Endo- to exo-isomerization of tetrahydrodicyclopentadiene catalyzed by commercially available zeolites

Enhui Xing, Zhentao Mi, Chengwei Xin,
Li Wang, Xiangwen Zhang*

The School of Chemical Engineering, Tianjin University, Tianjin 300072, PR China

Abstract

This paper presents the results of catalytic endo- to exo-isomerization of tetrahydrodicyclopentadiene. Several zeolites were tested and influences of calcinations temperatures, Si/Al ratio and cations of the zeolites on the reaction were investigated. The results showed that HY zeolites were more active than other zeolites and Y zeolites with other cations, because of its large pore size and relative strong acidity. In all HY zeolites with different Si/Al, H-USY is best. On one hand, H-USY has more moderate acids than others. On the other hand, the high thermal stability of H-USY makes it suitable choice for recycling catalysts. In all the zeolites tested, H-USY calcined at 450 °C was favorable. Regeneration of H-USY showed no decrease of exo-yield while had better exo-selectivity.
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1. Introduction

The exo-isomer of tetrahydrodicyclopentadiene (exo-THDCPD) is the major component of the high-energy-density liquid fuel referred to as JP-10 [1]. The endo-isomer (endo-THDCPD), which is the precursor of the exo-isomer, is also present in JP-10 as impurity [2]. Both endo- and exo-isomers have high volumetric energy content. Although most physical–chemical properties of endo- and exo-isomers are very similar, there is large difference in freezing point (endo 77 °C, exo −79 °C). Obviously, exo-isomer is suitable choice for liquid fuel usage, especially at low temperature. This single-component fuel takes advantage of the increased energy storage available through the strained cyclic geometric. JP-10 can satisfy the requirement of the fuels with low toxicity, low freezing point (−79 °C), suitable flash point (55 °C) and high volumetric energy content (39.6 MJ l^{-1}). Nowadays

JP-10 has been widely used as high-energy-density fuel, because of its excellent phys-chemical properties, low cost and easy production. In addition, exo-THDCPD is widely used as solvents for paints, diluents for surfactants, waxes and washing agents for semiconductor, blankets, etc. Also, exo-THDCPD is used as rolling oils, resin powders, lubricating oils, punching oils and cutting oils.

Endo-THDCPD can be partly converted into exo-THDCPD to be used as liquid fuels (Scheme 1).

In earliest studies [3,4], sulfuric acid was used to catalyze the endo- to exo-isomerization of THDCPD. Since 1960s, aluminum chloride has been the most widely used catalyst for the isomerization of endo-THDCPD [5], which suffered from several drawbacks: First, strong Lewis acidity of aluminum chloride led to low exo-selectivity and formation of deposits. Second, the reaction mixture should be separated by adding sodium hydroxide aqueous solution. Third, aluminum chloride often causes environmental problems and severe corrosion. There were other disadvantages such as catalysts recycling and the use of co-catalyst or solvent. Recently, some Japan patents have focused on production

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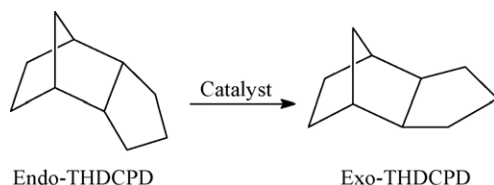
Scheme 1.

of exo-THDCPD through isomerization of tetrahydrodicyclopentadiene [6], still aluminum chloride was used as catalyst. Although better selectivity and yield were achieved with the use of solvents and co-catalysts, separation and environmental protection are still hard problems to be solved. Although the use of Pd(acac)$_2$ as catalyst brought yields of 99.5% of end product [7], its high cost limits its use on industrial scale. In 1980s, Cheng [8] and Olah [9] catalyzed endo-THDCPD to exo-THDCPD by liquid super acids. The problems of separation and corrosion are still hard to solve. In final, there still lies much need to develop new catalyst at low cost for exo-THDCPD production.

The expansion of zeolitic catalysts into many areas of organic synthesis also offers the possibility of their application for the rearrangement of polycyclic hydrocarbons. The utilization of zeolites for the synthesis of adamantane (ADM) improved the technology of this isomer of tetrahydrodicyclopentadiene. In many literatures [10–12], the isomerization of endo-THDCPD catalyzed by Y zeolites was reported. Nowadays, Y zeolites had replaced aluminum chloride to catalyze endo-THDCPD to adamantine on industrial scale [13]. In the adamantane production, exo-THDCPD was regarded as byproducts. No published literature has been found about exo-THDCPD formation catalyzed by zeolitic catalysts till now.

This paper presents the study of the isomerization of endo-THDCPD to exo-THDCPD using commercially available zeolites, but having different cations and Si/Al molar ratios. The aim is to find out the relationship between the properties of these zeolites, the calcinations temperature and the activity, exo-selectivity, especially relationship between the strength of acids and product distribution.

2. Experimental

2.1. Materials

Commercially available zeolites were used. All Y zeolites were produced by Wenzhou Catalyst Co., China. H-ZSM-5 and H-beta were provided by 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 (350–750 °C) in air to form acidically active H-type before catalytic runs. NH$_4$Y was activated for 2 h at 200 °C to preserve ammonium cations. The H-type zeolites were calcined at 200 °C.

2.2. Characterization

NH$_3$-TPD was performed on Autochem 2910 equipped with TCD detector. Analyzing conditions are as follows: carrier gas He, absorption temperature: 120 °C, linear heating rate: 10 °C min^{-1}, temperature range: 120–600 °C.

FT-IR spectra of adsorbed pyridine on zeolites were recorded on the transparent zeolite plate of thickness 10 mg cm^{-2} FT-IR spectrometer. Nicolet Magna-560 was used with a vacuum cell with CaF$_2$ windows.

2.3. Apparatus and procedure

The experiments were carried out in a mechanically stirred autoclave (150 ml). The autoclave was charged with 40.5 g endo-THDCPD and 8.000 g freshly activated catalysts (the particle size 0.45–0.90 mm). With stirring speed at 800 rpm, the experiments were carried out in this sealed autoclave at 195 °C. The catalysts were dried in vacuum oven at 120 °C for regeneration.

After filtration, the samples of the reaction mixture were analyzed by HP-4890 equipped with a HP-5 capillary column (length 30 m, diameter 0.53 mm, strength of the film 0.15 μm) and FID detector.

3. Results and discussion

3.1. The acidity characterization of zeolites

Adsorption of volatile amines such as NH$_3$, pyridine, n-butylamine, quinoline, etc., can be used to determine the number of acid sites on solid catalysts. Although NH$_3$-TPD curves cannot distinguish the difference between Broensted and Lewis acids, it can provide useful information about strength and distribution of acids [14].

NH$_3$-TPD curves of HY zeolites calcined at different temperature are shown in Fig. 1.
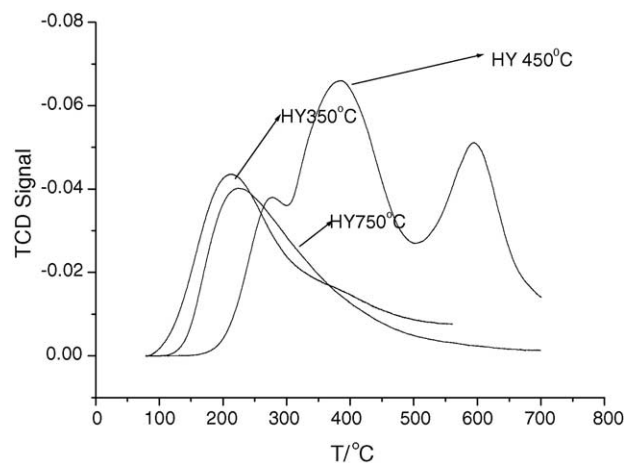

Fig. 1. NH$_3$-TPD curves of HY calcined at different temperatures.

Table 1
Characteristics of zeolites provided by producer

Zeolites	Si/Al ratio	Unit cell structure/10^{-10} m	Crystallinity (%)	Na$_2$O (wt.%)
NH$_4$Y	5.0	24.65–24.69	≥90	≤2.0
NaY	5.0	24.65–24.69	≥95	≤13.5
ReY	5.0	24.64–24.68	≥90	≤2.0
NH$_4$-USY	≥5.2	24.52–24.58	≥80	≤0.2
NH$_4$-SSY	9.0–12.0	24.49–24.53	≥78	≤0.2
H-beta	28.0–29.0	_[a]	≥90	_[a]
HZSM-5	50.0	_[a]	≥90	_[a]

[a] Data are not provided by producer.

As Fig. 1 shows, low calcinations temperature (350 °C) and high temperature (750 °C) of HY lead to weak acidity (T_{peak} around 200 °C). While calcined at 450 °C, possessing three distinguished acidic peaks at the graph, moderate acids (T_{peak} around 300 °C) and strong acids (T_{peak} around 400 °C). T_{peak} around 600 °C is attributed to the removal of surface hydroxyl groups in the form of water molecules, resulting in a decrease of Bronsted acid sites with a constant increase in Lewis acid sites [15]. Some literatures also showed that [14,16], when HY calcined above 560 °C, more and more Broensted-type acid sites were converted into Lewis acid sites with higher temperature and prolonged calcinations time, which results in the desorption of water molecules.

It is well known that zeolites in sodium and ammonia form have no acidity, which is also proved by NH$_3$-TPD and pyridine-adsorbed FT-IR spectroscopy.
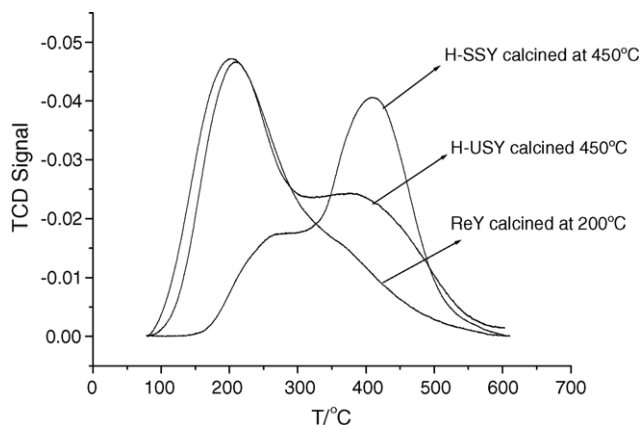

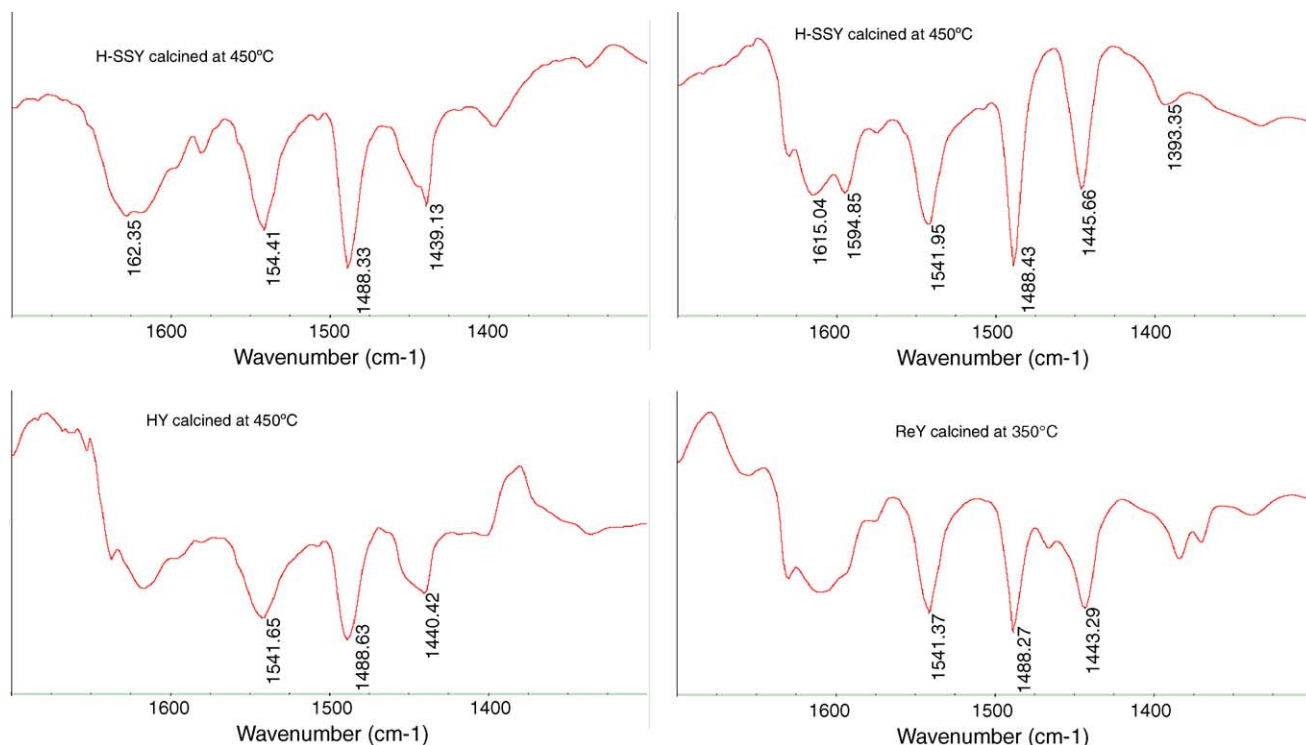Fig. 2. NH$_3$-TPD curves of different Y zeolites.

Fig. 3. The pyridine-adsorbed FT-IR spectroscopy of Y zeolites.

Table 2
The influence of zeolites type

Zeolites	Calcinations temperature (°C)	Endo-conversion	Exo-yield	Exo-selectivity	ADM-yield
HY	450	90.00	85.55	95.05	2.63
H-beta[a]	200				
HZSM-5[b]	200	Almost no activity			

[a] Reaction time for H-beta are 4 and 8 h.
[b] Reaction time for HZSM-5 are 4 and 8 h.

NH$_3$-TPD curves of H-USY, ReY and H-SSY calcined at 450, 200 and 450 °C, respectively are shown in Fig. 2.

As Fig. 2 shows, the acidity increased in the order ReY < H-USY < H-SSY. Weak acid sites (T_{peak} around 200 °C) dominated the acidity of ReY, with small number of moderate acids (T_{peak} around 300 °C). On the contrary, H-SSY had much more strong acids (T_{peak} around 400 °C) and some moderate acids. The acidity strength of H-USY was between ReY and SSY.

The pyridine-adsorbed FT-IR spectroscopy of zeolites show that both Bronsted (signals around 1540 cm^{-1}) and Lewis acids (signals around 1450 cm^{-1}) exit on the surface of the acidic catalysts calcined at moderate temperature. The literature reported that [4–6] both Bronsted acids (H$_2$SO$_4$) and Lewis acids (AlCl$_3$) could catalyze the endo- to exo-isomerization of endo-THDCPD. As for zeolitic catalysts, it needs to be further investigated (Fig. 3).

3.2. Isomerization of tetrahydrodicyclopentadiene

In rearrangement of endo-THDCPD to its exo-isomer, isomerization to adamantane also occurrs. In adamantane production catalyzed by Y zeolites, hydrogenolysis and various kinds of ring opening reations also take place simultaneously in the presence of hydrogen [10–12]. In our experiment, without hydrogen few hydrogenolysis and various kinds of ring opening reations occurred.

3.2.1. Activities of different types of zeolites

In the isomerization of large molecules, pore structure and size of the zeolites and the pore size are very important parameters. Zeolites H-beta, HY and HZSM-5 were tested.

HZSM-5 showed no activity for this skeleton rearrangement because of his relatively small pore size (0.53 × 0.56 nm, 0.51 × 0.55 nm). The reactant molecules could not penetrate into the pores, which was the preliminary step to be adsorbed on the acidic site and form carbonium.

Although the pore sizes of zeolites H-beta (0.57 × 0.75 nm, 0.56 × 0.65 nm) was large enough for endo-THDCPD to penetrate into the pores at 270 °C [12], while at 195 °C no conversion was observed after solving reactants in solid state with cyclohexane for GC quantitative analysis. The reason lies in the smaller pore sizes than endo-THDCPD (0.67 × 0.65 nm, estimated by ACD/ChemSketch 5.0 offered by Advanced Chemistry Development Inc.). The literature [12] showed that higher temperature (270 °C) would help the endo-THDCPD run into the pores of H-beta, but the activity of H-beta was still lower than HY. The main reason lies in the relative smaller pore size than HY zeolites (0.74 nm), which need higher reaction temperature to make the endo-THDCPD to penetrate into the inner pores of H-beta before endo-THDCPD molecules are adsorbed on the active sites and forms carbonium (Table 2).

3.2.2. The influence of cations

The framework of zeolites exhibits negative charges, which are balanced by cations. The types of the cations influence the properties of the zeolites, especially the strength of its acid centers.

Commercially available Y zeolites with four different cations, namely NaY, NH$_4$Y, ReY and HY were tested. The results are shown in Table 3.

Because of lack in acidity, proved by NH$_3$-TPD and pyridine-adsorbed FT-IR spectroscopy, NH$_4$Y and NaY were inactive for the transformation of endo-THDCPD, while HY showed distinctly higher activity than others. The activity of ReY was lower than HY. It is proposed that HY were more favorable for endo-conversion and exo-formation than those with other cations. Compared with moderate acids and strong acids, weak acids contribute little to this acid-catalyzed isomerization of endo-THDCPD to convert raw material to carbonium, then through skeleton rearrangement form exo-isomer and adamantane. That is the reason why the HY were more active than Y zeolites with other cations.

Table 3
The influence of zeolites cations

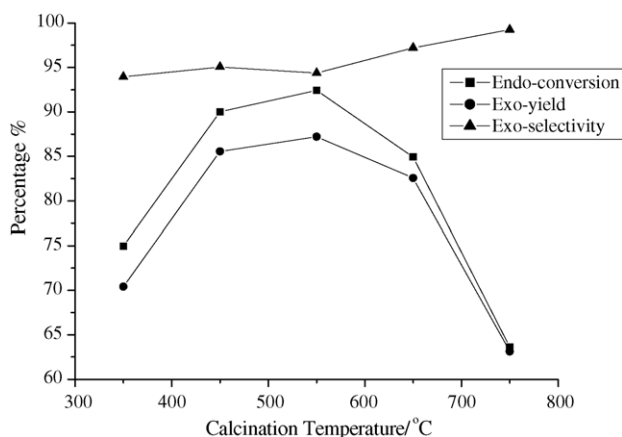| Zeolites	Calcinations temperature (°C)	Endo-conversion	Exo-yield	Exo-selectivity	ADM-yield
ReY	200	51.30	51.04	99.49	0.26
ReY	350	52.43	51.87	98.95	0.54
HY	450	90.00	85.55	95.06	2.63
HY	550	92.43	87.22	94.36	3.60
NaY	200				
NH$_4$Y	200	Almost no activity			
NH$_4$-USY	200				

Fig. 4. The effect of calcination temperature on catalytic activity and selectivity.

3.2.3. The influence of calcinations temperatures

As discussed above, isomerization of tetrahydrodicyclopentadiene belongs to acid-catalyzed reaction, so NH_4Y were always transformed into HY through calcinations prior to the catalytic run. Calcinations temperatures are the most influential factor to determine the acidity strength and distribution of HY. In order to check the effect of calcinations temperatures on the activity, NH_4Y zeolites were calcined at 350–750 °C to obtain acidically active HY. The results are shown in Fig. 4.

From Fig. 4, moderate calcinations temperatures should be proposed. As shown in Fig. 1, low calcinations temperature led to weak acidity, resulting in inadequate activity, while too high calcinations temperature caused the loss of activity too. It is showed that moderates and strong acids were more favorable than weak acids. For HY zeolites, 450–550 °C was proposed as suitable calcinations temperatures to get more moderate acids. As shown above, HY calcined at both 350 and 750 °C can catalyze the conversion of endo-THDCPD to form exo-THDCPD. Based on the research of Gene [10] and Xu [16], most of acids on HY surface calcined at 350 °C were Broensted acids, while calcined at 750 °C most are Lewis acids. From it, the strength of acids is more important than the types of acids.

3.2.4. The module of zeolites

Commercially available HY Zeolites with different Si/Al ratios, HY, H-USY and H-SSY were tested. NH_4Y (Si/Al ratio 5.0) treated at high temperature in presence of water

steam possess relative higher Si/Al ratio (NH_4-USY) than NH_4Y. Even higher Si/Al ratio (9.0–12.0) of NH_4-SSY was achieved by treating NH_4Y with dealuminated reagent. The experiment results are listed in Table 4.

Si/Al ratio was an important factor to influence the acidic sites. Reza's work [17] showed that higher Si/Al ratio leads to smaller unit cell structure (UCS), meaning fewer acidic sites/stronger acidity and longer distance between two neighboring acid sites. Based on the data provided by zeolites producer: the Si/Al ratio increase in the order HY < H-USY < H-SSY, UCS decrease in the order HY > H-USY > H-SSY. It is concluded that the acidity increase with the order HY < H-USY < H-SSY, while acidic site numbers decrease with the same order, which is also showed in Corma's review [14]. It is shown that acidity strength is more important than acidity numbers to the formation of exo-THDCPD. So modification of Y zeolites should be focused on the change of acidity strength and acidity distribution rather than acidity numbers. Considering reaction data, higher Si/Al ratio contributes little to the formation of exo-THDCPD, while favor the formation of adamantane and other byproducts. In the adamantane literature [10–12], it was suggested that strong Bronsted acid sites help the formation of adamantane and side reactions. From this point, H-USY with more moderate acidity is favorable choice for exo-THDCPD production. On the other point, because NH_4-USY was prepared by treating NH_4Y with water stream at high temperature, H-USY is more stable at high temperature than HY, which is promising and enduring in catalyst regeneration. H-USY was proposed to be the favorable zeolites catalyst for the isomerization of endo-THDCPD.

As acidic zeolites, ReY showed unsatisfied activity for endo-THDCPD isomerization. The reason will be discussed with the acidity characterization in Fig. 2. As Fig. 2 shows, the acidity increased in the order ReY < H-USY < H-SSY. That was why activity (measured by endo-THDCPD conversion) increased in the same order ReY < H-USY < H-SSY. On the contrary, the selectivity decreased with the increase of acidity, mainly reflected by the amount of adamantane (also increasing with acidity strength) and other side products. In adamantane production essays, it's also proved that strong Broensted acid favored the formation of adamantane and cracking byproducts. While in this paper it is found that for the formation of exo-THDCPD, moderate acids are needed. The low activity of ReY showed that weak acidity contributes unimportantly to the conversion of endo-THDCPD, while having better selectivity. Taking the results of HY calcined at differ-

Table 4
The influence of Si/Al ratio

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

Fig. 5. Time stream on reaction.

Table 5
The composition of reaction mixtures (wt%) of used H-USY

Cat	The composition of reaction mixtures (wt.%)			
	Endo-THDCPD	Exo-THDCPD	ADM	Others
Used	72.83	24.39	0.21	2.57

acidity Y zeolites (HY, H-USY, H-SSY), 2 h is long enough to complete the isomerization of endo-THDCPD.

3.2.6. Catalyst deactivation

The life of H-USY was investigated in this section. After reaction the H-USY was dried at $120\,^{\circ}$C for next catalytic run. The results were listed in Table 5.

As shown in Table 5, obviously after reaction, the catalysts were deactivated. The reason may lie in the formation of deposits, which blocked the channels of zeolites. The H-USY should be regenerated to recover their activities.

3.2.7. Catalyst regeneration

Because of fast deactivation of H-USY, it is important to investigate the stability and regeneration of the catalysts for industrial use. In this section, H-USY (calcined at $550\,^{\circ}$C) was selected to check the catalyst life and the possibility of regeneration. Because of deactivation, H-USY was calcined to recover its activity. In order to burn out the deposits on the inner surface, the catalysts were calcined in muffle with air at $550\,^{\circ}$C until no weight loss occurred. It is shown that 4 h is sufficient for the complete of regeneration. Lower regeneration temperature leads to long regeneration time or incomplete recovery of activity. The regeneration data are drawn in Fig. 6.

As Fig. 6 shows, activity decreased slowly with regeneration times, while the exo-yields showed no tendency of decrease with the lower ADM formation. In other words, exo-selectivity was improved by regenerating deactivated H-USY zeolites. Compared with $AlCl_3$ in catalyst regeneration, obviously H-USY zeolites were more promising.

3.2.5. The effect of reaction time

The previous results show that H-USY has better catalytic performance to convert endo-THDCPD to exo-isomers. In order to check the time stream on reaction, the catalytic isomerization was carried out for 45 min, 1.5 h, 2 h and 4 h, respectively. The results were drawn below.

As Fig. 5 shows, 2 h is sufficient for the isomerization of endo-THDCPD. Prolonged reaction time has almost no contribution to the isomerizaion. Below 2 h, endo-conversion, exo-yield increase with prolonging reaction hours. After 2 h, all data about catalytic activity were almost unchanged. Although the activity of used H-USY was cut down (data in Section 3.2.6), its low activity can convert endo-THDCPD with condition that the reaction is uncompleted. As shown in Fig. 5, prolonged reaction time makes no contribution to endo-conversion, exo-yield and exo-selectivity. For strong

ent temperatures into account, it is proposed that moderate acidity is more favorable, because of its high conversion and better exo-yield.
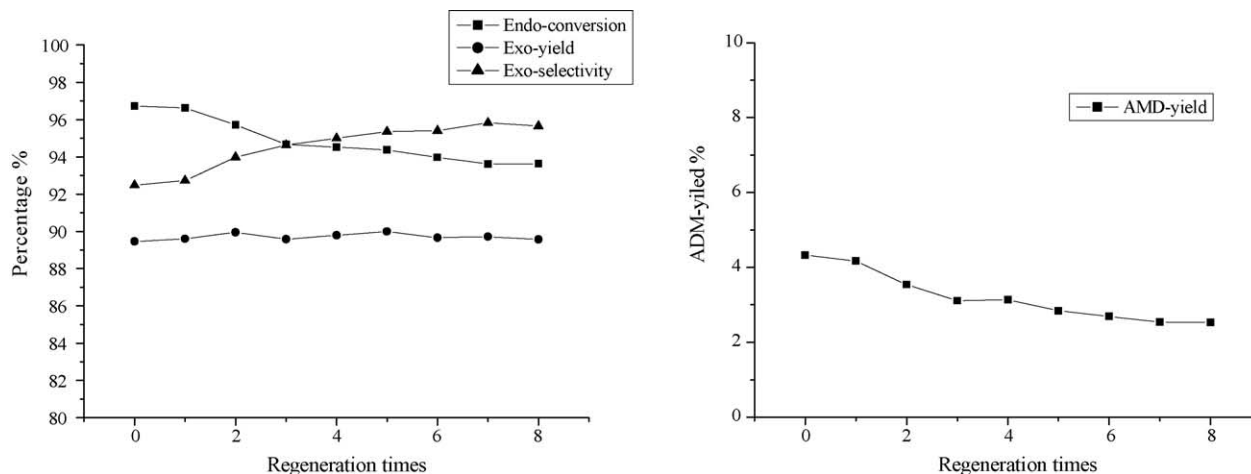

Fig. 6. The influence of catalyst regeneration.

4. Conclusion

The synthesis of exo-THDCPD by isomerization of endo-THDCPD on commercially available zeolites was studied. It was shown that pore size and acidity were most important factors to influence the activity and selectivity of the zeolitic catalyst. HY zelites (0.74 nm) were most active than zeolites with smaller pore sizes (H-beta and H-ZSM-5). Besides pore size, acidity is the other key factor. Calcinations temperatures, cations and Si/Al ratios were investigated. Moderate calcinations temperatures, which lead to more moderate acids favoring the formation of exo-THDCPD, are key factor to influence the acidity of the HY zeolites. In all Y zeolites with different cations, HY were most active. In all H-type Y zeolites with different Si/Al ratio, H-USY is best because of more moderate acids. What's more, H-USY's stability at high temperature seem promising in catalyst regeneration. In final H-USY calcined at 450 °C was best. As shown in papers, the strength of acids is most influential factor for the formation of exo-THDCPD. Weak acids have low conversion. In spite of high conversion, strong acids are not suitable choice for exo-THDCPD because strong acids help the formation of adamantane and other side products. As for moderate acids, it can catalyze endo-THDCPD to exo-THDCPD effectively with fewer byproducts' formation.

For H-USY, time course showed that 2 h is sufficient to complete reaction, and regeneration of catalyst leads to no decrease of exo-yields, but low endo-THDCPD conversion, that is selectivity increased with regeneration times.

It can be concluded that commercially available Y zeolites could be used for synthesis of exo-THDCPD, but without further modification such catalyst exhibit unsatisfactory activity for industrial application. The use of aluminum chloride as catalyst in exo-THDCPD production can be replaced by Y zeolites through modifications of zeolites. Theoretically, attention should be focused on the influence of acidity strength rather than the types and numbers of the acids. Even without the modification of HY zeolites, the results of H-USY were still promising to replace aluminum chloride for exo-THDCPD production.

References

[1] L.G. Cannell, US Patent 4059644 (1977), to Shell Oil Company; R.V. Norton, D.H. Fisher, US Patent 4286109 (1981), to Ashland Oil Inc.
[2] H.S. Chung, C.S.H. Chen, R.A. Kremer, J.R. Boulton, Energy Fuels 13 (1999) 641–649.
[3] C.A. Cohen, C.W. Muessig, US Patent 3381046 (1968), to Esso Research and Engineering Company.
[4] P.V.R. Schleyer, M.M. Donaldson, J. Am. Chem. Soc. 82 (17) (1960) 4645–4651.
[5] R.V. Norton, D.H. Fisher, G.M. Graham, P.J. Frank, US Patent 4355194 (1982), to Ashland Oil Inc.; E.J. Janoski, A. Schneider, R.E. Ware, US Patent 4288644 (1981), to Suntech Inc.; R.V. Norton, S.C. Howe, US Patent 4270014 (1981), to Ashland Oil Inc.; A. Schneider, R.E. Ware, E.J. Janoski, US Patent 4086284 (1978), to Suntech Inc.
[6] A. Tanaka, JP Patent 2002255866 (2002), to Nippon Zeon Co. Ltd.; A. Tanaka, JP Patent 2002302460 (2002), to Nippon Zeon Co. Ltd.; N. Ogoshi, T. Mase, Tanakaakira, K. Watanabe, JP Patent 2003128593 (2003), to Nippon Zeon Co. Ltd.
[7] U.M. Dzhemilev, R.A. Sadykov, M.G. Samokhina, RU Patent 2191172 (2003), to AS Bashkortostan Petrochem & Catalysis (ABAS-Soviet Institute).
[8] S.S. Cheng, K.F. Liou, Y.T. Lin, J. Chin. Chem. Soc. 33 (1986) 335–340.
[9] G.A. Olah, O. Farooq, J. Org. Chem. 51 (1986) 5410–5413.
[10] G.C. Lau, W.F. Maier, Langmuir 3 (1987) 164–173.
[11] K. Honna, M. Sugimoto, K. Kurisaki, Chem. Lett. (1986) 315–318.
[12] M. Navratilova, K. Sporka, Appl. Catal., A Gen. 203 (2000) 127–132.
[13] K. Tanabe, W. Hoelderich, J. Appl. Catal., A Gen. 181 (1999) 399–434.
[14] A. Corma, Chem. Rev. 95 (1995) 559–614.
[15] J. Datka, J. Chem. Soc., Faraday Trans. 77 (1981) 2877.
[16] R. Xu, W. Pang, K. Tu, Zeolite Molecular Sieves Structure and Synthesis, Jilin University Press, Jilin, China, 1987, p. 116.
[17] R. Sadeghbeigi, Fluid Catalytic Cracking Handbook, 2nd ed. Chinese version translated by China Petrochemical Press, p. 72.