AlCl₃ Supported Catalysts for the Isomerization of Endo-Tetrahydrodicyclopentadiene

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ABSTRACT

Two of zeolites such as Hβ and HY, and mesoporous HMCM-41 were used as supports to immobilize AlCl₃ for the investigation of the isomerization of endo-tetrahydrodicyclopentadiene (endo-TCD). The dependences of porous structure and surface acidity of the AlCl₃ immobilized catalysts on the activity and selectivity were studied. Based on characterization studies, both the large pore diameter and strong acid sites of the supported catalysts contributed to the high activities in the endo-TCD conversion. And specifically the stronger Lewis acid sites seems to be responsible for the higher selectivity onto exo-TCD, and the stronger Brönsted acid sites were crucial to the formation of adamantane through the further isomerization of exo-TCD.

Keywords: Tetrahydrodicyclopentadiene; Isomerization; Zeolite; Immobilization; Aluminium Chloride

1. Introduction

Endo-tetrahydrodicyclopentadiene (endo-TCD) has been typically formed through the dimerization followed by hydrogenation from dicyclopentadiene, and its isomers, both exo-tetrahydrodicyclopentadiene (exo-TCD) and adamantane (ADH), are very useful fine chemical products [1-3]. In industry, exo-TCD and ADH are produced through the rearrangement of endo-TCD by acid catalysis [4], as shown in Scheme 1. Due to the advantages of low reaction temperature and strong resistance to ward coke, AlCl₃ has been used as the most widely used catalyst [5], but it causes environmental problems such as severe corrosion and difficulty in separation from the reaction mixture. In the 1980s, liquid type superacids, such as CF₃SO₃H and SbF₅-graphite, were used to catalyze endo-TCD to exo-TCD [6]. However, the problems of separation and corrosion were still remained. Since the 2000s, ionic liquids [7] were used to isomerize the endo-TCD, which resulted in pretty good result, but the expensive price restricts its industrial application. Hence, there is a strong motivation to develop new catalyst system for the isomerization that has minimum environmental impact. On the other hand, during the past decades, zeolites have been drawn much attentions in the

Scheme 1. Exo-TCD and ADH are produced through the rearrangement of endo-TCD by acid catalysis.

rearrangement of endo-TCD [8,9]. However, the low activity of zeolites limits its industrial application. Since then, the immobilization of AlCl₃ on inorganic solid supports has been proposed [10-12]. In our previous study [13,14], we developed the catalysts of AlCl₃ immobilized on SiO₂, Al₂O₃ and MCM-41, and found that it could keep the excellent reactivities of traditional AlCl₃ catalyst at mild reaction conditions for endo-TCD isomerization, and the properties of supports strongly affected to the product selectivity. It is known that the reaction mechanism for the endo-TCD isomerization to exo-TCD and ADH is a carbenium ion skeleton rearrangement [4]. So, the pore structure and acid type of the catalyst seem to be important parameters in the conversion and product distribution. In the present report, Hβ and HY zeolites, and HMCM-41mesoporous material were used as catalyst supports to immobilize AlCl₃ for the purpose of dif-

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ferentiating both pore structures and acidities. Based on the property changes of supports after AlCl\textsubscript{3} immobilization, the influences of porous property, the type of acidities, and acidic strength of catalysts on both endo-TCD conversion and product selectivities in the endo-TCD rearrangement reaction were investigated.

2. Experiment

2.1. Catalyst Preparation

The H\textbeta and HY zeolites were purchased from Nankai Catalyst Co., China. HMCM-41 was prepared by the tetraethyl silicate (TEOS) in basic solution condensation with cetyltrimethylammonium bromide (CTAB) as a supramolecular template, and by ion-exchange with HNO\textsubscript{3} [15]. The immobilized AlCl\textsubscript{3} catalyst was prepared by a two-step method as described in our previous publications [13].

2.2. Catalyst Characterization

The BET surface areas and the pore properties of the catalysts were measured by nitrogen physisorption by using a Micromeritics Gemini 2395 instrument at 77 K. In-situ Fourier Transform Infrared Spectra (FT-IR) of chemically adsorbed pyridine were collected on a Nicolet 360 FT-IR spectrophotometer. All spectra were taken at a resolution of 2 cm\textsuperscript{-1} for 32 scans. Catalysts were activated in an IR cell at 550 °C under vacuum for 2 h, cooled down to room temperature, followed by exposure to pyridine at this temperature for 30 min. The samples were heated up to 150 °C or 250 °C and evacuated under vacuum (10\textsuperscript{-3} Torr) for 1 h to remove physically adsorbed pyridine. Finally, the spectra were recorded at the desired temperatures.

2.3. Catalyst Activity Test

The isomerization rearrangement reaction was carried out in a batch suspension reactor. The catalyst was charged into 20 ml n-heptane solution. The reaction temperature was controlled by an oil bath equipped with a thermostat and an electric stirrer. The reaction pressure of 1.0 MPa was set by the replacement of air by N\textsubscript{2} to keep the solvent in liquid phase. The reaction time was 3 h. The products were analyzed by an Agilent 6890 GC equipped with an HP-5 capillary column and FID detector of HP 6890/5973 GC-MS.

3. Results and Discussion

The physico-chemical properties of the catalysts are summarized in Table 1. The specific surface area and pore diameter of HMCM-41 were 1001 m\textsuperscript{2}/g and 2.33 nm, respectively, which were much higher than that of both HY and H\textbeta due to the mesoporosity. After AlCl\textsubscript{3} was loaded, the decreasing surface area, pore volumes, and pore diameters were observed for both AlCl\textsubscript{3}/zeolites and AlCl\textsubscript{3}/HMCM-41 catalysts. This was primarily due to the penetration of AlCl\textsubscript{3} into the pores of supports and located mostly inside of pores. Specially, HY showed the most drastic decresse in its surface area (46 m\textsuperscript{2}/g) and pore volume (only 0.02 cm\textsuperscript{3}/g) after AlCl\textsubscript{3} immobilization, indicating that the pore channel of HY seemed to be greatly blocked by the large amounts of AlCl\textsubscript{3} loading of 45.3%. However, the mass fractions of [-O-AlCl\textsubscript{2}] on the case of H\textbeta and HMCM-41 were 13.2% and 20.1%, respectively. So, they sustained pretty high pore volumes and surface areas even after immobilization of AlCl\textsubscript{3}. The mechanism of AlCl\textsubscript{3} immobilization onto the supports were proposed via the surface reaction of AlCl\textsubscript{3} with surface hydroxyl groups of the supports accompanied with HCl release [16,17]. Over 90% of the chloroaluminium species on the surface of the immobilized supports had the composition of [-O-AlCl\textsubscript{3}] [16]. So, the higher [-O-AlCl\textsubscript{3}] loading on HMC-M41 could be attributed to its higher surface area and more abundant surface hydroxyl groups.

The types of acid sites (Lewis and Brønsted) were studied by in-situ FT-IR adsorption of pyridine. The infrared spectra of the pyridine-adsorbed H\textbeta and HY (in Figure 1) revealed three peaks at ca. 1449 and 1540 cm\textsuperscript{-1} due to pyridine adsorbed on Lewis and Brønsted acid sites, respectively, and ~1480 cm\textsuperscript{-1} band corresponded to both Lewis and Brønsted (L+B) sites [18,19]. The infrared spectrum of the pyridine adsorbed HMCM-41 was somewhat different from those on HY and H\textbeta since it only showed Lewis acid sites at 1449 cm\textsuperscript{-1}. After immobilization of AlCl\textsubscript{3}, the amounts of acid sites on catalyst surfaces increased remarkably in all the cases. The infrared spectra of all the samples recorded after evacuation at 150 °C and 250 °C are indicating total acid sites and only strong acid sites, respectively, and the difference between them could be presumed to show weak acid sites of the catalysts. Based on the spectra in Figure 1, the adsorption capacities were the planimetered ac-

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area (m\textsuperscript{2}/g)</th>
<th>Pore Volume (cm\textsuperscript{3}/g)</th>
<th>Pore Size (nm)</th>
<th>Mass Fraction of [-O-AlCl\textsubscript{3}] (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HY</td>
<td>579</td>
<td>0.25</td>
<td>0.59</td>
<td>-</td>
</tr>
<tr>
<td>H\textbeta</td>
<td>478</td>
<td>0.16</td>
<td>0.58</td>
<td>-</td>
</tr>
<tr>
<td>HMCM-41</td>
<td>1001</td>
<td>0.58</td>
<td>2.33</td>
<td>-</td>
</tr>
<tr>
<td>AlCl\textsubscript{3}/HY</td>
<td>46</td>
<td>0.02</td>
<td>0.51</td>
<td>45.32</td>
</tr>
<tr>
<td>AlCl\textsubscript{3}/HMCM-41</td>
<td>291</td>
<td>0.12</td>
<td>0.52</td>
<td>13.20</td>
</tr>
<tr>
<td>AlCl\textsubscript{3}/HMCM-41</td>
<td>710</td>
<td>0.36</td>
<td>2.00</td>
<td>20.08</td>
</tr>
</tbody>
</table>
According to the peak areas and normalized with both surface areas and wafer thickness of the catalysts [20], and the calculation results are listed in Table 2. It can be found that the pure HMCM-41 possessed only weak Lewis acid sites. After immobilization of AlCl₃, it still lacked of strong Brønsted acid sites but owned abundant strong Lewis acid sites, which was as high as 11.50 (a.u.) cm⁻¹·cm²·mg⁻¹. HY showed fewer strong Brønsted acid sites and strong Lewis acid sites, but after immobilization of AlCl₃ on HY by forming AlCl₃/HY, both strong Brønsted acid sites and strong Lewis acid sites increased simultaneously. For Hβ, it exhibited both the strongest Brønsted and Lewis acidities among the three supports, and those properties were also enhanced after AlCl₃ immobilized on Hβ to form AlCl₃/Hβ. It is interesting that the amount of AlCl₃ loading on HY was much more than that on both HMCM-41 and Hβ, as shown in Table 1, but the number of total acid sites on AlCl₃/HY was lower than that on AlCl₃/Hβ and AlCl₃/HMCM-41. It is mainly because of huge pore block in the case of AlCl₃/HY.

Since the isomerization reaction of endo-TCD → exo-TCD → ADH is a consecutive reaction, the pore structure and surface acidity of solid acid catalyst were speculated to play important roles in the endo-TCD conversion and product selectivity. Table 3 shows the catalytic properties of supports and supported AlCl₃ catalysts for the isomerization of endo-TCD at 150°C and 250°C. Three pure supports showed no activity at 150°C. When reaction temperature was risen up to 250°C, HY and Hβ showed a certain degree of activity increase, while HMCM-41 still kept no activity. The results of FT-IR of pyridine adsorption listed in Table 2 shows that HMCM-41 had only weak Lewis acid sites, instead HY and Hβ owned both weak and strong acid sites. So, it can be suggested that the weak Lewis acid sites of solid acid catalyst might contribute insignificantly to the reaction.

For all the of AlCl₃ immobilized catalysts, the catalytic activities were greatly increased whether HY, Hβ and HMCM-41 as supports. Although the pores of AlCl₃/HY catalyst were largely blocked due to high AlCl₃ loading compared with the pure zeolites, it still allowed the reaction by the contribution of AlCl₃ on external surface.

The greatly enhanced activity over AlCl₃/Hβ could be ascribed to the increase in strong acidity of the catalyst as well as low blocking due to low loading of AlCl₃. The order of the strong acidity of the supported AlCl₃ catalysts are listed in Table 2 ranked as AlCl₃/Hβ > AlCl₃/HMCM-41 ≈ AlCl₃/HY, and the highest endo-TCD conversion of 95.7% was observed over AlCl₃/Hβ catalyst. It is noteworthy that the total strong acid sites on AlCl₃/HY and AlCl₃/HMCM-41 was quite similar, but the endo-TCD conversion of AlCl₃/HMCM-41 was much higher than that of AlCl₃/HY, which might be caused by the the diffusional limitation of partial pore blocking in the AlCl₃/HY catalyst. Therefore, the mesoporous structure of AlCl₃/HMCM-41 catalyst seems to be quite beneficial to the reactant diffusion to overcome the small amounts of Lewis acidity for the reaction.

The data in Tables 2 and 3 also show the dependence of surface acidity of catalyst on the product selectivity.

The ADH selectivities obtained at 250°C shows AlCl₃/Hβ > AlCl₃/HY ≈ Hβ > HY = AlCl₃/HMCM-41, which seemed to be corresponding to the amounts of strong Brønsted acid sites of catalysts (see Table 2). AlCl₃/Hβ possessed the large number of strong Brønsted acid sites, and its ADH yield reached 25.6%, while the others were lower than 4%. The AlCl₃/HY catalyst and Hβ support itself provided nearly the same amounts of strong Brønsted acid sites, and their ADH selectivities were almost same, which were 10.9% and 9.8%, respectively.
In contrast, AlCl₃/HMCM-41 showed only strong Lewis acidic sites and had no strong Brønsted acidity, then it exhibited the highest exo-TCD selectivity but the lowest ADH selectivity. Similar relationship between ADH selectivity and the amount of strong Brønsted acid sites could be found at the reaction temperature of 150 °C. These observations obviously indicate that strong Lewis acid sites of catalysts are attributed to the increases of selectivity of intermediate isomerization product, exo-TCD, and the strong Brønsted acid sites are responsible for the farther ADH formation.

The synthesis mechanism of exo-TCD and ADH goes through a carbenium ion rearrangement (Scheme 2). Endo-TCD is isomerized on an acid by two consecutive reactions: endo-TCD is first isomerized to form exo-TCD, and then ADH was formed through the isomerization of exo-TCD. The first isomerization of endo-TCD can be catalyzed by strong Lewis acids, while the second step of exo-TCD to ADH requires strong Bronsted acids.

### 4. Conclusion

We have prepared a series of AlCl₃ supported catalysts onto Hβ, HY, and HMCM-41 having different both porous structures and surface acidities. The dependence of the activity and selectivity in the conversion of endo-TCD to exo-TCD and ADH was studied by correlation with both porous property and surface acidity of the catalysts. The suitable pore diameter and strong acid sites of catalyst are requisite for the isomerization of endo-TCD. And the weak Lewis acid center of catalyst surface seemed to be no use to the catalytic activity for isomerization.
zation even at the high reaction temperature of 250°C. However, the strong acid sites controlled the distribution of the products distinctly. Strong Lewis acid sites are responsible to get the intermediate isomerization product of exo-TCD, and the strong Brønsted acid sites of catalyst are crucial for the formation of ADH. The result found herein is believed to be potentially important for the selective formation of exo-TCD or ADH by controlling acidity and its strength.

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