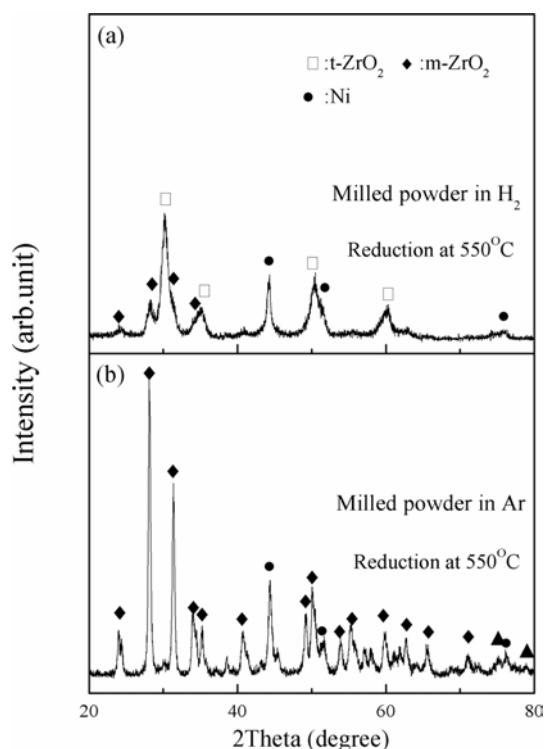


Fig. 5. XRD patterns of (a) Ni-ZrO₂-h and (b) Ni-ZrO₂-a powders after reduction.

3(b). In order to apply it as a catalyst, it is necessary to reduce only NiO in the composites to metallic Ni selectively. Fig. 4 shows the reduction behaviors of the two powders determined via TPR (temperature-programmed reduction) analysis. In the TPR analysis, the amount of hydrogen to be consumed by the reducing reaction of samples under heating was measured. The ranges of the reduction temperatures of NiO-ZrO₂-h and NiO-ZrO₂-a were approximately 300 to 500 °C and 300 to 600 °C,

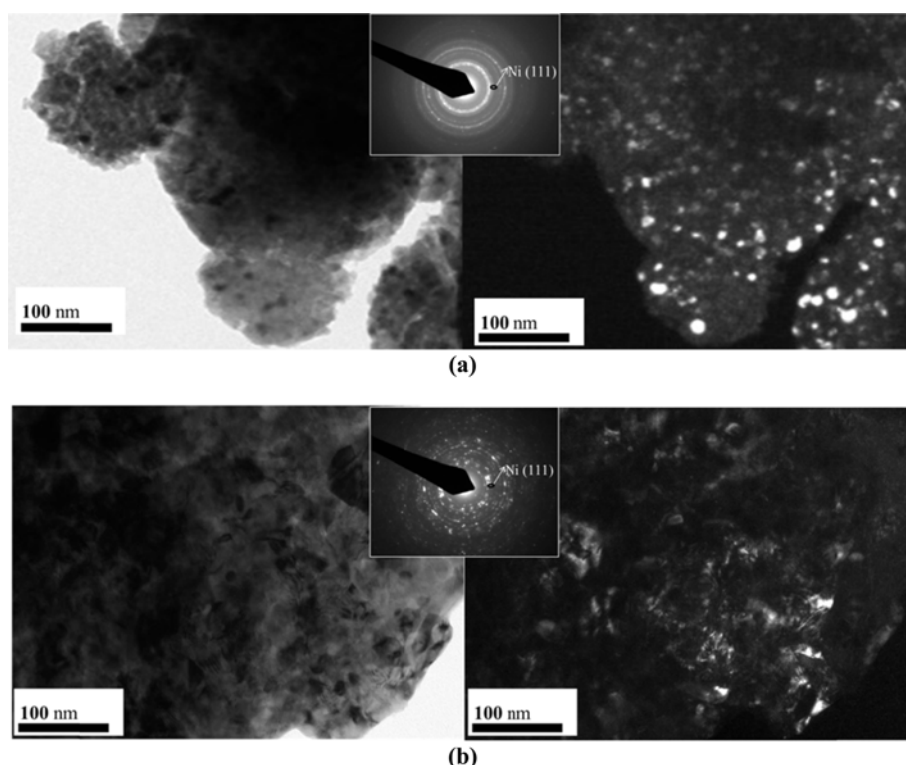


Fig. 6. TEM images of (a) Ni-ZrO₂-h and (b) Ni-ZrO₂-a powders after reduction.

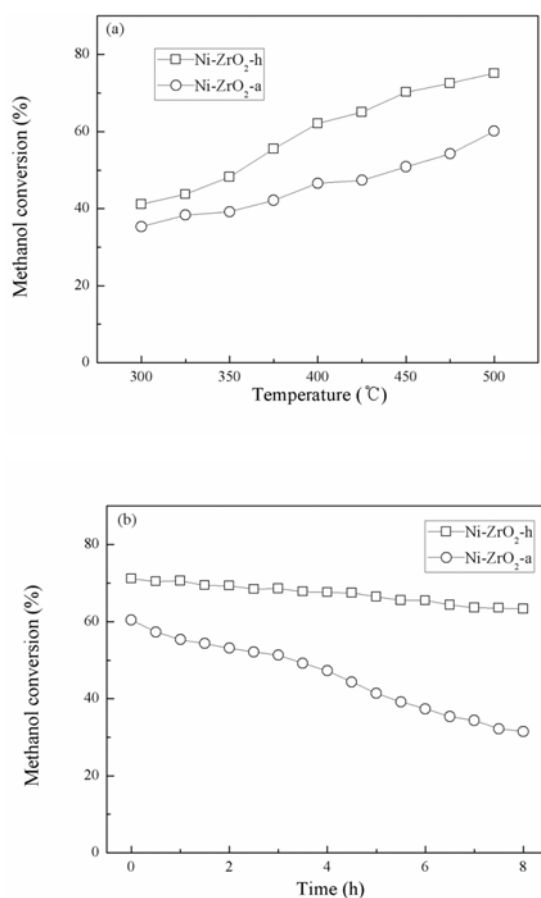


Fig. 7. The methanol conversion ratio as a function of the (a) reaction temperature and (b) reaction time at 500 °C for the Ni-ZrO₂-h and the Ni-ZrO₂-a catalysts.

respectively. Therefore, the NiO-ZrO₂-h and NiO-ZrO₂-a powders were annealed at 550 °C for 1 h in H₂. The NiO phase in the (a) NiO-ZrO₂-h and (b) NiO-ZrO₂-a composite was converted to metallic Ni by the reduction treatment, as shown in Fig. 5.

The microstructures of the samples reduced at 550 °C were investigated using TEM to obtain light field images, diffraction-mode images, and dark field images corresponding to the Ni (111) plane. The images show that the size of Ni particles in Ni-ZrO₂-h ranged from 5 to 20 nm, as shown in Fig. 6(a). However, metallic Ni planes in Ni-ZrO₂-a were not obviously separated as fine particles, as shown in Fig. 6(b). The mean sizes of the Ni particles in Ni-ZrO₂-h and Ni-ZrO₂-a calculated using equation (1) were about 16.9 nm and 28.4 nm, respectively.

Catalytic experiments of the production of hydrogen from a mixed solution of methanol and water were carried out. Fig. 7 shows the methanol conversion as a function of (a) the reaction temperature and (b) reaction time at 500 °C for the Ni-ZrO₂-h and Ni-ZrO₂-a catalysts. The methanol conversion ratio of Ni-ZrO₂-h was higher than that of Ni-ZrO₂-a for all temperatures. Furthermore, the catalytic activity of Ni-ZrO₂-h was almost maintained for 8 h, but that of Ni-ZrO₂-a decreased with time. This means that compared to Ni-ZrO₂-a, Ni-ZrO₂-h had good catalytic activity for the SRM (steam reforming of methanol) reaction and a more highly endurable structure.

Two important points should be noted regarding this work. First, we developed a different preparation process

Table 1. Specific surface areas (SSA) and Ni grain sizes (D_{Ni}) of the as-milled and Ni-ZrO₂ samples.

Condition	As-milled	After reduction	
Samples	SSA (m ² /g)	D_{Ni} (nm)	SSA (m ² /g)
Ni-ZrO ₂ -h	1.41	16.9	4.43
Ni-ZrO ₂ -a	0.27	28.4	0.99

for the Ni-ZrO₂ catalyst. The wet process requires multiple steps, increased handling requirements, and generates waste during the intermediate synthesis steps [13-14]. However, it is important to note that by employing the mechanochemical method developed in this study, the preparation process can be completed in only two steps with the synthesis of Ni-ZrH₂ or amorphous NiZr₂ and oxidation/reduction to Ni-ZrO₂ composites to overcome the disadvantages of the wet processes. The second notable observation is related to the differences of the catalytic performance between Ni-ZrO₂-h and Ni-ZrO₂-a. The activity of a catalyst is known to increase with decreasing particle size or increasing surface area. As indicated in Table 1, the results of the present study agree with this observation where Ni-ZrO₂-h had smaller Ni particle sizes and a greater specific surface area than Ni-ZrO₂-a. We conclude that separately dispersed metallic Ni fine particles and the large surface area of Ni-ZrO₂-h were crucial factors in its superior catalytic properties.

Conclusions

Ni-ZrO₂ catalytic materials were prepared by the selective oxidation of Ni-ZrH₂ composite and amorphous Ni-Zr alloy powders synthesized by means of ball milling of NiZr₂ alloys under pressurized H₂ and Ar atmospheres, respectively. When Ni-ZrH₂ composite and amorphous Ni-Zr alloy powders were oxidized at 550 °C, the Ni-ZrH₂ powder was converted to NiO + ZrO₂ (mixture of tetragonal and monoclinic), while the amorphous powder was not oxidized completely. Therefore, further oxidation was conducted at 800 °C. The size of Ni particles in Ni-ZrO₂-h ranged from 5 to 20 nm. However, metallic Ni planes in Ni-ZrO₂-a were not separated obviously as fine particles. The mean sizes of the Ni particles

in Ni-ZrO₂-h and Ni-ZrO₂-a obtained by XRD were about 16.9 nm and 28.4 nm, respectively. The methanol conversion ratio of Ni-ZrO₂-h was higher than that of Ni-ZrO₂-a at all temperatures. Furthermore, the catalytic activity of Ni-ZrO₂-h was almost maintained for 8 h while that of Ni-ZrO₂-a decreased with time.

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