Benzene hydrogenation activity of nickel catalysts prepared from amorphous Ni–Zr alloys

Takeshige Takahashi, Soh-ichro Higashi, Takami Kai
Department of Applied Chemistry and Chemical Engineering, Kagoshima University, Kagoshima 890, Japan

Hisamichi Kimura and Takeshi Masumoto
Institute for Material Research, Tohoku University, Katahira, Aoba-ku, Sendai 980, Japan

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The hydrogenation of benzene over amorphous Ni–Zr alloys with different Ni compositions ($Ni_{33}Zr_{67}$, $Ni_{40}Zr_{60}$, $Ni_{50}Zr_{50}$, $Ni_{70}Zr_{30}$, $Ni_{90}Zr_{10}$) produced by means of a rapid solidification technique was investigated. Although the catalytic activities of the alloys were very low in the virgin state, they gradually increased with increasing number of regeneration (oxidation and reduction) reaction cycles, and the activity approached a constant value after six regenerations. The benzene hydrogenation activity increased with nickel content up to 50%, but then decreased with Ni content. It was shown that the surface area measured by the nitrogen adsorption method had almost the same dependence on Ni content. These results suggest that the $Ni_{50}Zr_{50}$ alloy is easily relaxed by the regeneration, and Ni atoms effective for the hydrogenation are highly dispersed on the micro ZrO_2 crystals produced from the alloy by the oxidation.

Keywords: amorphous Ni–Zr alloy; benzene hydrogenation; catalytic activity; effect of Ni content

1. Introduction

Many studies have been reported concerning the catalytic activities of amorphous alloys for hydrogenation and/or oxidation [1–4]. Although some alloys had high activity for hydrogenation even in the virgin state, the activity of Pd–Zr and Pt–Zr alloys was gradually improved by repeated regeneration by oxidation and reduction [5]. The characterization of the regenerated alloy revealed that the increase in the catalytic activity of the regenerated alloy was due to an increase in the palladium dispersion on the zirconium oxide crystals produced by the oxidation treatment. However, it is not possible to prepare an arbitrary composition of Pd–Zr, because the melting point of the alloy, except for $Pd_{35}Zr_{65}$, is too high to synthesize by the rapid quenching method. On the other hand, the melting point of Ni–Zr alloys does not change with composition. Shimogaki et al. [6] reported the effect of Ni content of the amorphous Ni–Zr alloys on the catalytic activity of CO hydrogenation. They concluded that the production of ZrO_2 by the reaction of Zr and oxygen in carbon monoxide was responsible for the increases in the surface area of alloy and the catalytic activity.

In the present study, benzene hydrogenation runs were carried out over a catalyst prepared from amorphous Ni–Zr alloys with different compositions to elucidate the effect of Ni content on catalytic activity. The effect of oxidation on the surface state and catalytic activity was also examined by the characterization of the alloy surface.

2. Experimental

The uniform Ni–Zr alloys were prepared by melting of the prescribed masses of nickel and zirconium in an arc furnace under an argon atmosphere. Thin, long amorphous ribbons were prepared at the Institute for Material Science, Tohoku University, in an argon atmosphere by rapid quenching from the molten alloys using a single roll. The crystallization temperature of the amorphous alloy was about 873 K. The long alloy was cut with scissors into 1 mm long fragments. The hydrogenation runs were carried out in a previously described fixed-bed type quartz tubular reactor. The experimental procedures were essentially similar to that presented in a previous paper [7]. The alloy, put into the reactor, was oxidized at 623 K for 17 h and reduced at the same temperature for 3 h. Benzene supplied from a micro feeder at a constant flow rate was diluted with hydrogen to 10% in an evaporator. The vapor mixture of benzene and hydrogen was fed into the reactor. The effluent gas was trapped in chilled toluene, and the product was analyzed using a gas chromatograph equipped with a FID detector. Cyclohexane was the only product from the present benzene hydrogenation runs. Since the catalytic activity of the alloy decreased with time on stream (process time) by the deposition of coke on the catalyst surface, the used catalyst was regenerated under the same conditions already described.

The surface area of the alloy was measured by the nitrogen adsorption method, in which the BET equation was used for calculation. The hydrogen adsorption measurement was performed at 298 K; the Langmuir equation was used in the calculation. The catalyst pretreatment procedure for the measurements has been described in a previous paper [8]. The dispersion calculated from the quantity of adsorbed hydrogen was defined as the ratio of surface Ni atoms which were effective for hydrogen adsorption to the total amount of Ni atoms in the alloys.

3. Results and discussion

It was well known that the catalytic activity of an amorphous alloy increased with the oxidation temperature below the crystallization temperature and oxidation period. Furthermore, it was reported that the activity of an amorphous Pd–Zr alloy for the hydrogenation of carbon monoxide became about two orders of magnitude larger than the initial activity after 70 h of time on stream [3]. It was concluded that the increase in the catalytic activity was due to the preparation of an unknown complex oxide of palladium and zirconium under highly reducing reaction condition. In this study, the repeated use of the amorphous alloy was conducted to clarify the effect of oxidation of an amorphous alloy on the benzene hydrogenation activity.

Fig. 1 shows the effect of regeneration number on the catalytic activity of the $Ni_{40}Zr_{60}$ alloy. The catalytic activity gradually increases with the regeneration number and reaches a constant activity after five regenerations. When the oxidation of the amorphous alloy was carried out for 85 h, which corresponds to five time regenerations, under the same conditions as in fig. 1, the catalytic activity is almost the same as shown in fig. 1. This result suggests that the increase in the catalytic activity was due to the oxidation of zirconium.

Since the decrease in benzene conversion was approximately proportional to the square root of the process time except for the low conversion, the deactivation is represented as a function of process time by

$$x(t) = x(0)\exp(-\gamma t^{1/2}), \tag{1}$$

where $x(t)$ and $x(0)$ represent benzene conversion at any process time t and the conversion at $t = 0$, respectively. The conversion is defined as a dimensionless parameter. γ is the deactivation coefficient. Since this deactivation behavior is similar to the deactivation due to the coke deposition for the disproportionation reaction of cumene over a Co–Mo cracking catalyst [9], the catalyst could be deactivated by

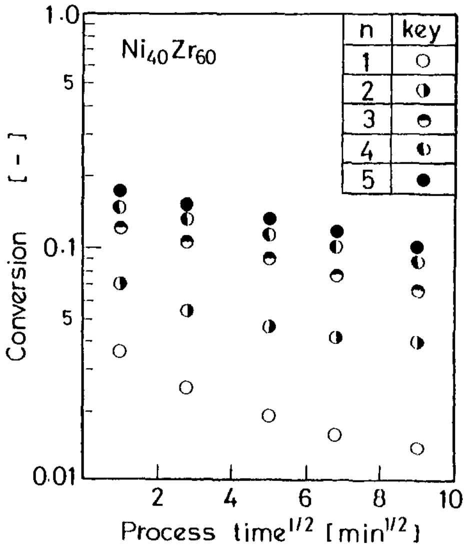

Fig. 1. Effect of regeneration number on benzene conversion over amorphous $Ni_{40}Zr_{60}$ alloy.

the coke deposition. Similar relationships as shown in fig. 1 are obtained for Ni–Zr alloys with different compositions. However, the constant activity was dependent upon the nickel content of the Ni–Zr alloy.

Fig. 2 shows the relationship between the benzene conversion and the square root of process time over the crystallized alloy prepared by the heating of the amorphous alloy in argon atmosphere at 865 K, which is 50 K higher than that of crystallization point, for 10 h. The crystallization was confirmed by an XRD measurement. Although the initial activity was higher than that of the amorphous alloy, the constant activity after five time regenerations is significantly lower than that of the amorphous alloy, as shown in fig. 1. The differences in the catalytic activity and the surface area between the amorphous alloy and crystallized alloy were observed in the reaction over $Pd_{35}Zr_{65}$ alloy [5].

Fig. 3 illustrates the effect of nickel content on the initial and constant benzene conversion over the amorphous Ni–Zr alloys. The conversions increase with the Ni content up to 50%, but they suddenly decrease with content over 50%. Fig. 4 demonstrates the relationship between alloy surface area after five regenerations and Ni content of the alloy. The surface area of $Ni_{30}Zr_{70}$ is 27 m^2/g and it increases with the nickel content up to 50%. The maximum surface area was 44 m^2/g for the $Ni_{50}Zr_{50}$ alloy. The value is almost the same as the area of the $Pd_{35}Zr_{65}$ alloy [5]. The surface area rapidly decreases with increasing Ni content over 50% as shown in fig. 3. These results indicate that the active nickel sites for the benzene hydrogenation increase with the number of regenerations. The XRD analysis shows that when the amorphous $Ni_{50}Zr_{50}$ alloy, which has a broad peak assigned to $NiZr_2$, was treated in an oxygen atmosphere at 623 K, new peaks assigned to NiO and ZrO_2

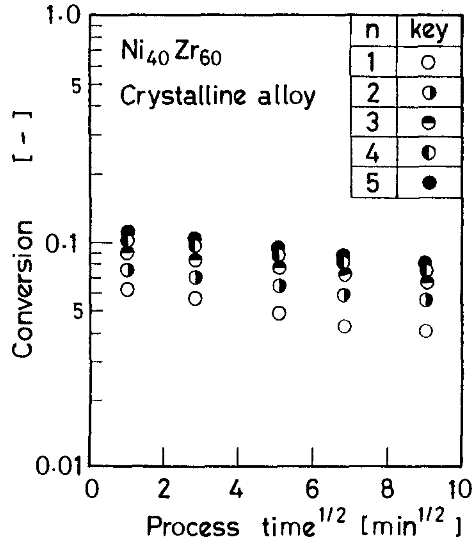

Fig. 2. Effect of regeneration number on benzene conversion over crystalline $Ni_{40}Zr_{60}$ alloy. Experimental conditions are the same as in fig. 1.

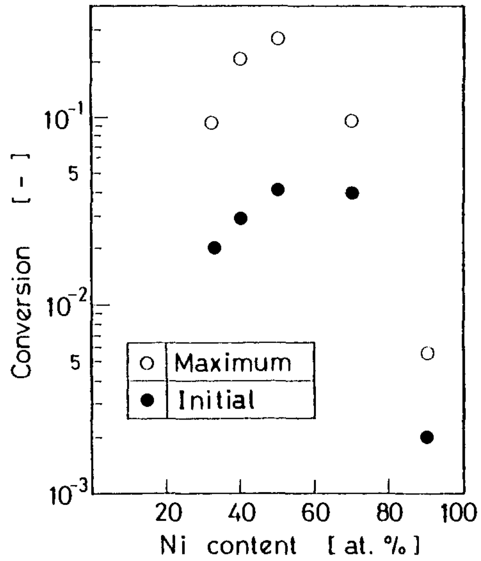

Fig. 3. Effect of nickel content on initial and maximum benzene conversion.

(mainly monoclinic) were observed. The NiO peaks disappeared and Ni peaks appeared with hydrogen treatment at 623 K for 3 h, but peaks representing ZrO_2 still remained. After the hydrogenation of benzene, peaks of Ni were still observed. As the peak height of monoclinic ZrO_2 increased with each repetition of the regeneration and reaction sequence, the ZrO_2 crystals were gradually produced by the oxidation. These results indicate that the surface area of the alloy increases with the growth of the crystals.

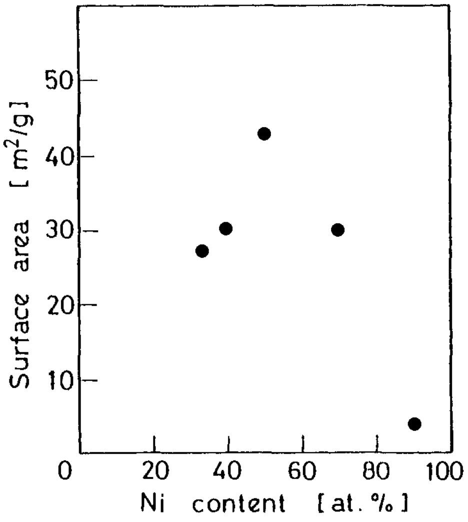

Fig. 4. Effect of nickel content on surface area of five times regenerated alloys.

The quantity of adsorbed hydrogen of the regenerated alloys was measured by a volumetrical method as described above. Since the dissociated hydrogen was adsorbed on the metal surface, the dispersion of nickel was calculated from the nickel content in the alloy and chemisorbed hydrogen quantity.

Fig. 5 demonstrates the relationship between the dispersion of Ni after five regenerations and Ni content. The curve in fig. 5 is similar to those in figs. 2 and 3. This result suggests that the crystal size of nickel is dependent on the surface area of the alloy.

Generally speaking, an integral reaction rate for the hydrogenation of benzene is represented by a Langmuir–Hinshelwood type equation in which adsorption equilibrium constants for hydrogen, benzene and cyclohexane should be evaluated [10]. To avoid the complexity, the reaction rate was measured by a differential method in this study. The reaction rate at low conversion level is represented by

$$-r = F\Delta x/\Delta W, \tag{2}$$

where $-r$ is disappearance rate of benzene (mol/(g s)), F is the molar feed rate of benzene(mol/s), Δx is the benzene conversion (–) and ΔW is the mass of the alloy (g). After a prescribed mass of the alloy after six time repetitions was placed into the reactor, the hydrogenation reaction was carried out under the same conditions as mentioned above. The conversion of benzene was adjusted to below 1% by the mass of the alloy. Since the turn-over frequency can sufficiently be calculated from the reaction rate obtained from eq. (2), we did not calculate the reaction rate constant and the adsorption equilibrium constants.

The turn-over frequency (TOF), which is defined as the reacted number of ben-

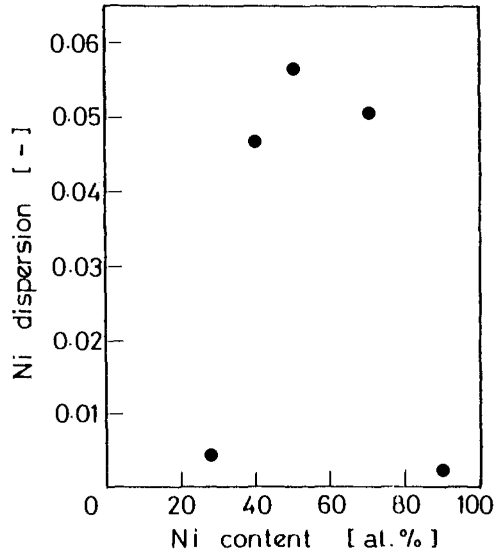

Fig. 5. Effect of nickel content on dispersion of five times regenerated alloys.

zene molecules per surface nickel atom per second (1/s), was calculated from the nickel dispersion and the reaction rate. The turn-over frequency is not dependent upon the nickel content as shown in fig. 6. This result suggests that the concentration of the surface nickel atoms changes with the content, but the activity of each nickel atom does not change with the nickel content.

To examine the effect of nickel content on catalytic activity and surface area, the change in mass of the Ni–Zr alloy by the oxidation was measured using a thermogravimetric balance. The prescribed mass (0.500 g) of the alloy was placed into a platinum perforated basket in a thermogravimetric balance. The alloy was heated at the rate of 5 K/min in air atmosphere from room temperature to 800 K. It should be observed that the mass of the alloy in the thermogravimetric balance increased with oxidation. Fig. 7 shows the relationship between the mass increase and oxidation temperature. The oxidation of the $Ni_{50}Zr_{50}$ alloy proceeds at the lowest temperature and this mass increase is maximum among the alloys. On the other hand, the mass of the $Ni_{90}Zr_{10}$ alloy does not change under the present oxidation conditions.

Since the amorphous Ni–Zr alloy has shorter repetitions of the Ni–Zr bond than the crystalline alloy [11], a broad peak assigned to $NiZr_2$ was observed in the X-ray diffraction pattern. The loose bonding between nickel and zirconium atoms is thermodynamically unstable compared to the crystalline form, then the amorphous alloy changes to crystalline alloy by heating at the crystallization temperature. The exothermic peak or peaks are observed by differential scanning calorimetry for the crystallization process. When the amorphous alloy is treated in an oxygen atmosphere even below the crystallization temperature, the oxygen could easily penetrate into the loose bond between nickel and zirconium. The amorphous alloy is divided into small blocks from the oxidizing layer. As a result,

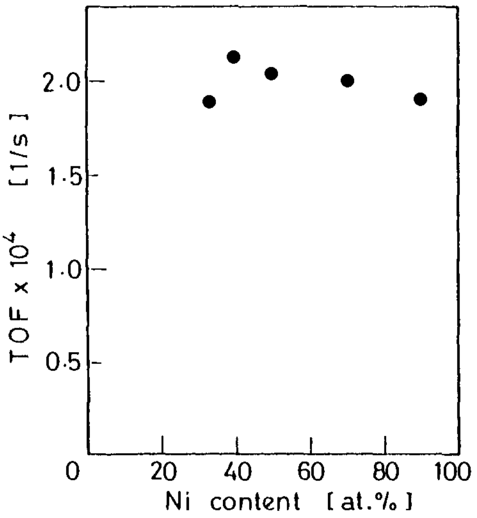

Fig. 6. Effect of nickel content on turn-over frequency of regenerated alloys.

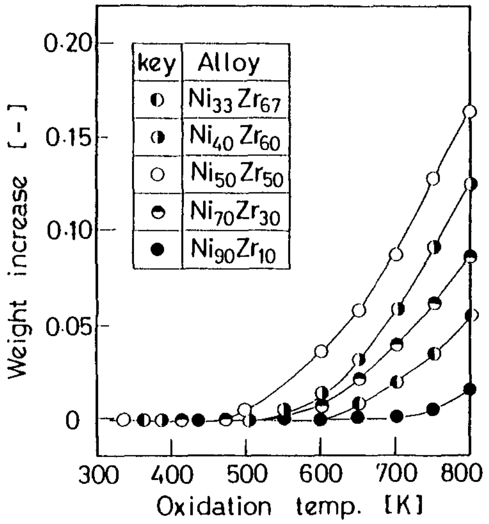

Fig. 7. Relationship between weight increase of Ni–Zr alloy and nickel content.

many cracks are developed on the alloy surface. Since oxygen diffuses into the small blocks from the cracks, the crystals of zirconium oxide and nickel oxide are prepared on the alloy surface.

Since the mass increase rate of amorphous $Ni_{50}Zr_{50}$ alloy was largest among the Ni–Zr alloys as shown in fig. 7, the structure of $Ni_{50}Zr_{50}$ could smoothly be reconstructed to the corresponding oxides by the treatment in oxygen atmosphere. The surface area and catalytic activity for the benzene hydrogenation were simultaneously increased with the repeated regenerations. It is found that a novel catalyst can be prepared using the amorphous alloys as precursor.

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