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# Greener synthesis route for Jet Propellant-10: the utilization of zeolites to replace $\text{AlCl}_3$ †

Enhui Xing, Xiangwen Zhang,\* Li Wang and Zhentao Mi

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This paper summarizes our recent developments in the utilization of H-type zeolites to replace  $\text{AlCl}_3$  in *exo*-tetrahydrodicyclopentadiene production. H-type Y zeolites with large pore size (0.74 nm) had sufficient activities for isomerization of *endo*-tetrahydrodicyclopentadiene (*endo*-THDCPD) to form *exo*-tetrahydrodicyclopentadiene (*exo*-THDCPD). As for acidity strength, the moderate strength of zeolite acidity was favorable. The incorporation of fluorine generated more moderate acids, which improved the catalytic performance of zeolites to *exo* yield = 92.58%, *exo* selectivity = 96.47%, and suppressed the adamantane (ADM) yield = 2.32%. When  $\text{NH}_4\text{F}/\text{SSY} = 6.57\%$ , calcined at 500 °C, this showed an equivalent performance as  $\text{AlCl}_3$ .

## 1 Introduction

In this contribution, we focus on the synthesis of the single-compound fuel, Jet Propellant-10. Its relatively simple composition of >98.5% *exo*-tetrahydrodicyclopentadiene (*exo*-THDCPD) (freezing point −79 °C) and *endo*-tetrahydrodicyclopentadiene (*endo*-THDCPD) (freezing point 80 °C) is responsible for its very high volumetric energy content ( $39.6 \text{ MJ L}^{-1}$ ) due to the strained cyclic geometry (Scheme 1).<sup>1,2</sup> This property, in combination with its low toxicity and suitable flashpoint (55 °C), explains its success as a fuel for short-range missiles. *Exo*-THDCPD is additionally used in other fuel mixtures (e.g. JP-9 and PF-1), and also as a solvent for paints, etc. The production of *exo*-THDCPD is summarized in Scheme 1.

Hydrogenation of dicyclopentadiene (DCPD) affords selectively *endo*-THDCPD. This compound needs to be isomerized to *exo*-THDCPD to meet the freezing point requirements of a jet fuel. Unfortunately, *exo*-THDCPD can be further isomerized to adamantane (ADM), a side-reaction which needs to be avoided as much as possible because of its high freezing point (above 269 °C). Whereas the isomerization reaction was originally catalyzed by the highly corrosive sulfuric acid,<sup>3,4</sup>  $\text{AlCl}_3$  has been predominantly used for this

purpose since 1960s.<sup>5</sup> Although the use of  $\text{Pd}(\text{acac})_2$  as a catalyst brought the yield up to 99.5%,<sup>6</sup> the high cost limited its application at an industrial scale. In 1980s, Cheng *et al.*<sup>7</sup> and Olah and Farooq<sup>8</sup> catalyzed *endo*-THDCPD to *exo*-THDCPD using liquid super acids. The problems of separation and corrosion are still to be solved. Therefore, there is still a strong need to develop new catalysts at low cost for *exo*-THDCPD production with minimum environmental impact.

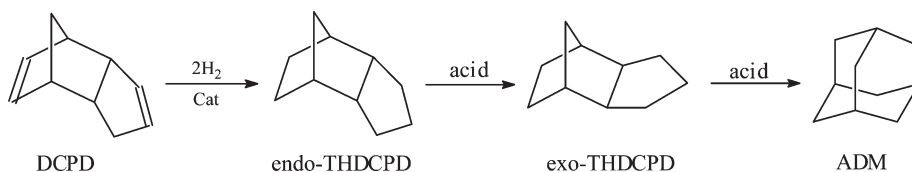
The synthesis of ADM from *endo*-THDCPD catalyzed by Y zeolites at the laboratory<sup>9–11</sup> and industrial scales<sup>12</sup> have been reported. In the synthesis of ADM, *exo*-THDCPD production would be promoted by the use of zeolites. This paper summarizes our recent developments in the utilization of H-type zeolites to replace  $\text{AlCl}_3$  in *exo*-THDCPD production.<sup>13,14</sup> It was shown that H-type zeolites have equivalent yields and better selectivity than  $\text{AlCl}_3$ , which could make *exo*-THDCPD production greener.

## 2 Experimental

### 2.1 Materials

Commercially available zeolites were used. All Y zeolites were produced by the Wenzhou Catalyst Co., China. H-ZSM-5 and H-β were provided by the Nankai Catalyst Co., China. The characteristics of these zeolites are given in Table 1. All zeolites in the ammonia form were activated for 2 h at  $T_f$  (ca. 450–600 °C) in air to form the corresponding H-type before catalytic runs. The H-type ZSM-5, β and ReY were calcined at 200 °C to eliminate adsorbed water molecules.

The fluorine loading of zeolites into H-type Y zeolites was carried out as follows: about 1 g of  $\text{NH}_4\text{-SSY}$  zeolites were



Scheme 1

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, P. R. China.  
E-mail: zliuying@public.tpt.tj.cn; Fax: +86 22 27402604;  
Tel: +86 22 27892340

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**Table 1** Characteristics of zeolites provided by producer

Zeolite	Si : Al ratio	Unit cell structure/ $10^{-10}$ m	Crystallinity (%)	Na <sub>2</sub> O (wt%)
NH <sub>4</sub> Y	5.0	ca. 24.65–24.69	≥90	≤2.0
ReY	5.0	ca. 24.64–24.68	≥90	≤2.0
NH <sub>4</sub> -USY	≥5.2	ca. 24.52–24.58	≥80	≤0.2
NH <sub>4</sub> -SSY	ca. 9.0–12.0	ca. 24.49–24.53	≥78	≤0.2
H-β	ca. 28.0–29.0	<sup>a</sup>	≥90	<sup>a</sup>
H-ZSM-5	50.0	<sup>a</sup>	≥90	<sup>a</sup>

<sup>a</sup> No data are available from vendor.

impregnated with 1.50 mL of an aqueous solution of NH<sub>4</sub>F (Tianjin Chem Reagents Co.). After drying at 120 °C overnight, the catalysts were activated stepwise in air at 250 °C for 4 h to decompose NH<sub>4</sub>F, and at  $T_f$  for a further 2 h. The subsequent activation at  $T_f$  helped fluorine to be incorporated into the skeleton of the zeolites, and to decompose NH<sub>4</sub><sup>+</sup> into NH<sub>3</sub> and H<sup>+</sup> to form acidic, active H-type Y zeolites.

## 2.2 Characterization

NH<sub>3</sub>-temperature-programmed desorption (TPD) was performed on an Autochem 2910 instrument equipped with thermal conductivity detectors (TCD). The conditions for the analysis were as follows: carrier gas He, absorption temperature 120 °C, linear heating rate 10 °C min<sup>-1</sup>, temperature range 120–600 °C.

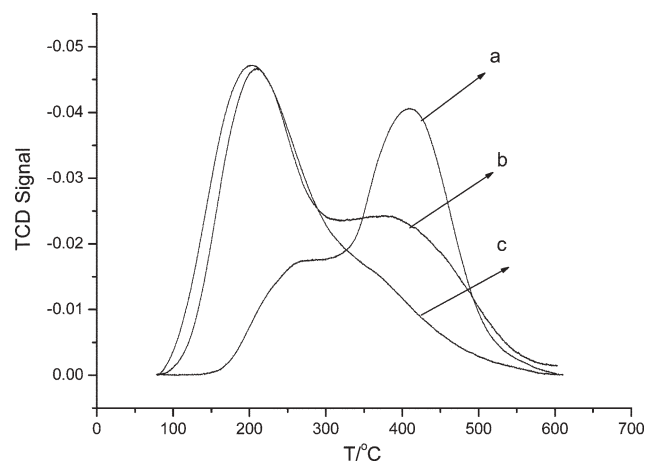
## 2.3 Apparatus and procedure

The experiments were carried out in a mechanically stirred autoclave at 195 °C. Samples of the reaction mixture were analyzed by a GC HP-4890 equipped with a HP-5 capillary column (length: 30 m; diameter: 0.53 mm; thickness of the film: 0.15 μm) and flame ionization detectors (FID).

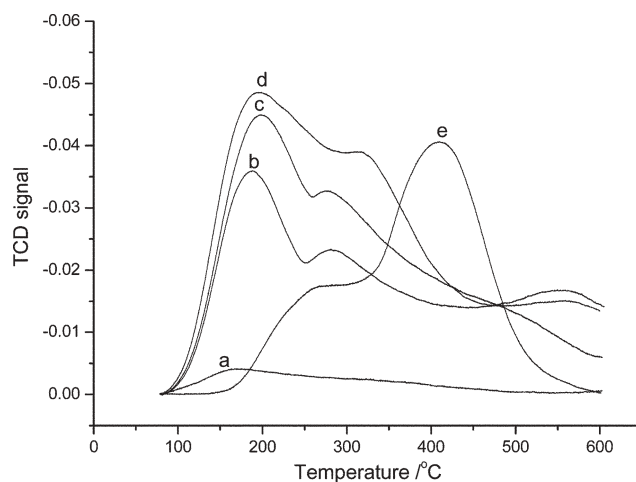
# 3 Results and discussion

## 3.1 Acidity characterization of zeolites

NH<sub>3</sub>-TPD curves of H-USY, ReY and H-SSY calcined at 450, 200 and 450 °C, respectively, are shown in Fig. 1.



**Fig. 1** NH<sub>3</sub>-TPD curves of different Y zeolites: (a) H-SSY calcined at 450 °C; (b) H-USY calcined at 450 °C; and (c) ReY calcined at 200 °C.



**Fig. 2** NH<sub>3</sub>-TPD curves of fluorine-modified H-SSY with different NH<sub>4</sub>F/SSY and calcination temperatures: (a) NH<sub>4</sub>F/SSY = 6.57%, 600 °C; (b) NH<sub>4</sub>F/SSY = 9.81%, 450 °C; (c) NH<sub>4</sub>F/SSY = 3.28%, 550 °C; (d) NH<sub>4</sub>F/SSY = 6.57%, 500 °C; and (e) NH<sub>4</sub>F/SSY = 0.00%, 450 °C.

As Fig. 1 shows, the acidity increases in the order ReY < H-USY < H-SSY. Weak acid sites ( $T_{peak}$  around 200 °C) dominate the acidity of ReY, with a small number of moderate acids ( $T_{peak}$  around 300 °C). On the contrary, H-SSY has much more strong acid sites ( $T_{peak}$  around 400 °C) and some moderate acid sites.

NH<sub>3</sub>-TPD curves of fluorine-modified H-SSY with different NH<sub>4</sub>F/SSY and calcination temperatures are shown in Fig. 2.

As shown in Fig. 2, the addition of fluorine decreases the strong acid sites and increases weak acid sites significantly. As for moderate acids, both NH<sub>4</sub>F/SSY and calcination temperature should be suitable to achieve the increase of the moderate acid sites. The formation of large amounts of weak acids can be explained by thermal dealumination to form aluminium oxide species with weak acidity. Although unmodified H-SSY showed high thermal stability during calcination, the involvement of fluorine can decrease the thermal stability of the zeolitic skeleton of H-SSY. It should be pointed out that a higher fluorine content calcined at a higher temperature [Fig. 2(a), NH<sub>4</sub>F/SSY = 6.57%, calcination temperature 600 °C] leads to the collapse of the zeolitic skeleton, which results in the almost complete loss of acidity. The complete loss of acidity can be reflected by both NH<sub>3</sub>-TPD and pyridine-adsorbed FT-IR. The loss of acidity, especially strong and moderate acid sites, is an indication of the collapse of the zeolitic skeleton. The complete loss of acidity could certainly decrease the catalytic activity of the zeolites, which will be discussed with the catalytic activity data in the following section.

## 3.2 Activities of different types of zeolites

During the isomerization of large molecules, the pore structure and size of the zeolites are very important parameters. Zeolites H-β, HY and H-ZSM-5 were tested in this study, as shown in Table 2.

All of these three H-types show sufficient acidity, but they have different zeolitic channels and cavities. For the cavities,

**Table 2** Influence of zeolite type

Zeolite	Calcination temperature/°C	Endo conversion (%)	Exo yield (%)	Exo selectivity (%)	ADM yield (%)
HY	450	90.00	85.55	95.05	2.63
H- $\beta^a$	200	Almost no activity			
H-ZSM-5 <sup>b</sup>	200	Almost no activity			

<sup>a</sup> Reaction times for H- $\beta$  were 4 and 8 h. <sup>b</sup> Reaction times for H-ZSM-5 were 4 and 8 h.

they are hard to measure and calculate. Combined with the calculated dimensions of the THDCPD isomers, the shape-selectivity of zeolitic catalysts was studied.<sup>14</sup> H-ZSM-5 and H- $\beta$  showed no activity for this skeleton rearrangement at 195 °C because of their relatively small pore size (H-ZSM-5: 0.53 × 0.56 nm, 0.51 × 0.55 nm; H- $\beta$ : 0.57 × 0.75 nm, 0.56 × 0.65 nm) when compared with the dimensions of *endo*-THDCPD (cross-section of minimum area 0.67 nm × 0.65 nm; kinetic diameters  $\sigma$  0.58 × 0.60 nm) (Fig. 3). The reactant needs to be adsorbed onto an acidic site, be protonated, and then be isomerized into the *exo*-THDCPD and ADM, which needs then to be desorbed again. For HY, the large size of the channels (0.74 × 0.74 nm) can provide sufficient windows for *endo*-THDCPD to penetrate into the inner surface of the HY zeolites, and then be adsorbed onto acidic centers to precede skeleton rearrangement for the formation of isomerized products. In conclusion, reactant selectivity can explain why H- $\beta$  and H-ZSM-5 lack isomerizing activity at 195 °C.

### 3.3 Acidic Y zeolites

Commercially available HY zeolites with different Si : Al ratios – HY, H-USY and H-SSY – were tested. The experimental results are summarized in Table 3.

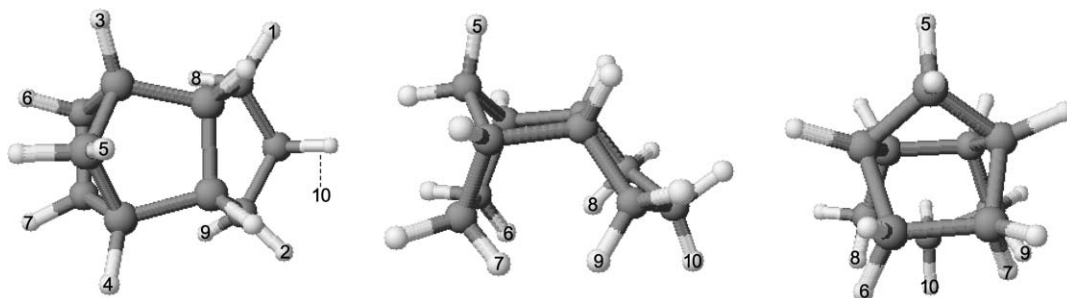
Corma's review<sup>15</sup> showed that a higher Si : Al ratio leads to a smaller unit cell structure (UCS), and thus fewer acidic sites, stronger acidity and longer distance between two neighboring acid sites. Based on the data provided by the zeolite vendor,

the Si : Al ratio increases in the order HY < H-USY < H-SSY; UCS decreases in the order HY > H-USY > H-SSY. So the acidity increases in the order HY < H-USY < H-SSY, and the number of acidic sites decreases in the same order. It is shown that acidity strength is more important than the number of acidic sites to the formation of *exo*-THDCPD. Therefore the modification of Y zeolite should be focused on the change in the acidity strength and acidity distribution rather than on the number of acidic sites.

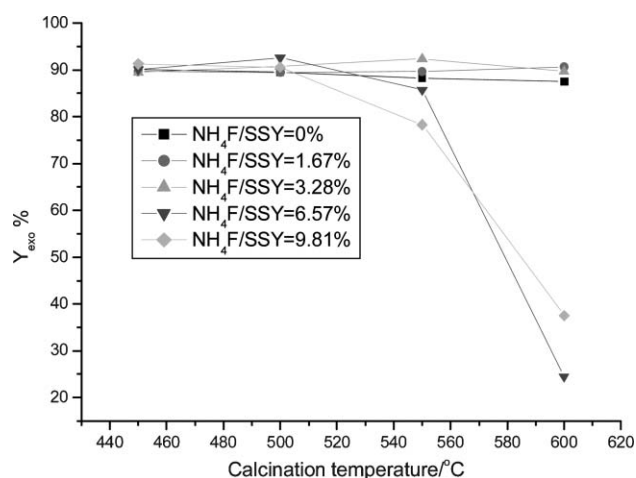
As an acidic zeolite, ReY showed unsatisfactory activity for *endo*-THDCPD isomerization. The reason will be discussed according to the acidity characterization in Fig. 1. As Fig. 1 shows, the acidity increases in the order ReY < H-USY < H-SSY. The activity (measured by *endo*-THDCPD conversion) increases in the same order ReY < H-USY < H-SSY. In contrast, the selectivity decreases with the increase in acidity, mainly reflected by the yields of ADM (also increasing with acidity strength) and other by-products. In ADM production studies, it has also been proved that strong Brønsted acids favor the formation of ADM and cracking of by-products. In this study it is found that for the formation of *exo*-THDCPD, moderate acids are needed. The low activity of ReY showed that weak acidity contributed insignificantly to the conversion of *endo*-THDCPD.

### 3.4 Zeolites modified by fluorine

In order to modify the surface acidity of the zeolites, fluorine was introduced as described for H-ZSM-5 modification by

**Fig. 3** Optimized 3D geometry of *endo*-THDCPD.**Table 3** Influence of Si : Al ratio

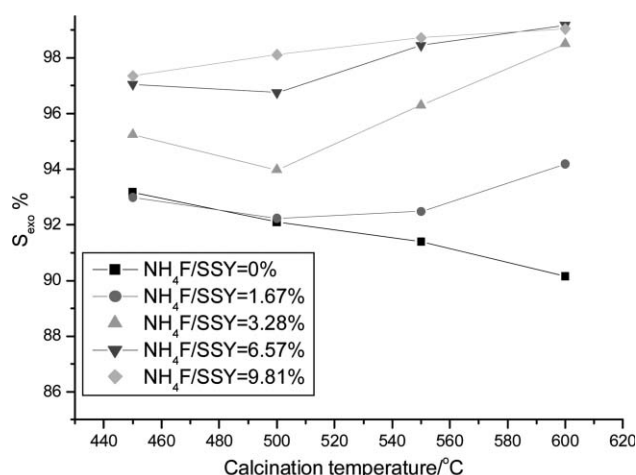
Zeolite	Si : Al ratio	Calcination temperature/°C	Endo conversion (%)	Exo yield (%)	Exo selectivity (%)	ADM yield (%)
HY	5.0	450	90.00	85.55	95.06	2.63
		550	92.43	87.22	94.36	3.60
H-USY	≥5.2	450	94.93	89.69	94.48	3.03
		550	96.73	89.46	92.48	4.33
H-SSY	ca. 9.0–12.0	450	95.83	87.55	91.36	4.40
		550	95.85	87.58	91.37	4.72



**Fig. 4** Influence of  $\text{NH}_4\text{F}/\text{SSY}$  and calcination temperature on  $Y_{\text{exo}}$ .

NH<sub>4</sub>F.<sup>16,17</sup> For fluorine incorporation, the calcination temperature and F content, measured by NH<sub>4</sub>F/SSY (mass ratio), were two key factors influencing the catalytic performance. However, NH<sub>4</sub>F/SSY is the most influencing factor in determining the content of fluorine incorporated into the zeolitic skeleton. As discussed in Section 3.2, the catalytic activity of fluorine-modified H-SSY is measured by  $Y_{exo}$  and  $S_{exo}$ , which correspond to the yield and selectivity of *exo*-THDCPD.

The influences of  $\text{NH}_4\text{F}/\text{SSY}$  and calcination temperature on  $Y_{exo}$  and also on  $S_{exo}$  are illustrated in Fig. 4 and Fig. 5, respectively. Generally speaking, the fluorine modification is positive in improving the *exo*-selectivity and suppressing the ADM formation since the addition of fluorine increases moderate acids. As shown in Fig. 5, the low concentration of fluorine shows a hardly noticeable effect on the catalytic performance, especially at lower calcination temperatures (450, 500 °C), while at higher calcination temperatures (550, 600 °C), the fluorine modification leads to an increase in *exo*-THDCPD yield and *exo*-selectivity. As shown in Fig. 5, with the improvement in *exo*-selectivity, suitable fluorine concentration and calcination temperature lead to a better *exo*-yield. The reason is attributed to the strengthening of moderate acids, such as Fig. 2(b), Fig. 2(c) and Fig. 2(d). Moderate fluorine loading



**Fig. 5** Influence of  $\text{NH}_4\text{F}/\text{SSY}$  and calcination temperature on  $S_{\text{exo}}$ .

and higher temperature lead to more moderate acids, which favor the formation of *exo*-THDCPD. In all, the best  $Y_{exo}$  (92.58%) is achieved for H-SSY with  $\text{NH}_4\text{F}/\text{SSY} = 6.57\%$ , calcined at 500 °C (Fig. 4). Compared with parent zeolites with the best yield (90.08%), the yield of *exo*-THDCPD is improved by 2.50%.

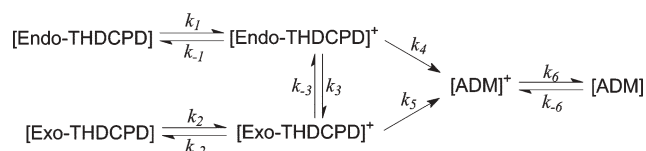
The involvement of fluorine as an electron-withdrawing component can change the surface acidity of zeolites toward the desired direction, in which moderate acids are needed to achieve better *exo*-yield. On one hand, the amount of moderate acids of fluorine-modified H-SSY [Fig. 2(b)–(e)] decreased in the order 2(d) > 2(c) > 2(b) > 2(e), which was reflected by the decreasing order of *exo*-yield: 2(d) (92.58%)  $\approx$  2(c) (92.34%) > 2(b) (91.28%) > 2(e) (90.08) (Fig. 4). The best catalyst is obtained with a calcination temperature of 500 °C and  $\text{NH}_4\text{F}/\text{SSY} = 6.57\%$ . Compared with unmodified H-SSY zeolites (best performance occurred at 450 °C, with  $X_{\text{endo}} = 96.66\%$ ,  $Y_{\text{exo}} = 90.08\%$ ,  $S_{\text{exo}} = 93.18\%$ ,  $Y_{\text{ADM}} = 3.60\%$ ), the conversion decreased by 0.19%. However  $Y_{\text{exo}}$  and  $S_{\text{exo}}$  were improved by 2.50 and 3.29% respectively, suppressing the formation of ADM by 1.28%. This desired tendency is achieved through forming more moderate acids with the addition of fluorine into the zeolitic skeleton.

In order to test the thermal durability of fluorine-modified zeolites, the best catalysts were regenerated for at least eight times and showed no noticeable decrease in yield and selectivity.

USY zeolites modified by fluorine were also tested, which showed improved performance.

### 3.5 Proposed mechanism of isomerization

Scheme 1 shows the traditional mechanism of THDCPD isomerization. Although there are hundreds of  $[\text{C}_{10}\text{H}_{15}]^+$  isomers, because of thermodynamic and kinetic unfavorable factors, other  $\text{C}_{10}\text{H}_{16}$  isomers could hardly be detected. All isomers detected are *exo*-THDCPD, *endo*-THDCPD and ADM. With the assumption that other  $[\text{C}_{10}\text{H}_{15}]^+$  are thermodynamically unstable or kinetically unfavorable, a simple mechanism for the isomerization of THDCPD is proposed, as shown in Fig. 6. The key scheme is the isomerization of  $[\text{C}_{10}\text{H}_{15}]^+$ . Although the yield of *exo*-THDCPD could reach 99% with liquid super acids as catalysts below room temperature, the purified *exo*-THDCPD (99%) could be partly isomerized to *endo*-THDCPD (Table 4), which means that the steps are reversible. According to Olah and Farooq,<sup>8</sup> 100% of  $[\text{ADM}]^+$  could exist in liquid super acids, which shows that step 4 and step 5 were irreversible. Also, heating ADM in the presence of zeolites does not lead to the formation of *endo*-THDCPD and *exo*-THDCPD, but to ring-opening products. Total conversion of *endolexo*-THDCPD to ADM can be achieved,<sup>7-11</sup> which also shows the step 5 was irreversible.



**Fig. 6** Mechanism of isomerization.



**Table 4** Equilibrium mixture at 200 °C

Reactant	The composition of reaction mixtures (wt%)			
	<i>Endo</i> -THDCPD	<i>Exo</i> -THDCPD	ADM	Others
<i>Endo</i> -THDCPD	3.20	87.55	4.24	5.01
<i>Exo</i> -THDCPD	3.24	86.71	4.56	5.49

Generally speaking, step 3 is kinetically favorable, which could proceed very quickly even at very low [*endo*-THDCPD]<sup>+</sup> concentration. Steps 4 and 5 are thermodynamically favorable, which means higher [THDCPD]<sup>+</sup> will lead to more thermodynamically stable [ADM]<sup>+</sup>.

Based on the isomerization mechanism, low concentration of [*endo*-THDCPD]<sup>+</sup> will favor the formation of *exo*-THDCPD until the equilibrium is established. Because Step 3 is exothermic, the reactions should proceed at low temperature to achieve high equilibrium yields. In all, the *exo*-THDCPD should be carried out with strong acids at low concentration and low temperature. For the formation of ADM, higher reaction temperature, more acidic numbers and stronger acidity are needed to convert [*endo*-THDCPD]<sup>+</sup> to [ADM]<sup>+</sup>.

According to the above mechanism, the best condition for *exo*-THDCPD production should be strong acids at low concentration and low reaction temperature. Although the use of liquid super acids can achieve higher yield and selectivity, the difficulty in separation and corrosion are the major problems. That is why Y zeolites are used at higher temperatures to achieve almost equivalent yield and selectivity as AlCl<sub>3</sub> does. For the ADM, strong acids at high concentration and higher reaction temperature will be needed. In some cases, even HCl is needed to improve the acidity of catalysts for ADM. In all, strong acidity, high concentration and high reaction temperature favor the formation of ADM.

## 4 Conclusion

The synthesis of *exo*-THDCPD by isomerization of *endo*-THDCPD on commercially available zeolites is studied. It is shown that pore size and acidity are the most important factors to influence the activity and selectivity of the zeolitic catalysts. HY zeolites (0.74 nm) are the most active with smaller pore sizes (H-β and H-ZSM-5). Besides pore size, acidity is the other key factor. Based on the proposed mechanism, the surface acidity of zeolites is modified toward the desirable direction. It is possible to enhance the moderate acids of H-type Y zeolites by incorporation of ammonium fluoride in relatively low concentrations and, subsequently, by stepwise activation at high temperature. The strengthening of moderate acids favors the *exo* yield, the decrease in strong acids leads to improved *exo* selectivity and suppressed ADM yield, which is desirable in *exo*-THDCPD production.

Fluorine-modified H-SSY (NH<sub>4</sub>F/SSY = 6.57%, calcination temperature 500 °C) shows the best isomerizing activity for *endo*-THDCPD, with a maximum *exo* yield of 92.58%, an improved *exo* selectivity of 96.74% and a suppressed ADM yield of 2.32%.

It can be concluded that fluorine-modified H-SSY shows potential use for the production of *exo*-THDCPD to take the place of AlCl<sub>3</sub> as the isomerizing catalyst for *endo*-THDCPD. The fluorine-modified zeolites show similar activities as AlCl<sub>3</sub> under solvent-free conditions. Catalyst recycling and reuse causes almost no harm to the environment or little corrosion. The easy separation appears more promising for commercial use in *exo*-THDCPD production.

## Acknowledgements

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