

Accepted Manuscript

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PII: S0926-860X(14)00362-7
DOI: <http://dx.doi.org/doi:10.1016/j.apcata.2014.05.028>
Reference: APCATA 14848

To appear in: *Applied Catalysis A: General*

Received date: 22-3-2014
Revised date: 25-5-2014
Accepted date: 26-5-2014



Please cite this article as: Z. Chen, Y. Feng, T. Tong, A. Zeng, Effects of acid-modified HBEA zeolites on thiophene acylation and the origin of deactivation of zeolites, *Applied Catalysis A, General* (2014), <http://dx.doi.org/10.1016/j.apcata.2014.05.028>

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Effects of acid-modified HBEA zeolites on thiophene acylation and the origin of deactivation of zeolites

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Highlights

- First report on thiophene acylation over acid-modified HBEA zeolite.
- Discussion about origin of deactivation of zeolite on thiophene acylation.
- Use of green renewable technology that can potentially be industrialized.

Abstract: The liquid phase Friedel-Crafts acylation of thiophene with acetic anhydride over HBEA zeolites modified by hydrochloric, nitric, and acetic acid was investigated in a trickle bed reactor. The catalytic stability of the HBEA zeolite was doubled after treatment with the hydrochloric and nitric acids due to the increase of the ratio of Brønsted to Lewis acid sites, the surface area, and the average pore diameter. The deactivated zeolites can be regenerated by calcination in a muffle furnace and the superior reusability of the zeolite HBEA was demonstrated after nine cycles. Moreover, the carbon deposit was proved to be one of the main reasons for the deactivation by using ^{13}C NMR MAS, ^{27}Al NMR MAS, and TGA.

Keywords: Friedel-Crafts acylation; Zeolite; Thiophene; Modification; Deactivation

1. Introduction

Friedel-Crafts acylation is an important reaction for synthesizing aromatic ketones, which are the key intermediates in the production of valuable industrial and fine chemicals^[1-6], such as pharmaceuticals^[7,8], insecticides^[8], plasticizers, dyes^[8] and perfumes. Traditionally, the catalysts used in the Friedel-Crafts acylation are Lewis acid (e.g. metal halides) or Brønsted acid (e.g. H_2SO_4 ^[9,10], HCl , HF ^[2]). However, a number of problems including the disposal of spent catalysts, corrosion, toxicity and product isolation, are involved^[1,11].

In view of the disadvantages of the conventional catalysts, the development of eco-friendly catalytic routes for various organic transformations has become an ongoing interest of catalytic researchers^[12,13]. Considerable efforts have been made to develop zeolites, such as ZSM-5^[14,15,16],

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H β ^[2,4,17,18], and HY^[18,19,20] for the acylation reaction. Harvey et al.^[21] reported H-Beta exhibited highly active catalyst for the acylation of anisole by acetic anhydride and phenyl acetyl chloride. Mild liquid-phase Friedel-Crafts acylation of heteroaromatic compounds such as thiophene, pyrroles and furans over zeolite beta were studied by Alvaro et al.^[22], and the beta zeolites were also found to have high catalytic activity in the acylation of thiophene in micro-reactor without solvent. In addition, indium modified zeolite beta has provided a way to obtain a good yield in the acylation of pyrroles. On the other hand, the study on the nature of active sites of zeolites was still in grope. Reddy et al.^[23] found the Friedel-Crafts acylation of furan and pyrrole was more active on Broensted acid sites. However, there was a correlation between the initial rates of reaction and the number of Lewis acid sites but not Broensted acid sites^[24].

What is also worth noticing is that modifications of zeolites are essential for obtaining higher catalytic stability and activity in the reaction process. Dealumination was one of the modifications used for promoting the performance of zeolites, which was obtained via hydrolysis of Al-O-Si bonds by organic acids, such as oxalic acid and citric acid^[25,26]. Zhao et al.^[27] reported that the beta zeolite modified with hydrochloric acid exhibited the most active performance and best catalytic stability in the anisole acetylation. However, the study of the effects of the modified zeolites with acids on the acylation of heteroaromatic compounds in a fixed bed reactor was scarcely seen.

In this paper, HBEA zeolites modified by typical simple organic acid (acetic acid) and inorganic acids (hydrochloric and nitric acid) were first investigated in Friedel-Crafts acylation of thiophene in a trickle bed reactor. The thiophene used in this work was distinguished from the general one due to its particular source of being purified from the by-products of coal coking process, and herein it was named as coking thiophene. In China, over 21,500 tons of coking thiophene could be get as a by-product from the industry of coal coking per year, and that is ten times than the amount of synthetic thiophene. Moreover, almost all coking thiophene was wrecked into pollutions. It is very urgent to find a solution to utilize the coking thiophene. Therefore, the aim of this paper was to provide an efficient approach to change coking thiophene into pharmaceutical intermediate 2-acetyl thiophene. And an attempt was made to analyze the effects of modified HBEA zeolites with its acids on the structure, acidity, catalytic stability and the origin of deactivation of zeolite HBEA was discussed as well.

2. Experimental

2.1 Materials

Thiophene (96%) was provided by Qiaoyou Chemical Co., Ltd and it contains impurities such as propionitrile (approximately 4%), trace of benzene and furan. Various acids, acetic anhydride (>99%) and tetraethyl ammonium hydroxide (TEAOH) were purchased from Aladdin reagent Co., Ltd. The commercial aluminosilicate was purchased from Nankai University Catalyst Co., Ltd. All materials were used without further purification.

2.2 Catalyst Preparation

The HBEA sample was made according to the method reported by Matsukata et al.^[28]. 50 g

HBEA (Si/Al=27.6) were subjected to acid treatments by stirring with 1.0 mol/L hydrochloric, nitric and acetic acid at 100 °C for 12 h, respectively. The acid-treated zeolites were washed by deionized water until the solution reached neutral, then dried at 120 °C for 2 h. After that, the zeolites were calcined at 450 °C for 5 h. The treated zeolites were named HA-BEA, NA-BEA and AC-BEA, respectively.

Each 10 g powder of HBEA, HA-BEA, NA-BEA and AC-BEA were mixed with 3 g Al₂O₃ and 4 g nitric acid solution (10 wt%) into homogenate and then extruded and cut into short cylinder within 4 mm in length and 3 mm in diameter. The granular zeolites were dried at 120 °C for 2 h, and then calcined at 450 °C for 5 h in a muffle furnace.

2.3 Catalyst Characterization

X-ray diffraction (XRD) analysis was recorded on a Bruker D8-S4 with Cu K α radiation, scanning from 5° to 50° (2 θ) range with a scanning rate of 5.21 °/min. The voltage and current used were 40 kV and 40 mA, respectively.

The bulk Si/Al molar ratios of the samples were determined by XRF. The BET surface area and total pore volume were determined using a Micromeritics ASAP2020 volumetric instrument at -196 °C using nitrogen adsorption isotherms. The pore size was determined by Horvath-Kawazoe method.

The acidity of all the zeolite samples was determined by the pyridine adsorption-desorption method performing on a Nicolet 750 infrared spectrometer coupled to a conventional high vacuum system. The samples were calcined at 450 °C for 120 min in an in situ IR gas cell under vacuum prior to pyridine adsorption. Then the temperature was cooled down to 90 °C. Pyridine was adsorbed for 30 min and then the physisorption pyridine was evacuated at 200 °C and 350 °C for 20 min, respectively. The IR spectra were obtained at 200 °C and 350 °C.

¹³C-NMR and ²⁷Al-NMR spectra were recorded on a Varian Infinity plus NMR (¹³C, ²⁷Al 300 MHz) spectrometer in order to investigate the kind of carbon deposit and the form of aluminum. The scanning frequency was 75.4 MHz and pulse delay was 5.0 second. Chemical shifts (δ) were reported in ppm on behalf of the kind of carbon deposit and the form of aluminum, respectively.

A PerkinElmer Diamond TG/DTA instrument was used to obtain TG/DTG profiles. For clarity, the differential TG curve (DTG) was presented. Each time, appropriate 10 mg of the samples were heated at a heating rate of 20 °C·min⁻¹.

2.4 Catalytic Reaction

The acylation reactions were carried out in a trickle bed reactor (Fig. 1) made of glass (inner diameter 10 mm) at 80 °C under atmospheric pressure. The catalyst (6.2 g) was preheated for 2 h at 200 °C in a drying oven before the reaction, and then placed in the center zone of the reactor. The reactants of thiophene and acetic anhydride mixture with a molar ratio of 1:2 were fed into the reactor by a metering pump, at a flow rate of 0.05 ml/min. Products were taken in regular intervals and analyzed by gas chromatography (Agilent 7890A) equipped with a FID detector using 30 m column of DB-17MS.

The organic compounds retained on the external zeolite surface and in the micropores were recovered at the end of the experiment. For that, the used catalyst underwent a double-extraction

methodology according to the description by Rohan^[29] and the remaining organic materials were analyzed by GC-MS. We found side products containing 3-acetylthiophene (0.1~0.3% relative to 2-acetylthiophene) and others (<0.01%) such as 1-(thien-2-yl)-1,3-butanedione and 1-(thien-2-yl)-1-propanone.

Since acetic anhydride was in excess, and the product isomer was hardly found by the spectral in comparison with the authentic samples, that is to say, the selectivity of the 2-acetylthiophene was approximately 100%. The conversion of thiophene was calculated by

$$X_{\text{Thiophene}} = \frac{\% \text{Thiophene}(\text{feed}) - \% \text{Thiophene}(\text{product})}{\% \text{Thiophene}(\text{feed})} \times 100$$

After the first cycle, the catalysts were collected together and dried at 120 °C for 2 h, then calcined at 450 °C for 5 h in a muffle furnace. Catalytic behavior of regenerated zeolite was investigated under the same conditions. The tests were repeated for nine times.

3. Results and discussion

3.1 Characterization of zeolites

XRD patterns of all zeolite HBEA samples are shown in Fig. 2. All of them showed that the reflections at 7.8° and 22.5°, typical of zeolite HBEA structure even after the acid modifications, indicating that the acid-treatment did not change the zeolite structure, and there were no other visible peaks can be observed. The modified zeolite samples all existed relatively high crystallinity as Table 1 showed. Table 1 also illustrates that the ratios of Si/Al of the zeolites HBEA, AC-BEA, HA-BEA and NA-BEA were 27.6, 33.7, 62.3 and 89.8, respectively, suggesting that the dealuminized extent of HBEA zeolite increased significantly after inorganic acid (HCl and HNO₃) treatments but slightly after organic acid (CH₃COOH) treatment.

Table 2 shows that the total BET surface areas and average pore diameters of NA-BEA and HA-BEA were larger than those of HBEA and AC-BEA, with NA-BEA having the largest surface area and HA-BEA having the largest average pore diameter. These results might be explained by the extent of dealumination of the zeolites after acid modification^[27] which can be confirmed by Si/Al ratio shown in Table 1.

The FT-IR spectra of the parent and acid-modified HBEA zeolites adsorbed pyridine probe molecule are compared in Fig. 3. Band at 3744 cm⁻¹ in Fig. 3A is assigned to silanol groups, characteristic of terminating silanols^[30]. Compared with HBEA, the band of terminating silanols at 3744 cm⁻¹ increased its intensity substantially for HA-BEA and NA-BEA, while there was only a little increase for AC-BEA. The information of Broensted and Lewis acid sites can be gained by the pyridine-IR spectra shown in Fig. 3B. Bands at 1545 and 1455 cm⁻¹ can be ascribed to pyridinium ions (PyH⁺, Broensted acid site) and coordinative bound pyridine (PyL, Lewis acid site), respectively^[27,30-33]. The band at 1489 cm⁻¹ was associated with adsorption on both Broensted and Lewis acid sites^[31]. A reliable assessment of the concentration of surface acid sites can be calculated by the integrated peak area^[32], and the results of Py-IR analysis of different samples are listed in Table 3. In comparison with unmodified HBEA zeolite, it is clear to see that acid-treated ones contained more Broensted acid sites, and the number of Lewis acid sites decreased remarkably after modifications except AC-BEA zeolite. Therefore, it can be concluded that the

hydrochloric acid and nitric acid treatments are able to etch most Lewis acid sites on or near the external surface but acetic acid treatment is not. This is validated by the absorbance fluctuation appeared at band 3744 cm^{-1} . Moreover, the ratios of Brønsted to Lewis acid site (B/L ratio) of HA-BEA and NA-BEA are far more than those of HBEA and AC-BEA zeolites.

3.2 Catalytic stability of the zeolites

The catalytic stability for the conversion of thiophene into 2-acetylthiophene has been investigated in a trickle bed reactor using the HBEA zeolites with and without modification. It is obviously observed that HA-BEA and NA-BEA zeolites exhibited higher catalytic stability than the parent HBEA and AC-BEA zeolites as shown in Fig. 4. In the presence of parent HBEA zeolite, the conversion of thiophene could keep up to 90% within 2510 min, which is similar to that of AC-BEA zeolite. The zeolites HA-BEA and NA-BEA maintained 4847 min and 5332 min respectively, and the highest conversion was found to be 99.9% at 200 min for both of them. In addition, the conversions with AC-BEA and parent HBEA zeolites decreased sharply after 820 min, while HA-BEA and NA-BEA still showed relatively higher conversion (>97%) after 3000 min. This distinction is in good agreement with results reported by Heinichen and Holderich^[4]. Fig. 4 and Table 1 indicate that the catalytic stability went up when increasing the ratio of Si/Al in a certain range. Besides, combining with Table 2, it can be clearly seen that higher catalytic stability of the catalyst are related to larger external surface area and average pore diameter, which could be conducive to the diffusion of the product.

Herein the performance of zeolites characterized in this work were compared with those of the best-performing ones reported by Kantam et al.^[34]. Better results (conversion of thiophene reached 91% and selectivity of 2-acetyl thiophene was 70% after 3 h) were got when using microcrystalline beta zeolite (particle size of 1~10 μm). Though there existing a huge difference in reactive mode between current work described above (continuous mode) and that in the literature (batch mode, in a flask), it can obviously reveal the superiorities of acylation reaction in continuous mode (conversion of thiophene was up to 90% within 5332 min and selectivity of 2-acetyl thiophene was close to 100%) under the similar conditions (80 °C, thiophene/acetic anhydride molar ratio=1:2).

3.3 Effects of the zeolites modified with acids

It is well known that Friedel-Crafts acylation reaction over zeolites is catalyzed on the Brønsted or Lewis acid sites, this makes no essential difference with the general catalytic mechanism of traditional Brønsted or Lewis acid to some extent. The acidic properties of zeolites are closely linked to the quantity, nature, and distribution of the aluminum atoms attached to or trapped in pores and cavities of zeolites. Brønsted acid sites have external -OH groups, while the Lewis sites are exposed three-fold coordinated Al^{3+} ions^[35].

Zeolites HBEA treated by acids exhibited different catalytic stabilities in acylation of thiophene (Fig. 4). Among these zeolites, NA-BEA and HA-BEA gave higher catalytic stability, while AC-BEA and HBEA were less effective. It was of interest to see that catalytic stability increased with the increase of the ratio of Si/Al without a linear relationship (Table 1), which was due to the different levels of dealumination by acids. Donk et al.^[36] reported a mild acid-leaching

step using either inorganic acids or organic acid, improved the porous properties by dissolving the extraframework material. However, during the severe treatment with strong inorganic acids, aluminum is removed from the framework. And similar conclusions have been obtained by other groups^[37,38]. In this work, hydrochloric acid and nitric acid treatments were more intense than acetic acid treatment, which may remove additional framework aluminum species. Structural characteristics of zeolites can be significantly affected by acid-modification. Though all of the zeolites possessed high crystallinity (Fig. 2 and Table 1), the XRD patterns at 7.8° and 22.5° of NA-BEA and HA-BEA zeolites were stronger than those of AC-BEA and HBEA, which may favor the acylation reaction. In addition, NA-BEA and HA-BEA zeolites had larger external surface area and average pore diameter (Table 2), because of the removal of most extra-framework aluminum through hydrochloric acid and nitric acid treatments and hence the formation of some intergranular pore or new unchoked channels. It should be noticed that all the acid treatments are mild so that the integrity of the zeolite crystal would not be destroyed. And the channels were unchoked in the gentle acid treatments, which may contribute to maintain high zeolite crystallinity.

The increase of external surface area and average pore diameter were not only conducive to better distribution of acid sites on zeolites surface, as well as fully diffusion of reactants and products. Besides, external surface areas of NA-BEA and HA-BEA zeolites augmented visibly compared with HBEA, but not the internal. Hence, it seems that the external surface is primarily active catalytically. It has been reported that Broensted acid sites present both on the internal and external surface, while Lewis acid sites are predominantly presents on the internal surface^[39,40]. Thus, possessing large external surface may contribute to adding Broensted acidity, which is beneficial to the acylation reactions.

Combined with Fig. 4, the correlation of catalytic stability with acidity reveals that the ratio of Broensted to Lewis acid sites seems to be of great importance for the acylation reaction (Table 3). That is NA-BEA and HA-BEA zeolites with more Broensted but less Lewis acid sites exhibited higher stability, while AC-BEA with both large Broensted and Lewis acid sites displayed unsatisfactory results. With further analysis of the ratio of Broensted to Lewis acid sites for HBEA (0.71~0.64), AC-BEA (0.95~0.91), HA-BEA (4.07~4.23) and NA-BEA (4.32~4.46), which is highly consistent with the acylation results ranked by catalytic stability as follows

$$NA - BEA \approx HA - BEA > AC - BEA \approx HBEA$$

The reasons may be that some Broensted acid sites which were covered by neutral or non-acidic amorphous substance on the external surface would be exposed through the hydrochloric and nitric acid treatments, and most extra-framework aluminum which represents Lewis acid sites was etched simultaneously^[41], resulting in producing more Broensted acid sites but less Lewis acid sites, with higher ratio of Si/Al. With regard to acetic acid, a kind of weak organic acid, probably due to the gentle treatment, only some amorphous substance was removed, resulting in the release of Broensted acid sites which were covered before. Therefore, the number of Broensted acid sites increased but the number of Lewis acid sites was nearly unchanged, that is, the total amount of acid sites of HBEA increased. Canizares and Carrero^[42] reported that extra-framework aluminum could decrease the accessibility of active sites to reactant molecules, which reduces the contact time but favors the formation of by-products. Thus, hydrochloric and nitric acid treatments could enhance the catalytic stability of the catalysts, but acetic acid treatment could not.

To summarize, the dealuminated catalysts with a higher ratio of Brønsted to Lewis acid sites have lower acid site density (and higher acid strength) and exhibit higher catalytic stability. Hence, it can be proposed that acid treatment affects the coordination state of aluminum and therefore change the number and type of acid sites. And an ideal catalyst with an outstanding activity and stability may not possess Brønsted acid sites as much as possible but a high ratio of Brønsted to Lewis acid sites, as well as a large external surface area and average pore diameter.

3.4 Regeneration and reusability of the zeolites

Reusability of HBEA, AC-BEA, HA-BEA and NA-BEA zeolites was investigated and the results are given in Table 4. The regenerated zeolites almost displayed the same trend profiles with the reactive time and performances as their origins. In this paper, the catalyst was regarded as deactivation when the conversion of thiophene was below 90%.

Table 4 also shows that the zeolites HBEA before and after modification could be regenerated and recycled through calcination at high temperature. The average lifetime of HBEA was kept at 2911 min before the deactivated point during the nine times reaction processes, and 6.2 g HBEA zeolite help to produce 1310 g primary products, such as 2-acetyl thiophene, acetic acid, etc. That is to say, the treated capacity of the parent zeolite was up to 211 g, which was roughly equal to the capacity of AC-BEA zeolite (3061 min, 222 g). As expected, the average lifetime and treated capacity of HA-BEA (4863 min, 353 g) and NA-BEA (4893 min, 356 g) zeolites were better than those of the parent zeolite HBEA and AC-BEA.

It indicates that the activity and stability of the zeolite can be regenerated efficiently and satisfactorily, which means that most of the acid sites can be regenerated to its original states. Therefore, the zeolites HBEA are expected to replace the traditional Lewis acid and Brønsted acid catalysts to solve the manufacturing and environmental problems.

3.5 The origin of deactivation

In order to study the reasons for deactivation of zeolites, the analytical methods of the ^{13}C MAS NMR, ^{27}Al MAS NMR and TGA were taken.

The ^{13}C MAS NMR spectra of the deactivated and regenerated zeolites are shown in Fig. 5. Derouane et al.^[43] first studied the formation and stability of coke deposits by the method of ^{13}C MAS NMR during the conversion reaction of methanol to hydrocarbons. Carbon deposit mainly includes fat carbon, olefin carbon, aromatic carbon and poly aromatic carbon, etc. The peak signal of fat carbon is between 10 ppm and 40 ppm, the signal between 125 ppm and 145 ppm belong to aromatic carbon, while between 130 ppm and 200 ppm was the characteristic signal of poly aromatic. For the deactivated zeolites, the carbon deposit in the channel and surface was very severe, which mainly consisted of fat hydrocarbon, cyclic compound and aromatic oligomers. It was clearly exhibited that there was no carbon depositing on the surface and inside channel for the regenerated samples, which meant the organics accumulated in zeolites were basically removed through regeneration in a muffle furnace. As a consequence, the HBEA zeolite can be reused in the acylation of thiophene.

The influence of carbon deposit on zeolites framework could be characterized by ^{27}Al MAS NMR. The state of aluminum framework changed when the zeolites channel was filled with

carbon deposit. There are two peaks in Fig. 6 corresponding to tetrahedral and octahedral Al sites^[44] in the range of -10 to 40 and 40 to 80 ppm, respectively. The tetrahedral Al concentration tended to decrease on the deactivated zeolite compared to the regenerated and the parent ones, while the octahedral Al concentration kept constant. This indicated that the change of tetrahedral Al results from the adsorption of carbon deposit in the zeolites. Besides, the tetrahedral Al represents Brønsted acid sites, while the octahedral Al is on behalf of Lewis acid sites. Therefore, Fig. 6 may indicate that the Brønsted acid is responsible for the Friedel-Crafts acylation reaction of thiophene with acetic anhydride.

TGA (Thermogravimetric Analysis) was employed to investigate the amount of carbon deposit in the surface and channel of the zeolites. As shown in Fig. 7, both of the samples had a peak of weight loss in the range of 50~150 °C mainly caused by surface moisture adsorbed from air, hydrated water and adsorbed organic with low boiling point in the reaction process. There was no weight loss for the regenerated zeolite over 150 °C, but the peaks of weight loss existed in the range of 200~300 °C and 350~400 °C for the deactivated zeolite. At the range of 200~300 °C, the peak of deactivated zeolite represented the high boiling point organic, such as 2-acetyl thiophene, while at the range of 350~400 °C, the peak represents the oligomers, such as poly thiophene, poly propionitrile, poly 2-acetyl thiophene, et al. Besides, Chica et al.^[44] reported that thiophene oligomers formed during adsorption and their size depended on spatial constraints within zeolite channels, and moreover oligomerization occurred on Brønsted acid sites at 90 °C. Fig.7 shows that the carbon deposit from deactivated zeolite mainly focused on the range of 200~300 °C, about 11.7% weight loss in this scope and 1.8% in the range of 350~400 °C. In summary, the carbon deposit rate of the regenerated zeolite was zero, while the number for deactivated zeolite was up to 13.5%.

4. Conclusions

The catalytic stability of zeolite HBEA in trickle bed reactor can be greatly improved by dealumination through various acids treatments, especially by hydrochloric and nitric acid. It is found that the ratio of Brønsted to Lewis acid sites, external surface area and average pore diameter play important roles in the significant increase of catalytic stability. And HBEA zeolites still exhibit excellent reusability even after eight cycles. The main reason for deactivation is the carbon deposit through the comparison between the deactivated and regenerated zeolites.

Acknowledgements

This work is supplied by The National Key Technology R&D Program of China (2007BAB24B05) and Shanxi Qiaoyou Chemical Co. Ltd.

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Figure Captions

Fig.1. Acylation of thiophene in trickle bed reactor apparatus diagram.

Fig.2. XRD patterns of the parent and acid-modified HBEA zeolites.

Fig.3. FTIR spectra of pyridine-adsorbed parent and acid-modified HBEA zeolites (Pyridine adsorption at 90 °C and desorption at 200 °C).

Fig.4. Catalytic stability tests for acylation of thiophene with acetic anhydride over the parent and acid-modified HBEA zeolites in a trickle bed reactor (experimental conditions: 80 °C, thiophene/acetic anhydride molar ratio=1:2, 6.2 g of catalyst).

Fig.5. ^{13}C MAS NMR of the deactivated and regenerated samples

Fig.6. ^{27}Al MAS NMR of the parent, deactivated and regenerated samples

Fig.7. TG/DTG curves of the deactivated and regenerated samples

Table Captions

Table 1 Properties of XRD on the parent and acid-modified HBEA zeolites.

Table 2 BET surface area, micropore volume and average pore diameter of the parent and acid-modified HBEA zeolites.

Table 3 Result of IR spectra of Py adsorbed on the parent and acid-modified HBEA zeolites after desorption at different desorption temperatures.

Table 4 Results of the treated capacity of the parent and acid-modified HBEA zeolites.

Fig.1

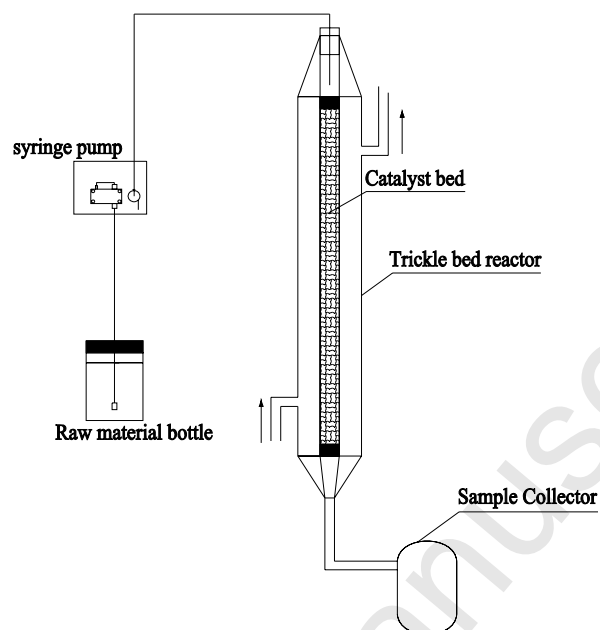


Fig.2

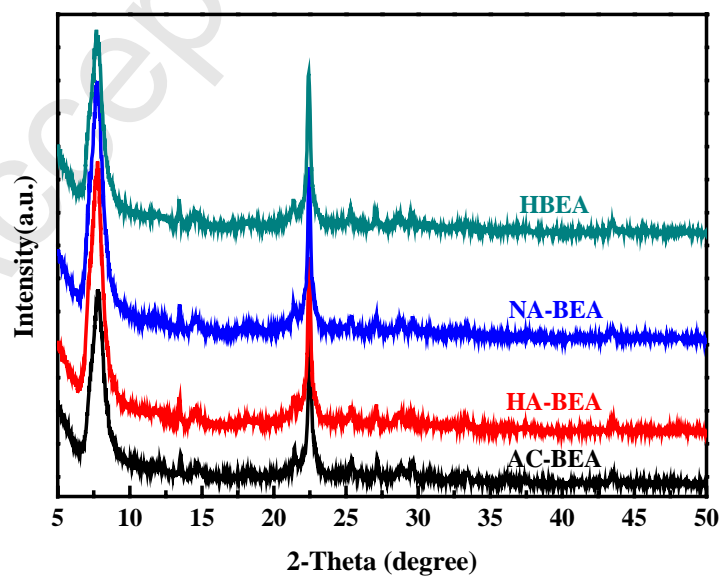


Fig.3

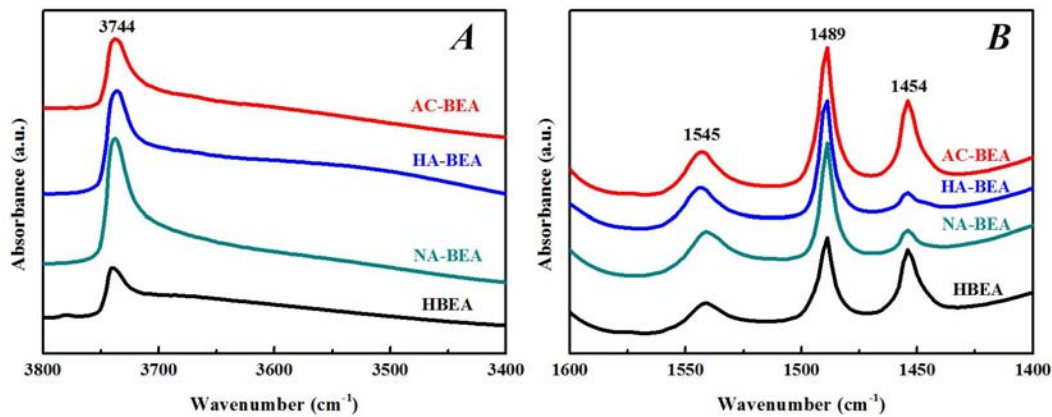


Fig.4

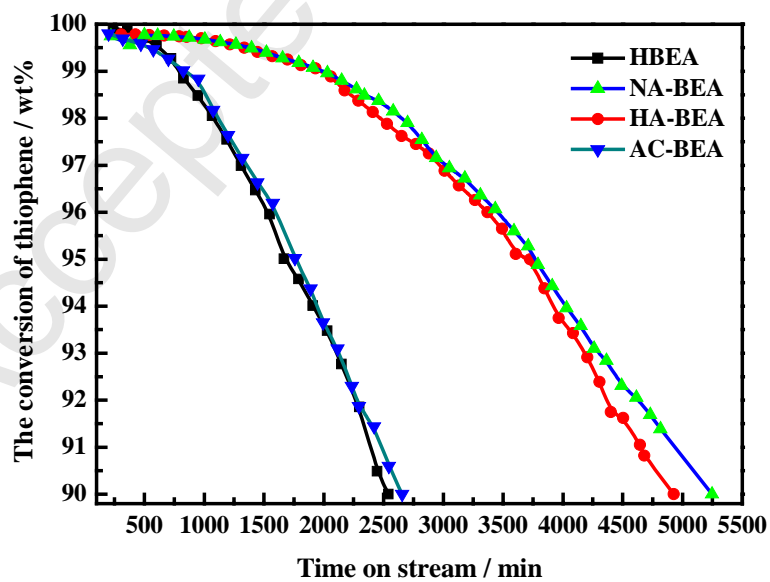


Fig.5

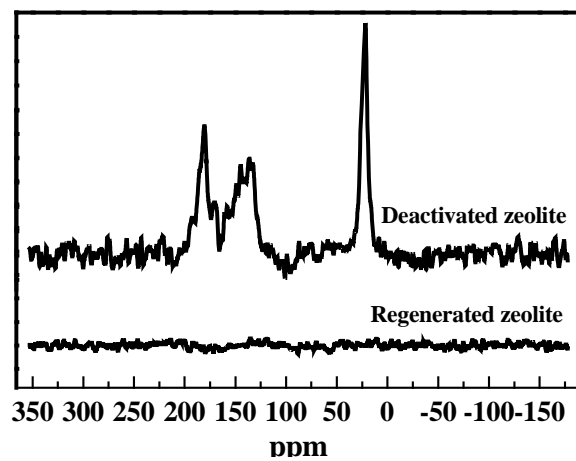


Fig.6

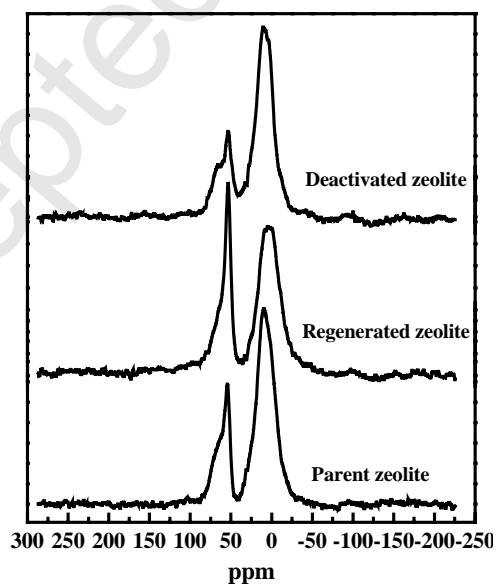


Fig.7

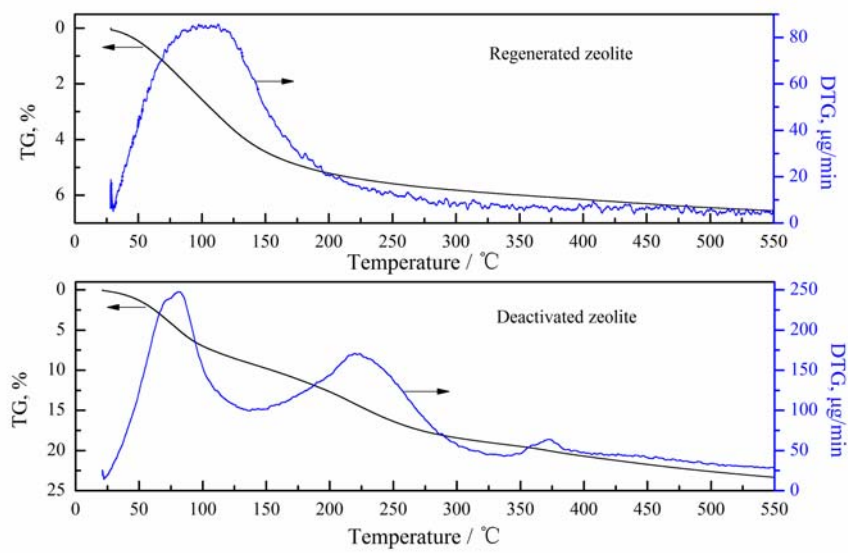


Table 1 Properties of XRD on the parent zeolite HBEA and modified with various acids.

Catalyst	Bulk Si/Al ratio ^a	XRD crystallinity ^b (%)
HBEA	27.6	100
AC-BEA	33.7	99
HA-BEA	62.3	99
NA-BEA	89.8	99

^a Determined by XRF; ^b XRD signal $2\theta=7.8^\circ$, and 22.5° .

Table 2 BET surface area, micropore volume and average pore diameter of zeolite HBEA and modified zeolite HBEA with various acids.

Sample	Surface Area ^a (m ² /g)			Micropore Pore Volume ^b (cm ³ /g)	Average Pore Diameter ^c (nm)
	Total	Micropore	External		
HBEA	542	449	93	0.209	0.56
AC-BEA	558	425	133	0.198	0.59
HA-BEA	585	419	166	0.194	0.74
NA-BEA	597	432	165	0.201	0.66

^a Surface area determined by the BET method;

^b Micropore pore volume determined by the t-plot method;

^c Micropore diameter determined by Horvath-Kawazoe method.

Table 3 Result of IR spectra of Py adsorbed on the zeolite HBEA and modified zeolite HBEA with acid after desorption at different desorption temperatures.

Sample	200 °C			350 °C		
	B acid site (mmol/g)	L acid site (mmol/g)	B/C ^a	B acid site (mmol/g)	L acid site (mmol/g)	B/C ^a
HBEA	0.334	0.331	0.71	0.228	0.252	0.64
AC-BEA	0.517	0.384	0.95	0.398	0.306	0.91
HA-BEA	0.502	0.087	4.07	0.396	0.066	4.23
NA-BEA	0.571	0.093	4.32	0.472	0.074	4.46

^a B/C: the ration of B acid site to L acid site.

Table 4 Results of the treated capacity of the parent zeolite HBEA and modified zeolite with various acids.

Catalyst	Regeneration time	Deactivated point	Catalyst dosage / g	Lifetime / min	The amount of initial product / g	The treated capacity of catalyst /g
HBEA	0	90.0%	6.2	2510	125.5	20.2
	1	90.0%	6.2	2139	107.1	17.3
	2	90.0%	6.2	2981	149.1	24.0
	3	90.0%	6.2	3042	152.2	24.5
	4	90.0%	6.2	3024	151.2	24.4
	5	90.0%	6.2	3117	155.8	25.1
	6	90.0%	6.2	2916	145.8	23.5
	7	90.0%	6.2	3523	176.2	28.4
	8	90.0%	6.2	2943	147.1	23.7
Average / Total				2911 /--	--/ 1310	--/ 211
AC-BEA	0	90.0%	6.2	2655	132.8	21.4
	1	90.0%	6.2	2913	145.7	23.5
	2	90.0%	6.2	3439	172.1	27.8
	3	90.0%	6.2	3935	196.8	31.7
	4	90.0%	6.2	2990	149.5	24.1
	5	90.0%	6.2	3100	155.1	25.0
	6	90.0%	6.2	3000	149.9	24.2
	7	90.0%	6.2	2586	129.3	20.9
	8	90.0%	6.2	2930	146.5	23.6
Average / Total				3061 /--	--/ 1378	--/ 222
HA-BEA	0	90.0%	6.2	4847	242.6	39.1
	1	90.0%	6.2	5705	286.2	46.2
	2	90.0%	6.2	5899	295.1	47.6
	3	90.0%	6.2	5447	273.1	44.0
	4	90.0%	6.2	4641	232.0	37.4
	5	90.0%	6.2	5212	260.6	42.0
	6	90.0%	6.2	3813	190.7	30.8
	7	90.0%	6.2	4110	205.5	33.1
	8	90.0%	6.2	4097	204.9	33.0
Average / Total				4863 /--	--/ 2191	--/ 353
NA-BEA	0	90.0%	6.2	5332	267.2	43.1
	1	90.0%	6.2	5508	275.7	44.5
	2	90.0%	6.2	5212	260.8	42.1
	3	90.0%	6.2	5075	253.8	40.9
	4	90.0%	6.2	4824	242.2	39.1
	5	90.0%	6.2	4788	240.4	38.8
	6	90.0%	6.2	4483	225.2	36.3
	7	90.0%	6.2	4574	229.2	37.0
	8	90.0%	6.2	4244	212.3	34.2
Average / Total				4893 /--	--/ 2207	--/ 356