Preparation and Characterization of Porous Boehmite Particles and Pt/γ-Alumina

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Abstract: Hydrogenation reactions are utilized in various applications ranging from large-scale series catalyst processes in the oil refinery industry to small-scale batch processes in the pharmaceutical and fine chemical industries. Catalysts that consist of active materials often have inferior mechanical strength or thermal stability and are costly because they contain novel metals. Catalysts containing dispersed active materials in a suitable support are used to overcome these shortcomings. Porous Boehmite was fabricated, and the possibility of utilizing a metal catalyst used in hydrogenation reactions to impregnate the porous Boehmite was investigated. In addition, several properties, such as the metal particle size and the hydrogenation reaction rate, of the catalysts incorporating different supports were studied.

Keywords: boehmite, platinum, alumina, catalyst preparation

Introduction

Hydrogenation reactions are utilized in various applications ranging from large-scale series catalyst processes in the oil refinery industry to small-scale batch processes in the pharmaceutical and fine chemical industries. Hydrogenation is used in processes such as those producing cooking oil and in the manufacturing process that utilizes benzene to make cyclohexane. Consequently, the hydrogenation process varies depending on which reactants are used. Hydrogenation processes that add the hydrogen in carbon-carbon double or triple bonds make amines or alcohols. Other processes involving hydrogenation include the reactions producing methanol and ammonia through hydrogenation of carbon monoxide and nitrogen, respectively. Because there are several types of reactants, there may be many different characteristics of the hydrogenation reaction. Transition metal catalysts are mainly used in hydrogenation reactions. Although it is inexpensive, nickel catalyst is most widely used when a high hydrogenation vitality is required. Although they are expensive, palladium and platinum active materials are often utilized when high hydrogenation vitality and selectivity are needed [1-4]. Catalysts that consist of active materials often possess poor mechanical strength or thermal stability, and are costly because they contain novel metals. Therefore, catalysts containing dispersed active materials in a suitable support are used to overcome these shortcomings. A support material that is not involved in the catalytic reaction is commonly used. Using support materials that have a large surface area, as well as superior mechanical strength and thermal stability, allows a reduction in the amount of expensive novel metals, which may be filed into thin slices in the support used while still obtaining desired properties. In the 1950s, a synergistic effect resulting from using platinum catalyst dispersed in aluminum oxide was observed due to the interaction of platinum with acid sites of aluminum oxide. Consequently, because the support may possess dual functionality, there has been much interest in the interactions of support and active materials. The interactions between the support and metal are complicated because they involve multiple phenomena, such as the size of the impregnated metal particles, poisoning depending on contamination of the support, the arrangement of the support and metal, and whether adsorbed molecules overflow from the metal [5-9]. The most com-
mon preparation methods of supported metal catalysts, such as impregnation, ion-exchange, co-precipitation, and deposition-precipitation, involve two main steps: (i) introduction of the metal precursor on the support and (ii) transformation of the precursor to the active metallic phase. Due to the high number of variables generally involved in both steps, it is very difficult to have complete control over all parameters and, therefore, reproducible results are not easily achievable. Moreover, the above preparation methods generally lead to metallic clusters that are non-uniform in size on the support surface [10]. The synthesis of metal particles with a controlled and narrow size distribution is a critical factor for those catalytic reactions that are dependent on the dimensions of the active metal particle. The specific properties of nano-sized metal particles in catalysts are usually associated with a change in their electronic properties relative to the bulk samples. This change is a result of size effects, giving rise to an increase in the surface energy and a characteristic high surface-to-volume ratio. These features lead to an enhancement of the particle’s catalytic properties, because large fractions of the active metal atoms are on the surface and, thus, are accessible to reactant molecules and available for catalysis [11,12]. A precursor of γ-Alumina in the form of Boehmite has one hydrate per mole of aluminum oxide; it is commonly used in supports and catalysts for purifying exhaust and chemical catalysts for manufacturing ethylene oxide, as an adsorbent, and a precursor of ceramic products. Porous Boehmite was fabricated and the possibility of utilizing a metal catalyst for hydrogenation to impregnate the porous Boehmite was investigated in this study. In addition, the properties, such as the metal particle size and the hydrogenation reaction rate, of the catalysts with different supports were studied [13-18].

Experimental

Firstly, an aluminum nitrate aqueous solution (Solution A) and an ammonia water solution (Solution B) were prepared. Three mixing procedures (P2jet, P1jetAB, and P1jetBA) were used in this study, details of the methods are listed in Table 1. The P2jet method included pouring solutions A and B together in distilled water with equal quantities of the two solutions. In the P1jetAB method, solution A was poured into a mixture of solution B and water. Finally, in the P1jetBA method, solution B was poured into the mixture of solution A and water. Here, pouring was performed by continuous flow using a micro feeding pump to form nano-sized particles with the pore volume and feeding flux held constant at 2.5 mL/min. The reactor temperature was kept constant at 90 °C for 2 h in the reactor containing an attached stirrer. Support A had residual materials that were washed with distilled water and ethanol using a centrifugal separator operated at 6,500 rpm. Support B was the Support A material that had been dried at 100 °C for 24 h. Support C was the Support B product that had been calcined at 520 °C for 2 h in a 100 mL/min air flow. Finally, Support D was commercial γ-alumina (Strem).

Pt/γ-Alumina catalysts were synthesized by impregnation of different supports. The required amount of 8 wt% liquid H2PtCl6, dissolved in 50 mL of water was directly impregnated onto the four types of supports. As a rule, the metal loading on the support corresponded to 5 wt%. The temperature was increased to 70 °C and the mixture was stirred vigorously in a closed beaker for 3 h. Then, after adsorption equilibrium had been reached, the excess water was removed using a rotary evaporator. The catalyst was then dried overnight in air at 120 °C, followed by calcination in a 100 mL/min air flow for 2 h. Reduction was accomplished using a 50 mL/min H2 flow for 2 h at 400 °C. The hydrogenation of a mixture of 1-hexene and n-heptane at a 1-hexene/n-heptane molar ratio of 1:8 was carried out using a fixed bed reactor under continuous flow and atmospheric pressure. The sample amounts used were 0.375 g. The reaction temperature investigated was 30 °C. The products were analyzed online by a gas chromatograph equipped with a flame ionization detector.

The porous properties of the as-prepared and heated samples were obtained from the adsorption-desorption N2 isotherms (ASAP2020, Micromeritics) studied at -203 °C. The specific surface area (S, m2/g) was calculated by a BET method using the data determined in the relative pressure (P/P0) range from 0.05 to 0.30. The pore size distribution was calculated by the BJH method using the desorption isotherm (0.05 ≤ P/P0 < 1). The total pore volume (V, mL/g) was obtained using the maximum desorption at P/P0=0.99. TEM was used to determine the particle size and shape of the platinum nanoparticles supported on alumina (JEM2010, JEOL). XRD analysis was performed to determine the crystal structure of the samples (PW 1730, Philips).

Results and Discussion

The zeta potential was investigated to determine the most suitable pH within the range of 5 to 9. Ionic precursors, such as metal ions, or nonionic precursors, such as alkoxide, form primary particles extending the hydrolysis or condensation process, and these materials grow or form secondary particles by cohesion. Brownian motion, van der Waals forces, and steric interactions that cause repulsive forces similar in magnitude to the attractive forces present should exist between solids to prevent co-
Table 1. Porous Properties of Powders Obtained Using Various Conditions

<table>
<thead>
<tr>
<th></th>
<th>Specific surface area (m²/g)</th>
<th>Total pore volume (mL/g)</th>
<th>Micro pore volume (mL/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Support A</td>
<td>308.54</td>
<td>0.3001</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P2jet (60 °C**, 10 mL/min*)</td>
<td>386.46</td>
<td>1.2052</td>
<td>0.02313</td>
<td>10</td>
</tr>
<tr>
<td>P1jetAB (60 °C**, 10 mL/min*)</td>
<td>275.55</td>
<td>0.1562</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Support C calcined at 520 °C</td>
<td>326.32</td>
<td>1.3600</td>
<td>0.00493</td>
<td>13</td>
</tr>
<tr>
<td>Calcined at 900 °C</td>
<td>154.77</td>
<td>0.8800</td>
<td>0.00390</td>
<td>18</td>
</tr>
<tr>
<td>Calcined at 1100 °C</td>
<td>103.15</td>
<td>0.6600</td>
<td>0.00214</td>
<td>22</td>
</tr>
<tr>
<td>Support D (Strem)</td>
<td>185.00</td>
<td>0.4300</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Feed rate; **reaction temperature

hesion of particles and to maintain particle stability. Derived cohesion between particles is more important than colloid stability to form pores. The effect of the zeta potential on the precipitated pH was measured. The surface charges were positive in the pH range 5 ~ 9, with an isoelectric point found at pH 9. At this point, there was no electrostatic repulsive force and cohesion may occur. Dispersion is important in forming stable colloidal particles that have large specific surface areas. However, this research focused on the porous Boehmite formed by experiments at pH 9, where derived cohesion of primary particles may occur. The specific surface areas of the samples at pH values of 7, 8, and 9 were 135.92, 174.81, and 308.54 m²/g, respectively, as determined by BET analysis. The pore volumes of the samples at pH values of 7, 8, and 9 were 0.1024, 0.1278, and 0.3001 mL/g, respectively. TEM images of the particles formed as a function of the mixing procedure, obtained at a 10 mL/min feeding rate, are shown in Figures 1 (a), (b), and (c).

In the case of (a), which utilized the P2jet mixing procedure, fibrillar particles were obtained and pores formed between the particles. The specific surface area of the sample was 308.54 m²/g with a pore volume of 0.3001 mL/g, corresponding to inter-fibrillar porosity. In the case of (b), in which the P1jetAB mixing procedure was used, fibrillar particles were not observed, and the particles were densely formed. The specific surface area of the sample was 275.55 m²/g, and the pore volume was 0.1562 mL/g because spaces between the particles were not formed. In the case of (c) using the P1jetBA mixing procedure, fibrillar particles were partially observed. The pore volume was 0.07 mL/g more than that obtained when using the P2jet method as determined from BET analysis. However, this difference was negligible and, therefore, the P2jet mixing procedure was selected, which improved the specific surface area and pore volume. In addition, the TEM results confirm that particles and pore volumes of a more equal size existed when using the P2jet method. The P2jet mixing procedure was not a batchtype process. Although this method involved consecutively feeding two aqueous solutions until the reaction ended, the pH could be maintained because the same quantities of the two solutions were poured simultaneously. This method created primary particles of equal size because of the super saturation of the reacted system. In addition, the particles formed had a low-density porous structure as a result of the ability to maintain the pH at the isoelectric point, where cohesion of primary particles may have occurred. Aggregations of fibrillar particles were formed at temperatures above 60 °C, but the fibrillar shape was not observed, and the particles were not densely cohered at 30 °C. Also, the pore volume decreased to a greater extent than did the specific surface area. Therefore, the porous properties were affected by the shape of the particles. By increasing the temperature from 60 to 90 °C, the shape of the primary particles changed. Porous Boehmite particles, which had high specific surface areas and uniform nano-sized particles, were prepared for use as metal catalyst supports. The particle properties were affected by the pH, mixing procedure, temperature, and feeding rate. The P2jet-type method allowed the pH to be uniformly maintained during the precipitation, which improved the specific surface area and pore volume of the particles. Increasing the temperature and decreasing the feeding rate resulted in particles having large specific surface areas and pore volumes. Also, fibrillar-shaped particles were observed when using a reaction temperature at or above 60 °C. Typical isotherms for alumina treated at 100, 500, 900, and 1100 °C are shown in Figure 2; pore property data are given in Table 1.

All of the samples exhibited a type-IV isotherm based on the BDDT classification [19]. Typical type-IV sample characteristics of mesoporous materials, such as high
BET values and a marked hysteresis associated with capillary condensation in the mesopore range ($2 \sim 100$ nm), were observed. The specific surface area values increased upon decreasing the calcination temperature. An increase in the total pore volume, therefore, resulted from a decrease in the number of pores and an increased pore size at 500°C. Because the particles and pores had collapsed and sintered, the number of pores decreased. It was thought that the particles and pores were not collapsed and agglomerated at temperatures above 900°C, but the specific surface area and pore volume decreased. It is assumed that there was no change of structure when the calcination temperature was increased from 100 to 500°C, as shown in Figure 3. Secondary particles existed in the pore spaces.

The XRD patterns of the synthesized and commercial

Pt/γ-Alumina samples are shown in Figure 4. It was confirmed that the main peak of Pt appeared at 40° ($2\theta$). The peak was very small when the sample was
impregnated with Pt in a slurry support and Boehmite dried at 100 °C. However, the peaks were very high when the samples were impregnated with Pt in a support calcined at 500 °C and impregnated with Pt in a commercial-Alumina. Because the dry, calcined, and hydrogenation conditions were the same after impregnation, and the Pt content was the same, the peak heights were expected to correlate with the particle size.

Figure 5 shows the Pt particle size as a function of the synthesis conditions. The catalyst made with a Pt-impregnated slurry support had angstrom-sized metal particles. The Pt-500 catalyst synthesized with a Pt-impregnated slurry support had nano-sized particles. Finally, the commercial Pt/\(\gamma\)-Alumina had 1 ∼ 2 nm-sized Pt particles. In terms of the hydrogenation of 1-hexene, Figure 6 shows that the catalyst derived from slurry was the most effective, followed by Pt-500, commercial Pt, Pt-100, and commercial Pt/Alumina catalyst.

**Conclusions**

Porous Boehmite particles were prepared as platinum catalyst supports having a high specific surface area and uniform nano-sized particles. These properties were affected by the pH, mixing procedure, temperature, and feeding rate. The P2jet-type mixing process maintained the pH uniformly during the precipitation; it was used to improve the specific surface area and pore volume of the particles. By increasing the temperature and decreasing the feeding rate, this method generated large specific surface areas and pore volumes. Also, it resulted in fibrillar-shaped particles at reaction temperatures above 60 °C. Catalysts that use slurry support showed superior performance in terms of their hydrogenation behavior, and had the smallest Pt size. As a result, we determined that the hydrogenation reaction performance was directly related to the size of Pt. The Pt formed by impregnation at 500 °C was smaller than the Boehmite support. Therefore, the catalyst performance was related to size.

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**References**

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