Hydrogenation of Benzene over Catalyst Prepared from Amorphous Pt–Zr Alloy

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The hydrogenation of benzene in a fixed-bed type reactor operated at atmospheric pressure over amorphous Pt–Zr alloys with different platinum composition (Pt₂⁰Zr₈₀, Pt₅₃Zr₴₇, Pt₃₂Zr₆₈) produced by a rapid solidification technique was investigated. Although the catalytic activity of the alloys was very low at virgin state, it gradually increased with increasing number of regeneration (oxidation and reduction)-reaction cycles. The activity approached a constant value after 5 or 6 regenerations. The hydrogenation activity of Pt–Zr alloy is higher than those of Pd–Zr and Ni–Zr alloys with the same composition. Furthermore, the turnover frequency of Pt–Zr defined as the reacting molecule per active site per second is also higher than those of Pd–Zr and Ni–Zr alloys. The hydrogenation order of the turnover frequency in the present study is almost the same as the order of the hydrogenation of olefins over the corresponding catalysts prepared from impregnation method. The characterization of the platinum catalyst prepared from the amorphous alloy revealed that the dispersion of platinum is higher than the impregnated catalysts, even though the platinum content of the former catalyst is much higher than that of latter. It is considered that this is a remarkable feature of the amorphous alloy catalyst.

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1. Introduction

The hydrogenation of benzene is an important reaction to synthesize cyclohexane as a raw material of Nylon-6. Recently, the hydrogenation of an aromatic compound in light oil is focused to reduce a particulate material in an exhaust gas from a diesel engine. Many catalysts including nickel and precious metals were used for the hydrogenation.

Many studies have been reported concerning the catalytic activities of amorphous alloys for hydrogenation.¹⁻³ Oxidation,⁴⁻⁵ NO reduction⁶ and methanol steam reforming reaction.⁷ Although some amorphous alloys had high activity even in a virgin state, the activity of Pd–Zr and Ni–Zr alloys was gradually improved by repeated regeneration by oxidation and reduction.⁸ The characterization of the regenerated Pd–Zr alloy revealed that the increase in the catalytic activity of the regenerated alloy was due to an increase in the palladium dispersion on the nano-size crystals of zirconium oxide produced by the oxidation treatment. The same improvement of catalytic activity was observed for the hydrogenation over a catalyst prepared from amorphous Ni–Zr alloys.⁹

In the present study, benzene hydrogenation runs were carried out over a catalyst prepared from amorphous Pt–Zr alloys with different compositions to elucidate the effect of platinum content on catalytic activity. Furthermore, the hydrogenation activity was compared with that over nickel and palladium catalysts.

2. Experimental

The uniform Pt–Zr alloys (Pt₂⁰Zr₈₀, Pt₅₃Zr₴₇ and Pt₃₂Zr₆₈) were prepared by melting of the prescribed masses of platinum and zirconium in an arc furnace under an argon atmosphere. Thin, long amorphous ribbons were prepared at the Institute of Material Science, Tohoku University, in an argon atmosphere by rapid quenching from molten alloy using a single copper roll. The crystallization temperature of the amorphous alloy was measured by differential scanning colorimetry (DSC). The observed crystallization is dependent on the composition of alloys from 776 to 873 K.

The hydrogenation runs were carried out in a fixed-bed quartz reactor. The experimental procedure were essentially similar to that presented in a previous paper.⁸ The long Pt–Zr alloy was cut with scissors into 1 mm fragments. 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%. The mixture of benzene and hydrogen was fed into reactor. The reaction was continued at 473 K for 2 h. The effluent gas was trapped into chilled toluene at a prescribed time intervals, and the products were analyzed using a gas chromatograph equipped a FID detector. Cyclohexane was the only product from the present benzene hydrogenation runs. Since the catalytic activity of the alloy increased with process time (time on stream) due to the deposition of coke on the catalyst surface, the used alloy was regenerated under the same conditions already described to obtain a constant activity.

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 in which the Langmuir equation was used for calculation. The catalyst pretreatment procedure for the measurement has been described in a previous paper. The dispersion of platinum was calculated from the hydrogen adsorption.
3. Results and Discussion

Figure 1 shows the effect of regeneration number on benzene conversion over Pt₂₃Zr₇₂ amorphous alloy at 473 K. Since the hydrogenation rate of benzene was represented by a Langmuir–Hinshelwood type equation, the apparent hydrogenation rate was a maximum around 473 K. The benzene conversion gradually increases with the regeneration number and reaches a constant conversion after six regenerations. The benzene conversion decreased with process time (time on stream) due to the coke deposition on the catalyst surface. The catalyst deactivation was represented by eq. (1), which was obtained from the catalyst deactivation of cumene cracking over a commercial cracking catalyst. \( x(t) = x(0) \cdot \exp(-\beta t^{1/2}) \).

Where, \( x(t) \) is benzene conversion at any process time, \( x(0) \) is initial benzene conversion, \( \beta \) is catalyst deactivation coefficient and \( t \) is process time. Similar relationship as shown in Fig. 1 are obtained for Pt–Zr alloys with different compositions. However, the constant activity was dependent on the platinum content in Pt–Zr alloy.

Figure 2 demonstrates the effect of platinum on the initial and constant benzene conversion. The conversion monotonously increases with the platinum content. Figure 3 shows the relationship between alloy surface area after six regenerations and platinum content of the alloy. The surface area of the alloys is independent on the platinum content. These results suggest that since the surface area was constant among the alloys, the active sites for benzene hydrogenation increase only with platinum content. The XRD analysis revealed that when the amorphous Pt–Zr alloys, which has a broad peak assigned PtZr₂, were treated in an oxygen atmosphere at 623 K, new peaks assigned to PtO and ZrO₂ (mainly monoclinic) were observed. The peaks due to PtO disappeared with hydrogen treatment at 623 K for 3 h, but the peaks assigned to ZrO₂ still remained. The peak assigned to Pt was observed after the hydrogenation instead of PtO. As the peak height of ZrO₂ increased with each repetition of the regeneration and hydrogenation sequence, the ZrO₂ was produced by the oxidation of zirconium in the alloy. Furthermore, the characteristic exothermic peaks corresponding to the change from amorphous state to crystallized state were not observed on DSC measurement. The TEM observation of the used alloy revealed that the layers of nano-size crystals of ZrO₂ were produced by the oxidation. These results supported that zirconium in the amorphous Pt–Zr alloy perfectly changed to zirconium oxide after 6 time regenerations and the increase in the surface area was due to the development of nano-size.
ZrO₂ crystals by the oxidation of the alloy.

Table 1 shows the relationship between the dispersion of platinum after five regenerations and platinum content. Table 1 also lists nickel and palladium dispersions after five or six regenerations under the same conditions. Although the dispersions of platinum are about 0.5, the nickel dispersion is below 0.1 and palladium dispersion is 0.2. Generally speaking, the dispersion of nickel on a nickel catalyst is lower than that of precious metals, because nickel atoms are agglomerated such as an island over a support. However, the platinum dispersion of the amorphous alloy is higher than that of a conventional impregnated catalyst, even though the platinum content is very large. This is a remarkable feature of the amorphous alloy catalyst.

Table 2 lists the turnover frequency (TOF) of the benzene hydrogenation over various amorphous alloy catalysts. Turnover frequency is defined as the molecule number reacted at unit second for unit active site. This means a measure of intrinsic hydrogenation activity of the active sites. The TOF of Pt–Zr alloy was largest among the alloys listed in Table 2. The TOFs of the crystalline alloy catalyst and a conventional platinum catalyst prepared from an impregnation method are almost same as those obtained from the amorphous alloys. It is known that the benzene hydrogenation rate does not depend on the structure of an active metal. As the result, the TOF is only decided by a kind of active metal. The order of the TOF is coincided with the order of olefin hydrogenation measured in liquid phase. It is found that platinum atom has the largest activity for the benzene hydrogenation.

The mass change of the amorphous Pt₃₀Zr₇₀ alloy by the oxidation was measured using a thermogravimetric balance. The prescribed mass of the alloy was placed into the platinum perforated basket in the thermogravimetric balance. The alloy was heated at the rate of 5 K·min⁻¹ in an 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. Figure 4 demonstrates the relationship between the mass increase and oxidation temperature. The oxidation of Pt–Zr alloys proceeds at the same temperature and the temperature is lower about 100 K than the crystallization temperature. Figure 4 also shows the oxidation behavior of the crystalline Pt₃₀Zr₇₀ alloy. The crystalline alloy was produced by the heating of the amorphous alloy at 50 K than the crystallization temperature for 17 h. The mass increase in the crystalline alloy is not observed in the present oxidation conditions. These results indicate that oxygen can easily diffuse into the amorphous alloy with relaxed structure. On the other hand, since the structure of the crystalline alloy should be very tight, oxygen did not penetrate into the lattice. The result was supported by the measurement of gravity of an amorphous alloy and a crystalline alloy, that is, the gravity of the crystalline alloy was larger than that of the amorphous alloy. As a result, the mass increase rate of the crystalline is smaller than that of the amorphous alloy.

### Table 1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Surface area [m² g⁻¹]</th>
<th>Platinum dispersion [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>am Pt₃₀Zr₇₀</td>
<td>37.0</td>
<td>0.46</td>
</tr>
<tr>
<td>am Pt₃₂Zr₇₀</td>
<td>39.5</td>
<td>0.52</td>
</tr>
<tr>
<td>am Pt₃₅Zr₆₈</td>
<td>38.4</td>
<td>0.47</td>
</tr>
<tr>
<td>cryst Pt₃₀Zr₇₀</td>
<td>12.5</td>
<td>0.14</td>
</tr>
<tr>
<td>am Pd₃₅Zr₆₈</td>
<td>48.0</td>
<td>0.33</td>
</tr>
<tr>
<td>am Ni₅₀Zr₅₀</td>
<td>32.4</td>
<td>0.085</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Benzene conversion [-]</th>
<th>Turnover frequency [s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>am Pt₃₀Zr₇₀</td>
<td>0.64</td>
<td>1.9 × 10⁻²</td>
</tr>
<tr>
<td>am Pt₃₂Zr₇₀</td>
<td>0.73</td>
<td>9.4 × 10⁻³</td>
</tr>
<tr>
<td>am Pt₃₅Zr₆₈</td>
<td>0.84</td>
<td>2.3 × 10⁻²</td>
</tr>
<tr>
<td>cryst Pt₃₀Zr₇₀</td>
<td>0.41</td>
<td>1.1 × 10⁻²</td>
</tr>
<tr>
<td>am Pd₃₅Zr₇₀</td>
<td>0.47</td>
<td>3.0 × 10⁻³</td>
</tr>
<tr>
<td>am Ni₅₀Zr₅₀</td>
<td>0.23</td>
<td>2.5 × 10⁻⁴</td>
</tr>
<tr>
<td>conv. Pt(1mass%)/Al₂O₃</td>
<td>0.21</td>
<td>1.0 × 10⁻²</td>
</tr>
</tbody>
</table>

Conventional Pt/Al₂O₃ was prepared by an impregnation method.

### Fig. 4

Relationship between mass increase of alloy and oxidation temperature.

4. Conclusions

The hydrogenation of benzene was carried out over the catalyst prepared from amorphous Pt–Zr alloy. The hydrogenation activity of Pt–Zr alloy catalyst was higher than that of Pd–Zr and Ni–Zr catalysts with the same composition. The platinum dispersion of the amorphous alloy catalyst was higher than that of a conventional impregnated catalyst supported on zirconium oxide, even though the platinum content of Pt–Zr alloy was larger than that of the impregnated catalyst. This means that the catalytic reactor size could be reduced using the amorphous alloy catalyst.

A novel hydrogenation catalyst will be prepared using the amorphous alloy as precursor.
Acknowledgments

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REFERENCES