Catalytic hydrogenation of tetrahydrophthalic anhydride

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Catalytic hydrogenation reaction of tetrahydrophthalic anhydride (THPA) to hexahydrophthalic anhydride (HHPA) has been studied. The effects of temperature, pressure, time and solvent on catalytic reaction have also been investigated. Raney Ni (T-1) has high activity towards hydrogenation of THPA to HHPA. The amount of HHPA formed constantly increases with increasing temperature in the experimental temperature range (70-100°C). The experimental results show that conversion of THPA and selectivity to HHPA reach 88% and 100%, respectively under the appropriate reaction conditions (T-1 Raney Ni, 7%, H2 pressure: 4.5 MPa, 45% DMF solution, reaction time 3.0h, temperature 95°C).

Hexahydrophthalic anhydride (HHPA) is an essential material for products of top grade quality coatings. The coatings tend to cause low pollution, low energy consumption, having high solid content and high durability. HHPA may replace aromatic acids for preparing polyester paint, polyurethane paint, amino-polyester paint, amino-alcohol acid paint and powder coatings. These coatings can remarkably reduce the viscosity, improve the brightness, gloss and solid content, and enhance strongly the climate durability of coatings. Furthermore, HHPA may be used as epoxy resin firming agent in the field of electrical appliances. HHPA may be prepared by phenolic anhydride hydrogenation or THPA hydrogenation. Because the former technology is complicated, this method is generally not adopted. Only a few of patents briefly describe THPA hydrogenation reaction giving HHPA. This paper reports the details of the hydrogenation of THPA to HHPA. The effects of temperature, pressure, time and solvent on catalytic reaction have also been investigated.

Experimental

THPA was a Merck Com. product. The catalyst used was Ni-Al alloy, which was a product of Shanghai Dechang Company. All solvents were dried and distilled by usual methods prior to use.

Catalytic reactions were carried out in a 500mL stainless steel pressure container. Catalyst (28 g), THPA (100 g) and solvent (35-80 g) were added. Nitrogen gas was passed through the container five times, then hydrogen gas was passed two times. When hydrogen pressure and the reaction temperature reached the assigned number, the reaction occurred.

Conversion of THPA and selectivity to HHPA (mass percentage) were determined by iodine value and IR spectra.

Results and discussion

Although olefin hydrogenation is a thermodynamically feasible reaction, it cannot occur without a catalyst. Because hydrogen molecule is extremely stable, H-H bond does not easily break as a result of polarization. Many transition metal elements (Ni, Pd, Pt, Co, Fe, Rh, Ru and Cu) exhibit catalytic activity towards olefin hydrogenation reaction. The activation of hydrogen molecule has two routes including hydrogen molecule as electron acceptor or electron supplier. In general, Raney Ni is used as the catalyst of olefin hydrogenation reaction.

Comparison of hydrogenation activities for THPA of different catalysts

The data in Table 1 show that Raney Ni can catalyse the hydrogenation reaction of THPA. The conversion of HHPA linearly increased with increasing Raney Ni activity in the reaction system. Our experimental results show clearly that Raney Ni(T-1) is a suitable catalyst for THPA hydrogenation to HHPA. If the activity of Raney Ni is very high, the catalyst is easily poisoned and also the hydrogenation reaction is too violent. Thus, Raney Ni means the T-1 type in the following discussion.

Reaction conditions: reaction temperature: 95°C, Raney Ni: 7%, reaction time: 2.0h, DMF, H2: 3.0 MPa, selectivity to HHPA: 100%.

Effect of H2 pressure on hydrogenation of THPA

Hydrogen gas is one of the reactants. Hydrogen pressure directly influenced the reaction results. The
Table 1—Comparison of hydrogenation activities for THPA of different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Preparation conditions</th>
<th>Conversion of THPA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-1</td>
<td>0°C, 25% NaOH, reaction time: 2-3h, washed with ethanol</td>
<td>19</td>
</tr>
<tr>
<td>W-2</td>
<td>25°C, 20% NaOH, reaction time: 2h, washed with ethanol</td>
<td>31</td>
</tr>
<tr>
<td>W-3</td>
<td>50°C, 20% NaOH, reaction time: 40min, washed with ethanol</td>
<td>41</td>
</tr>
<tr>
<td>W-4</td>
<td>50°C, 20% NaOH, reaction time: 1.5h, washed with ethanol</td>
<td>46</td>
</tr>
<tr>
<td>T-1</td>
<td>85°C, 10% NaOH, reaction time: 1.5h, washed with ethanol</td>
<td>53</td>
</tr>
<tr>
<td>T-2</td>
<td>90°C, 10% NaOH, reaction time: 1.5h, washed with ethanol</td>
<td>56</td>
</tr>
</tbody>
</table>

Table 2—Effect of H2 pressure on hydrogenation of THPA

<table>
<thead>
<tr>
<th>H2 pressure</th>
<th>Conversion of THPA (%)</th>
<th>Selectivity to HHPA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>15.9</td>
<td>100</td>
</tr>
<tr>
<td>3.0</td>
<td>43.6</td>
<td>100</td>
</tr>
<tr>
<td>4.0</td>
<td>48.8</td>
<td>100</td>
</tr>
<tr>
<td>5.0</td>
<td>52.8</td>
<td>100</td>
</tr>
<tr>
<td>6.0</td>
<td>55.9</td>
<td>100</td>
</tr>
</tbody>
</table>

amount of HHPA increased linearly with increasing H2 pressure in the observed reaction system (Table 2).

Reaction conditions: reaction temperature: 90°C, Raney Ni: 6.5%, reaction time: 2.0h, DMF solution (45%).

Effect of catalyst amount on hydrogenation of THPA

We studied the effect of the amount of catalyst Raney Ni on hydrogenation results of THPA. When Raney Ni amount was below 1%, the hydrogenation reaction did not occur. The amount of HHPA increased linearly with increasing Raney Ni content in the observed reaction system. When Raney Ni amount was above 7%, the yield of HHPA remained stable. Thus, 7% Raney Ni in the reaction system was appropriate considering the production cost. Also, the hydrogenation reaction was too violent to control if the amount of catalyst Raney Ni was very large.

Effect of reaction temperature on hydrogenation of THPA

The reaction temperature has considerable effect on hydrogenation of THPA to HHPA. The amount of HHPA constantly increased with increasing temperature in the experimental temperature range (70-100°C). But THPA easily polymerizes if reaction temperature is above 100°C.

Effect of solvents on hydrogenation of THPA

The effect of different solvents on hydrogenation of THPA was observed (90-95°C, 6.5% Raney Ni, H2 pressure: 3.3 MPa, reaction time 2.0 h). Because THPA has low solubility in benzene or toluene, the yield of HHPA is very low. THPA has larger solubility in DMF than that in THF; the yield of HHPA became to 51%. The amount of HHPA constantly increased with increase in polarity of the solvents in the reaction system. Furthermore, the hydrogenation reaction of THPA is very slow if the solvent content is below 25%.

To conclude, Raney Ni has high activity for the hydrogenation of THPA to HHPA. The good catalytic reaction results (the yield of HHPA: 88%, the selectivity: 100%) are obtained under suitable reaction conditions (45% DMF solution, temperature 95°C, 7% Raney Ni, H2: 4.5 MPa, reaction time: 3.0h). No byproduct has been detected in the reaction. These results show that this catalytic system has high catalytic efficiency and fine selectivity to the end product. Also the reaction materials are easily obtained and the price is low. These results offer a practical technology route for industrial production of HHPA.

Acknowledgement

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References