

AlCl₃ Supported Catalysts for the Isomerization of *Endo*-Tetrahydrodicyclopentadiene

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Received February 21, 2013; revised March 22, 2013; accepted March 30, 2013

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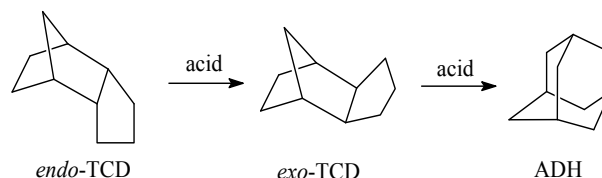
ABSTRACT

Two of zeolites such as H β 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 Brønsted 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, H β and HY zeolites, and HMCM-41 mesoporous 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_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 $\text{H}\beta$ 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_3 [15]. The immobilized AlCl_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^{-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^{-5} 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_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 $1001\text{ m}^2/\text{g}$ and 2.33 nm, respectively, which were much higher than that of

Table 1. Physico-chemical properties of supports and AlCl_3 supported catalysts.

Catalyst	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)	Mass Fraction of [-O-AlCl ₂](%)
HY	579	0.25	0.59	-
$\text{H}\beta$	478	0.16	0.58	-
HMCM-41	1001	0.58	2.33	-
AlCl_3/HY	46	0.02	0.51	45.32
$\text{AlCl}_3/\text{H}\beta$	291	0.12	0.52	13.20
$\text{AlCl}_3/\text{HMCM-41}$	710	0.36	2.00	20.08

both HY and $\text{H}\beta$ due to the mesoporosity. After AlCl_3 was loaded, the decreasing surface area, pore volumes, and pore diameters were observed for both $\text{AlCl}_3/\text{zeolites}$ and $\text{AlCl}_3/\text{HMCM-41}$ catalysts. This was primarily due to the penetration of AlCl_3 into the pores of supports and located mostly inside of pores. Specially, HY showed the most drastic decrease in its surface area ($46\text{ m}^2/\text{g}$) and pore volume (only $0.02\text{ cm}^3/\text{g}$) after AlCl_3 immobilization, indicating that the pore channel of HY seemed to be greatly blocked by the large amounts of AlCl_3 loading of 45.3%. However, the mass fractions of [-O-AlCl₂] on the case of $\text{H}\beta$ 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_3 . The mechanism of AlCl_3 immobilization onto the supports were proposed via the surface reaction of AlCl_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-AlCl₂] [16]. So, the higher [-O-AlCl₂] loading on HMCM-41 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 $\text{H}\beta$ and HY (in **Figure 1**) revealed three peaks at ca. 1449 and 1540 cm^{-1} due to pyridine adsorbed on Lewis and Brønsted acid sites, respectively, and $\sim 1480\text{ cm}^{-1}$ 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 $\text{H}\beta$ since it only showed Lewis acid sites at 1449 cm^{-1} . After immobilization of AlCl_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-

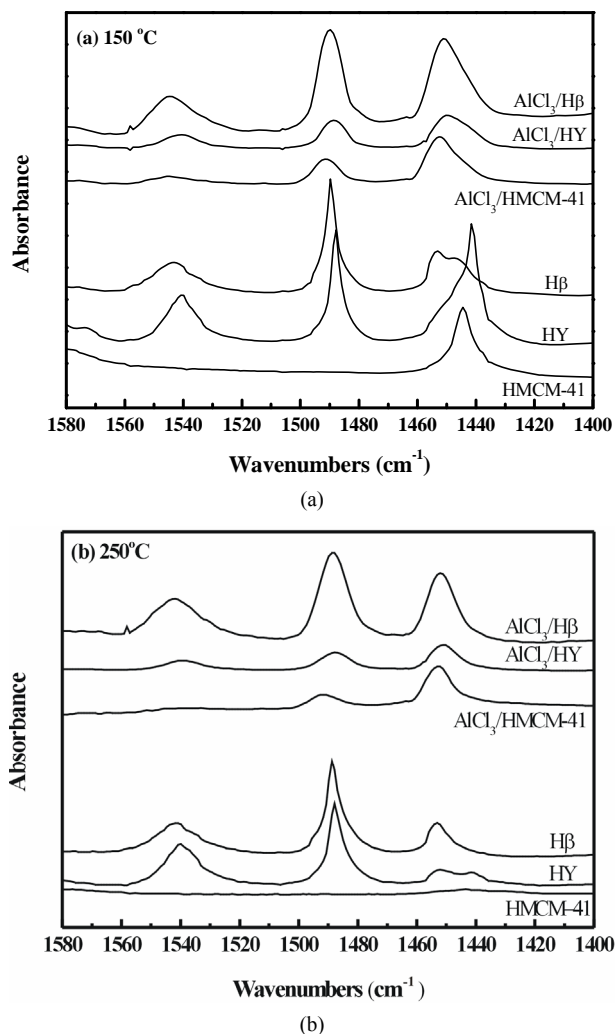


Figure 1. The infrared spectra of the pyridine-adsorbed over catalyst.

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 AlCl_3 , it still lacked of strong Brønsted acid sites but owned abundant strong Lewis acid sites, which was as high as $11.50 \text{ (a.u.)} \cdot \text{cm}^{-1} \cdot \text{cm}^2 \cdot \text{mg}^{-1}$. HY showed fewer strong Brønsted acid sites and strong Lewis acid sites, but after immobilization of AlCl_3 on HY by forming AlCl_3/HY , both strong Brønsted acid sites and strong Lewis acid sites increased simultaneously. For $\text{H}\beta$, it exhibited both the strongest Brønsted and Lewis acidities among the three supports, and those properties were also enhanced after AlCl_3 immobilized on $\text{H}\beta$ to form $\text{AlCl}_3/\text{H}\beta$. It is interesting that the amount of AlCl_3 loading on HY was much more than that on both HMCM-41 and $\text{H}\beta$, as shown in Table 1, but the number of total acid sites on AlCl_3/HY

was lower than that on $\text{AlCl}_3/\text{H}\beta$, and $\text{AlCl}_3/\text{HMCM-41}$. It is mainly because of huge pore block in the case of AlCl_3/HY .

Since the isomerization reaction of $\text{endo-TCD} \rightarrow \text{exo-TCD} \rightarrow \text{ADH}$ 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 AlCl_3 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 $\text{H}\beta$ 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 $\text{H}\beta$ 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 AlCl_3 immobilized catalysts, the catalytic activities were greatly increased whether HY, $\text{H}\beta$ and HMCM-41 as supports. Although the pores of AlCl_3/HY catalyst were largely blocked due to high AlCl_3 loading compared with the pure zeolites, it still allowed the reaction by the contribution of AlCl_3 on external surface.

The greatly enhanced activity over $\text{AlCl}_3/\text{H}\beta$ could be ascribed to the increase in strong acidity of the catalyst as well as low blocking due to low loading of AlCl_3 . The order of the strong acidity of the supported AlCl_3 catalysts are listed in **Table 2** ranked as $\text{AlCl}_3/\text{H}\beta > \text{AlCl}_3/\text{HMCM-41} \approx \text{AlCl}_3/\text{HY}$, and the highest endo-TCD conversion of 95.7% was observed over $\text{AlCl}_3/\text{H}\beta$ catalyst. It is noteworthy that the total strong acid sites on AlCl_3/HY and $\text{AlCl}_3/\text{HMCM-41}$ was quite similar, but the endo-TCD conversion of $\text{AlCl}_3/\text{HMCM-41}$ was much higher than that of AlCl_3/HY , which might be caused by the diffusional limitation of partial pore blocking in the AlCl_3/HY catalyst. Therefore, the mesoporous structure of $\text{AlCl}_3/\text{HMCM-41}$ 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 $\text{AlCl}_3/\text{H}\beta > \text{AlCl}_3/\text{HY} \approx \text{H}\beta > \text{HY} \approx \text{AlCl}_3/\text{HMCM-41}$, which seemed to be corresponding to the amounts of strong Brønsted acid sites of catalysts (see **Table 2**). $\text{AlCl}_3/\text{H}\beta$ possessed the large number of strong Brønsted acid sites, and its ADH yield reached 25.6%, while the others were lower than 4%. The AlCl_3/HY catalyst and $\text{H}\beta$ 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, $\text{AlCl}_3/\text{HMCM-41}$ showed only strong

Table 2. Absorption intensities of FT-IR of pyridine adsorbed on acid sites of the catalysts.

Catalysts	Integrated absorption intensity [(a.u.) $\times \text{cm}^{-1} \times \text{cm}^2 \times \text{mg}^{-1}$]								
	Total acid			Strong acid			Weak acid		
	Total	B acid	L acid	Total	B acid	L acid	Total	B acid	L acid
HY	7.61	2.45	5.16	2.72	1.81	0.91	4.89	0.64	4.25
$\text{H}\beta$	10.21	4.52	5.69	5.12	3.74	1.38	5.09	0.78	4.31
HMCM-41	4.49	0	4.49	0	0	0	4.49	0	4.49
AlCl_3/HY	17.65	4.86	12.79	11.12	3.43	7.69	6.53	1.43	5.10
$\text{AlCl}_3/\text{H}\beta$	52.35	18.84	33.51	33.25	14.86	18.39	19.10	3.98	15.12
$\text{AlCl}_3/\text{HMCM-41}$	18.48	2.13	16.35	11.50	0	11.50	6.98	2.13	4.85

Table 3. Comparison of the catalyst performances in the isomerization of endo-TCD.

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)			Yield (%)	
			<i>Exo</i> -TCD	ADH	Others	<i>Exo</i> -TCD	ADH
HY	150	0	0	0	0	0	0
$\text{H}\beta$	150	0	0	0	0	0	0
HMCM-41	150	0	0	0	0	0	0
AlCl_3/HY	150	15.6	98.4	0.8	0.8	15.4	0.1
$\text{AlCl}_3/\text{H}\beta$	150	37.9	95.4	3.1	1.5	36.1	1.2
$\text{AlCl}_3/\text{HMCM-41}$	150	64.4	99.3	0.6	0.1	63.9	0.4
HY	250	14.8	94.2	2.1	3.7	14.0	0.3
$\text{H}\beta$	250	37.3	88.3	9.8	1.9	33.0	3.7
HMCM-41	250	0	0	0	0	0	0
AlCl_3/HY	250	36.5	85.7	10.9	3.4	31.2	4.0
$\text{AlCl}_3/\text{H}\beta$	250	95.7	71.0	26.8	2.2	67.9	25.6
$\text{AlCl}_3/\text{HMCM-41}$	250	76.3	97.3	2.1	0.6	74.3	1.6

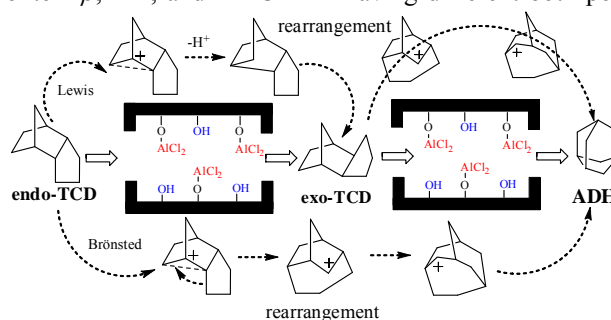
Lewis acidic sites and had no strong Brönsted acidity, then it exhibited the highest *exo*-TCD selectivity but the lowest ADH selectivity. Similar relationship between ADH selectivity and the amount of strong Brönsted acid sites could be found at the reaction temperature of 150°C. These observations 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 Brönsted 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 Brönsted acids.

4. Conclusion

We have prepared a series of AlCl_3 supported catalysts

onto $\text{H}\beta$, HY, and HMCM-41 having different both po-



Scheme 2. The synthesis mechanism of *exo*-TCD and ADH.

rous 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 isomeri-

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.

5. Acknowledgements

Supports of this work by the National Natural Science Foundation of China (21076031) and the Fundamental Research Funds for the Central Universities (DUT12-ZD219) are gratefully acknowledged. Sang-Eon Park thanks Dalian University of Technology for a "Seasky" professorship.

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