Liquid phase hydrogenation of cyclohexene over Pt/aluminum borate catalyst

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The hydrogenation of cyclohexene over Pt catalysts supported on alumina, activated carbon, and aluminum borate is investigated in a liquid phase batch reactor at a temperature of 60°C and a hydrogen pressure of 1 atm. The dispersion of Pt metal on these catalysts was determined by hydrogen adsorption in gas volumetry. Under the conditions employed in this study, the aluminum borate-supported catalyst was found to possess the highest activity. This can be attributed to its high metal dispersion and high turnover frequency.

Keywords: Platinum, liquid phase hydrogenation, cyclohexene hydrogenation, aluminum borate

1. Introduction

Hydrogenation of unsaturated hydrocarbons has been known to be an important industrial process. It is usually catalyzed by two classes of solids: noble metals, such as platinum, palladium, ruthenium, rhodium, and metal sulfides, such as WS_2 and MoS_2. Generally, these catalysts have been supported on γ-Al_2O_3 and activated carbon [1,2]. Recently, some studies have suggested [3–5] that the nature of the support might play a significant role in determining catalytic activity. Explanations have been given in terms of the interactions between the metal crystallites and the carrier.

Aluminum borate has been reported to be a good support for hydrodesulfurization catalysts [6]. It has a unique pore structure, high surface acidity, and high hydrothermal stability [7,8]. In the present study, platinum supported on γ-Al_2O_3, activated carbon, and aluminum borate carriers have been prepared, characterized and tested in the liquid phase hydrogenation of cyclohexene.

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2. Experimental

Catalyst preparation

The synthesis of aluminum borate (AB) with Al/B atomic ratio of 20 followed the method of Peil et al. [9]. The pH of the solution during synthesis was controlled at 9.00. After synthesis, AB was calcined at 500°C overnight. For comparison, conventional supports, such as γ-alumina and activated carbon (all from Strem Chemicals), were also used as a support for platinum.

Supported catalysts were obtained by incipient-wetness impregnation of $Pt(NO_3)_2$ aqueous solution. The Pt metal loading was 1 wt%. The catalyst was then reduced under a stream of hydrogen, the temperature was programmed at 1°C/min from room temperature to 400°C, then remained for 2 h. The reduced catalyst was used immediately in order to prevent air oxidation of the metal. All catalysts were characterized by volumetric H_2 chemisorption measurement at ambient temperature.

The hydrogenation of cyclohexene was performed in a CSTR pyrex reactor at 50°C under 1 atm hydrogen pressure. Ethanol was used as a solvent. It was determined that a stirrer speed of 600 rpm was more than sufficient to eliminate film resistances from influencing the observed reaction rates. Similarly, it was determined that catalyst particles with an average diameter of 90 μm were sufficient to eliminate internal mass diffusional resistances from influencing the observed reaction rates. All reaction runs were conducted with a stirrer speed of 600 rpm, while the catalyst particles did not exceed 90 μm in diameter. After certain interval, the reaction mixture was withdrawn and analyzed by HP 5890 gas chromatography with a flame ionization detector.

3. Results and discussion

Table 1 lists the hydrogen uptake and metal dispersions of the catalysts. The results indicate that AB support gives the highest hydrogen uptake and Pt metal dispersion. This is possibly due to the high concentration of acid sites on AB. In a previous paper [8], we have reported that the acid concentration is increased significantly with the incorporation of boron into the alumina support.

Table 1
Hydrogen uptake of Pt catalysts

Catalyst	H_2 uptake (μmol/g)	Pt dispersion (%)
Pt/C	10.9	42.5
Pt/Al_2O_3	11.2	43.7
Pt/AB	14.2	55.4
$Pt/B\text{-}Al_2O_3$	7.6	29.6

Table 2
The reaction rate and turnover frequency of Pt catalysts in cyclohexene hydrogenation (reaction condition: 50°C, 1 atm H_2 pressure)

Catalyst	Activity (mol/g s)	TOF (1/site s)
Pt/C	2.27×10^{-3}	104
Pt/Al_2O_3	2.29×10^{-3}	102
Pt/AB	2.25×10^{-2}	732
$Pt/B\text{-}Al_2O_3$	3.83×10^{-3}	252

The specific activity of Pt/AB is ten times higher than those of Pt/carbon and Pt/Al_2O_3. This can be attributed to its high metal dispersion and high turnover frequency. The different TOFs on AB, alumina, and activated carbon supported catalysts may be due to the promotion effect of boron. Boron is the promoter for most hydrogenation catalysts [10,11]. The interaction of boron with Pt metal affects the electronic structure of the metal and the activity for hydrogenation. In order to verify the effect of boron on AB supported catalysts, we impregnated Pt/Al_2O_3 with boric acid, the TOF increased twice, as shown in table 2. The electronic effect of boron in AB may strengthen the metal–hydrogen bond and increase the hydrogenation capability of the metal. The results of this study indicate that aluminum borate can be used as a support for hydrogenation catalysts. It demonstrates an excellent hydrogenation capability, compared to the conventional alumina and activated carbon.

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