



Direct amination of isobutylene over zeolite catalysts with various topologies and acidities

Shangyao Gao^{a,b}, Xiangxue Zhu^{a,*}, Xiujie Li^a, Yuzhong Wang^a, Sujuan Xie^a, Songwei Du^c, Fucun Chen^a, Peng Zeng^d, Shenglin Liu^a, Longya Xu^{a,*}

^a Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

^c PetroChina Jinzhou Petrochemical Company, Jinzhou 121001, Liaoning, China

^d China Huanqiu Contracting and Engineering Corporation, Fushun 113006, Liaoning, China

ARTICLE INFO

Article history:

Received 17 January 2017

Revised 18 March 2017

Accepted 27 March 2017

Available online 24 April 2017

Keywords:

Isobutylene

Amination

Tert-butylamine

Zeolite catalysts

ZSM-5

ABSTRACT

The atomically economic and green chemical reaction of direct amination of isobutylene to tert-butylamine, particularly under the relative mild reaction conditions available for future industrial use, was carried out over zeolite catalysts possessing different topological structures, from one dimensional to three dimensional pore system, and from small 8-member ring pore (MRP) to medium 10 MRP and further to large 12 MRP zeolites, to disclose the relationship between the zeolite properties/topologies and their amination performance systematically under the mild reaction conditions. It was discovered that the pore structure and the acidities of zeolite catalysts played crucial roles in the isobutylene amination process, and suitable pore diameter (larger than 0.5 nm or with large side pockets/cups in the outside surface) and a certain number of mid-strong acid sites are indispensable to catalyze the amination reaction, while too strong acid strength was not conducive to the process of isobutylene amination. Among them, zeolites with topologies of BEA, MFI, MEL, MWW and EUO exhibited good amination performance, with which the isobutylene conversion was higher than 12.61% (>46.42% of the equilibrium conversion) under the studied mild reaction conditions. Due to the good amination performance and the large adjustable Si/Al₂ ratio range, ZSM-5 was selected to further study the effect of acidity on the amination performance systematically under the mild reaction conditions, and the activity-acidity relationship in the amination process was disclosed: the amination activity (isobutylene conversion) had a linear correlation with the amount of mid-strong B acidity under the studied conditions over ZSM-5 catalyst, which can provide guidance for further developing high-efficient amination catalyst under mild reaction conditions available for future industrial use.

© 2017 Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier B.V. and Science Press. All rights reserved.

1. Introduction

Tert-butylamine is an important class of compound which is used as intermediate in a variety of applications including pharmaceuticals, agricultural chemicals, rubber chemicals, and water treatment chemicals [1]. Various methods for the synthesis of tert-butylamine were developed over the past decades, including hydrolysis of tert-butylurea, hydrocyanic acid process, amination of halogenated hydrocarbons, etc. [2,3]. Among them, using strong acid and alkali, discharging massive wastes and using highly toxic materials cannot be avoided [4,5]. Compared with the methods

above, direct amination of isobutylene to produce tert-butylamine with 100% atom efficiency is an environmentally friendly single step process utilizing cheap and readily available feedstocks of isobutylene and ammonia, offering environmental benefit to the chemical industry [1,6–9]. Zeolites can catalyze a wide variety of reactions [9–12] and Deeba et al. reported that the activity of catalysts for direct amination of isobutylene was correlated with the number of strong acid sites in heterogeneous systems [13–15]. However, in ref. [13–15] the amination reaction of isobutylene was performed under 0.1 MPa and the isobutylene conversion was lower than 1.73%, which was far from those of industrial use (generally under high pressure, as discussed in Section 3), and what being the truth under the industrial reaction conditions was not disclosed. BASF first made direct isobutylene amination process industrialized over a zeolite-based catalyst, but the condition was

* Corresponding authors.

E-mail addresses: zhuxx@dicp.ac.cn (X. Zhu), lyxu@dicp.ac.cn (L. Xu).

Table 1. Composition and characteristics of the zeolites with various structures.

Code	Zeolites	Pore diameter (Å)	Member-ring	Dimensional	Si/Al ₂ ratio ^a
EUO	EU-1	4.1 × 5.4 with large side pockets (6.8 × 5.8) [20]	10 × 12	1	36
MWW	MCM-22 MCM-49	4.0 × 5.5/4.1 × 5.1 with 12-ring cup (7.1 × 18.2) [21]	10 × 12	2	28 26
BEA	Beta	6.6 × 6.7/5.6 × 5.6	12	3	30
MOR	Mordenite	2.6 × 5.7/6.5 × 7.0	8 × 12	1	10
MEL	ZSM-11	5.3 × 5.4	10	3	48
MFI	ZSM-5	5.1 × 5.5/5.3 × 5.6	10	3	33–412
MTT	ZSM-23	4.5 × 5.2	10	1	91
FER	ZSM-35	3.5 × 4.8/4.2 × 5.4	8 × 10	2	29
AEL	SAPO-11	4.0 × 6.5	10	1	^b

^a The Si/Al₂ molar ratio was measured by XRF.^b The mole composition of SAPO-11, 1.6Al₂O₃:1.0SiO₂:1.4P₂O₅, measured by XRF.

rather harsh due to the fact that the reaction pressure was as high as 28 MPa [16], which was not conducive to the manufacture of the reactor and related equipment, as well as the reduction of process energy consumption. The rest of the reported literatures on the reaction are mostly found in patents and the relationship between the zeolite structures and acidities and the amination performance, especially under the relative mild reaction conditions available for future industrial use, need to be further explored.

As pointed out in our previous study based on the thermodynamics calculations results, developing a highly efficient catalyst under mild reaction conditions (relative lower pressure and temperature) is preferred for the amination process [17]. In the present study, the isobutylene amination reaction was carried out over various zeolites possessing different topological structures, from one dimensional to three dimensional pore system, and from small 8 MRP to medium 10 MRP and further to large 12 MRP zeolites, which were representative of the industrially commonly used micropore zeolites, to clarify the relationship between the zeolite properties or topologies and their amination performance, especially under the mild amination reaction conditions. Moreover, due to the good amination performance and the large adjustable Si/Al₂ ratio range, ZSM-5 was selected to further study the effect of acidity on the amination performance systematically under the mild amination reaction conditions, providing guidance for further developing high-efficient amination catalyst and reaction conditions optimization.

2. Experimental

2.1. Catalyst preparation

Each zeolite, Beta, ZSM-5, ZSM-11, ZSM-23, ZSM-35, MOR, MCM-22, MCM-49, EU-1 and SAPO-11, provided by Division of Fossil Energy Conversion of DNL, DICP, CAS, was calcined at 823 K for 3 h under static air to remove the organic template, followed by ion exchange in 0.8 mol/L NH₄NO₃ solution at 353 K for three times, converting the zeolites into their NH₄-forms. After the ion exchange, the zeolite samples were washed with deionized water, dried at 393 K, pressed binder-free, crushed to 20–35 mesh particles and then calcined under static air at 823 K for 2 h to convert the zeolite to their H-forms. The compositions and characteristics of the zeolites are listed in Table 1.

2.2. Characterization

Ammonia temperature-programmed desorption (NH₃-TPD) was performed in a U-shaped quartz glass micro-reactor (i.d. = 4 mm) with helium (He) as the carrier gas. The effluent was monitored by an online gas chromatograph (Shimadzu GC-8A) equipped with a TCD detector. Typically, the sample (0.14 g) was pretreated at 878 K for 0.5 h, then cooled down to 423 K and saturated with NH₃. After

a stable baseline had been obtained, the sample was heated from 423 K to 878 K at a ramp rate of 19.8 K/min.

The Brønsted and Lewis acid sites of samples were determined by pyridine adsorption followed by infrared (Py-IR) measurements on a VERTEX70 IR spectrometer. Samples were pressed into self-supported wafers, followed by evacuation at 723 K for 1 h (1×10^{-2} Pa) in IR cell. After the sample was cooled down to 313 K, a spectrum was recorded as background. Subsequently, the wafers were exposed to pyridine vapor for 5 min at 313 K and then outgassed at 423 K for 30 min. The spectra were collected at 313 K. The amount of Brønsted and Lewis acid sites in per gram catalyst were calculated by a method determined by CA Emeis [18].

N₂ adsorption was carried out at 77 K with an automatic Micromeritics ASAP 2020 apparatus. The fresh samples were pretreated under vacuum at 623 K for 6 h.

2.3. Catalyst evaluation

The direct amination of isobutylene to tert-butylamine was carried out in a stainless steel fixed bed reactor, in which the mode of operation was down-flow. All the samples were pressed, crushed and sieved into 0.38–0.85 mm particles before they were loaded into the reactor. 5 g of catalyst was loaded in the center of the reactor and pretreated at 773 K for 1 h in N₂. The set pressure was maintained with N₂. After the reactor was cooled down to reaction temperature (493–573 K), liquid ammonia was pumped in to fully fill the reactor before isobutylene was introduced as Ref. [19]. The products were analyzed on-line after 2 h time on stream by an Agilent 7980B gas chromatograph equipped with a flame ionization detector (FID) and a PONA capillary column.

3. Results and discussion

As pointed out by the thermodynamic study of direct amination of isobutylene to tert-butylamine in our previous paper, isobutylene amination is thermodynamically unfavorable and temperature-sensitive due to its exothermic nature and isobutylene equilibrium conversion decreases significantly with temperature rise (the value of K_p of isobutylene amination is less than 0.04 in the range of 473 K to 573 K), while a high pressure and $n(\text{NH}_3)/n(\text{i-C}_4\text{H}_8)$ molar ratio promote the transformation of isobutylene to tert-butylamine [17]. Developing a highly efficient catalyst under mild reaction conditions is preferred for the isobutylene amination process. Against the results from thermodynamics calculation, mild reaction conditions, viz. 523 K, 5.0 MPa, $n(\text{NH}_3)/n(\text{i-C}_4\text{H}_8)$ molar ratio of 4 and WHSV of isobutylene 0.5 h⁻¹, were selected to evaluate amination performance of the samples in the present work, and under the above conditions, the thermodynamics equilibrium conversion of isobutylene in amination reaction is about 27.16% [17].

Table 2(a). Acid sites distribution of the zeolites with various structures.

Zeolites	S_{BET} (m^2/g)	V_{total} (cm^3/g)	Total acid (mmol/g)	Mid-strong acid (mmol/g) ^a	Weak acid (mmol/g)
MOR	492	0.23	1.19	0.64 (836) ^b	0.55 (524)
ZSM-35	387	0.22	0.90	0.46 (785)	0.44 (525)
Beta	428	0.60	0.71	0.34 (673)	0.37 (527)
ZSM-5 (R50)	437	0.31	0.53	0.33 (719)	0.20 (503)
ZSM-11	437	0.51	0.48	0.30 (713)	0.18 (505)

^a Mid-strong acid concentration determined by NH_3 -TPD above 623 K.

^b Data presented in parentheses were the desorption peak temperature (K) of NH_3 -TPD profiles.

3.1. Influence of the zeolite pore structure on the catalytic performance

3.1.1. Physicochemical characteristics of the zeolites with different structures

To clarify the relationship between the zeolite properties and their amination performance, especially under the mild reaction conditions, first, the isobutylene amination reaction was carried out over various zeolites (as list in Table 1) possessing different topological structures, from one dimensional to three-dimensional pore system, and from small 8 MRP to medium 10 MRP and further to large 12 MRP zeolites, which were representative of the industrially commonly used micropore zeolites.

Among them: (1) Beta zeolite is a typical three dimensional large pore zeolite with 12 MRP, which is widely used in petrochemical processes, such as FCC process and esterification process [22,23]; (2) ZSM-5 and ZSM-11 are typical three-dimensional medium pore zeolites with bidirectional 10 MRP, which are widely used in shape-selective processes, such as xylene isomerization and aromatization processes [24–26]; (3) MCM-22/MCM-49 has 10 MRP and independent 12-member ring cavities connected by 10-member ring windows, and they have been used in the alkylation of benzene with ethylene and propylene [27–29]. EU-1 has 10 MRP with large side pockets. EU-1 exhibits good performance in m-xylene transformation process [30,31]; (4) ZSM-23 and SAPO-11 are one-dimensional zeolites with unidirectional 10 MRP. The channels of MOR are bidirectional 12×8 MRP and the size of 8 MRP channels is so small that most of the reactant molecules cannot enter into [32]; (5) The ZSM-35 framework topology is composed of bidirectional 10×8 MRP. The 10 MRP channels running parallel to the [001] direction are 5.4×4.2 Å in diameter and the 8 MRP channels running parallel to [010] direction are 4.8×3.5 Å in diameter [33].

It is generally considered that, among the zeolite samples with different topologies tested, ZSM-5, ZSM-11, ZSM-23, SAPO-11 and ZSM-35 are medium microporous zeolites, Beta and MOR are large microporous zeolites with 12 MRP, while MCM-22/MCM-49 and EU-1 have the characteristics of both 12 MRP and 10 MRP. Besides, the kinetic diameter of isobutylene is about 5.1 Å, which is bigger than the diameter of 8 MRP. Therefore, zeolites with only 8 MRP, like SAPO-34, were not tested in the present study.

Due to the differences in the zeolite nature, there existed a suitable Si/Al₂ ratio for the synthesis of particular zeolite, and the Si/Al₂ ratios of the samples used in the present work were also listed in Table 1.

The acidities of the zeolites with different structures were measured by NH_3 -TPD technique and the results are shown in Fig. 1 and Table 2. All samples presented two ammonia desorption peaks, SAPO-11 excepted. The two desorption peaks were corresponding to weak acid site and mid-strong acid site of zeolite, respectively. The difference of the maximum desorption-peak temperature represented the difference in the strength of acid sites of different zeolites. SAPO-11 showed only one desorption peak at 563 K, which indicated that the acid sites of SAPO-11 were mainly weak acid sites.

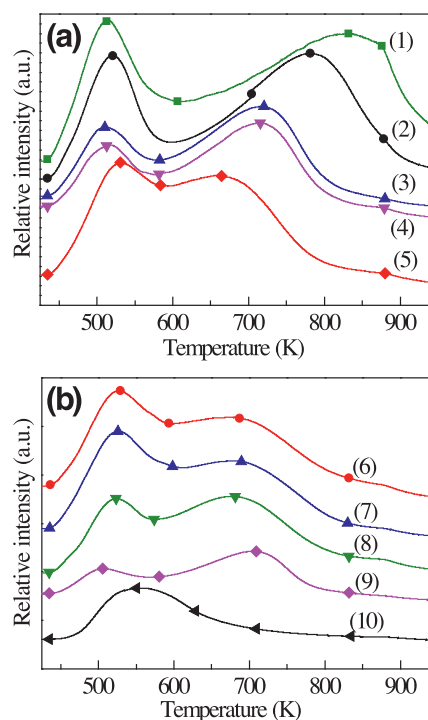


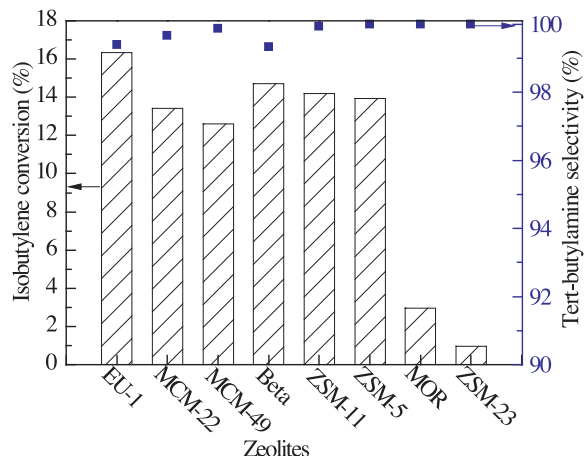
Fig. 1. TPD profiles of the zeolites with various structures. (1) MOR, (2) ZSM-35, (3) ZSM-5 (R50), (4) ZSM-11, (5) Beta, (6) MCM-22, (7) MCM-49, (8) EU-1, (9) ZSM-23, (10) SAPO-11.

As shown in Table 2(a), the results of NH_3 -TPD indicated that, among the zeolites studied, Beta, MOR and ZSM-35 had high acid concentrations. The total acid concentrations of Beta, MOR and ZSM-35 were 0.71 mmol/g, 1.19 mmol/g, 0.90 mmol/g and mid-strong acid concentrations of them were 0.34 mmol/g, 0.64 mmol/g, 0.46 mmol/g, respectively. For MOR zeolite, not only did it have the highest total acid concentration and mid-strong acid concentration, but it also had the highest acid strength. As can be seen in Fig. 1(a) and Table 2(a), the high-temperature (HT) peak of MOR centered at 836 K, which was 117 K higher than that of ZSM-5 (R50). ZSM-5 (R50) showed two desorption peaks at 503 K and 719 K respectively, the total acid concentration and mid-strong acid concentration of it were 0.53 mmol/g and 0.33 mmol/g respectively. ZSM-11 and ZSM-5 (R50) were both 10 MRP zeolites with similar pore size, similar Si/Al₂ molar ratio. ZSM-11 showed two desorption peaks at 505 K and 713 K respectively, and the total acid concentration and mid-strong acid concentration of it were 0.48 mmol/g and 0.30 mmol/g respectively, which were similar with those of ZSM-5 (R50).

MCM-22, MCM-49 and EU-1 had similar Si/Al₂ ratio and total acid concentrations. As shown in Table 2(b) and Fig. 1(b), the total acid concentrations of them were 0.57 mmol/g, 0.56 mmol/g and 0.56 mmol/g respectively. However, the mid-strong acid concentration of EU-1 was 0.29 mmol/g, which was slightly more than

Table 2(b). Acid sites distribution of the zeolites with various structures.

Zeolites	S_{BET} (m^2/g)	V_{total} (cm^3/g)	Total acid (mmol/g)	Mid-strong acid (mmol/g)	Weak acid (mmol/g)
MCM-22	584	1.09	0.57	0.25 (675)	0.32 (526)
MCM-49	498	0.45	0.56	0.24 (675)	0.32 (526)
EU-1	419	0.27	0.56	0.30 (678)	0.26 (525)
ZSM-23	242	0.28	0.22	0.15 (714)	0.07 (503)
SAPO-11	162	0.18	0.22	0.04 (723)	0.18 (563)

**Fig. 2.** Isobutylene conversion and tert-butylamine selectivity on zeolites with different structures. The Si/Al_2 of ZSM-5 was 50.

that of MCM-22 and MCM-49. The mid-strong acid concentrations of MCM-22, MCM-49 were 0.25 mmol/g and 0.24 mmol/g respectively. The ammonia desorption peaks' temperatures of the three zeolites were also basically the same, which showed that they had the same strength of the acid sites. Due to the relative high Si/Al_2 ratio, ZSM-23 had less acid concentration. Its total acid concentration and mid-strong acid concentration were 0.22 mmol/g and 0.15 mmol/g respectively. The two desorption peaks of ZSM-23 centered at 503 K and 714 K respectively. Meanwhile, the results, shown in Table 2(b) and Fig. 2(b), indicated that SAPO-11 presented only one low temperature desorption peak at 563 K, which meant that almost no mid-strong acid sites in SAPO-11. The total acid concentration of SAPO-11 was the lowest in the studied samples.

The results of N_2 adsorption revealed that, except ZSM-23 and SAPO-11, the rest of samples showed relative high surface area, which was about 380–584 m^2/g . The surface area of ZSM-23 and SAPO-11 was low and was 242 m^2/g , 162 m^2/g , respectively. MCM-22 had the largest pore volume among studied samples, 1.09 cm^3/g , which was twice more than that of MCM-49. The pore volume of MCM-49 and ZSM-11 was 0.45 cm^3/g , 0.51 cm^3/g , respectively. SAPO-11 showed the lowest pore volume, 0.18 cm^3/g . The pore volume of the rest of samples was about 0.20–0.40 cm^3/g .

3.1.2. Catalytic performances of zeolites with different pore structures in isobutylene amination reaction

Under the mild reaction conditions of 523 K, 5.0 MPa, $n(\text{NH}_3)/n(i\text{-C}_4\text{H}_8)$ molar ratio of 4 and WHSV of isobutylene 0.5 h^{-1} , the selectivity of isobutylene to tert-butylamine in amination reaction is more than 99.3% on each zeolite catalyst, the conversions of isobutylene to tert-butylamine over ZSM-35 and SAPO-11 samples were too low (0.01% and 0, respectively) to detect the by-products, and only trace by-products hydrocarbons of oligomerization and isomerization products were detected in the isobutylene amination reaction, which could effectively simplify the industrial device of the product separation process and was another advantage of the isobutylene amination to tert-butylamine

process on zeolite catalyst. As a result, only the conversion of isobutylene in the amination process was used to compare the performance of the studied samples due to their high selectivity to the desired tert-butylamine product in the following part.

Fig. 2 presents the isobutylene conversion and tert-butylamine selectivity under the above mild reaction conditions in the amination process on each zeolite catalyst with time-on-stream (TOS) of 6 h. We can see that tert-butylamine selectivity on each zeolite catalyst was more than 99.3%. Among the samples studied, zeolites of Beta, EU-1, MCM-22, MCM-49, ZSM-11 and ZSM-5 (R50) all showed relative high isobutylene conversion, higher than 12.61% (up to above 46.42% of the equilibrium conversion under the reaction conditions), under the mild reaction conditions; especially, on the EU-1 zeolite sample, the value of isobutylene conversion was as high as 16.32% (about 60.08% of the equilibrium conversion).

However, the isobutylene conversion in the amination process over SAPO-11, ZSM-35 and ZSM-23 zeolites was only 0, 0.01% and 0.94%, respectively. The low isobutylene conversion over SAPO-11 could be ascribed to its weak acidity, which was illustrated by the TPD profile of SAPO-11 in Fig. 1(b). The acidity of ZSM-23 and ZSM-35 zeolites was different from that of SAPO-11 and a certain amount of mid-strong acid sites was detected in ZSM-23 and ZSM-35 zeolites, especially for the latter sample. But the catalytic performance was not significant. This was attributed to their relative narrow pore size, which could not accommodate the intermediates formed in the isobutylene amination process and thus inhibited the formation of tert-butylamine in the pores. A few of tert-butylamine formed on the external surface of the zeolites.

An interesting phenomenon can be seen from Fig. 2 that the MOR zeolite, having 12-member ring large pore and a large amount of acid sites with mid-strong acidity (Table 2(a)), only gave a low value of isobutylene conversion 2.94% under the studied reaction conditions, why?

One reason was that about 55% of acid sites were located in the 8 MRP (0.28×0.57 nm) channels of the MOR zeolite [34], the narrow pore size restricting the formation of tert-butylamine from isobutylene and ammonia. The other reason may be that the acid strength of the acid sites in the 12 MRP of MOR was excessively strong [33,34], as indicated by the NH_3 -TPD profiles in Fig. 1(a), of which the HT peak' temperature was 117 K higher than that of ZSM-5 (R50). To a certain extent, the activity of a catalyst depends on the strength of chemisorption. To be active, the catalyst should be extensively covered by adsorbate, which is the case if chemisorption is relative strong. On the other hand, if the strength of the substrate-adsorbate bond becomes too great, the activity declines either because the other reactant molecules cannot react with the adsorbate or because the adsorbate molecules are immobilized on the surface [35]. Proper acidity and acid strength of zeolites do favor to the absorption of reactants. The acid sites with super strong acid strength in the 12 MRP of MOR adsorbed the alkaline ammonia molecules tightly and prevented the adsorption of isobutylene, suppressing the formation of tert-butylamine. Moreover, the super strong acidity of MOR was not conducive to desorption of the alkaline tert-butylamine product formed. All the above resulted in the low conversion of isobutylene on MOR.

From the above results, we can see that relative large pore channels (Table 1) and/or the void space in the zeolites and

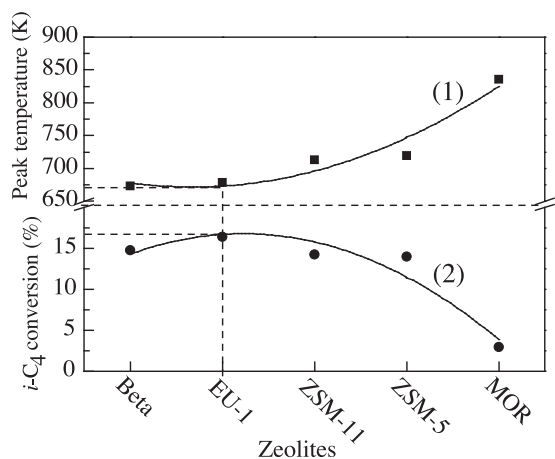


Fig. 3. Isobutylene conversion on large-pore zeolites. (1) Isobutylene conversion (%), (2) peak temperature (K).

suitable acidities, viz. acid sites with proper concentration and strong acid strength, are two indispensable factors for the zeolites to catalyze the isobutylene amination to tert-butylamine effectively, just as the samples of Beta, EU-1, MCM-22, MCM-49, ZSM-11 and ZSM-5 (R50) zeolites. However, too strong acid strength was not beneficial for the process of isobutylene amination.

According to the results that about 45% of acid sites were located in the 12 MRP channels of the MOR zeolite and the value of the acid sites with mid-strong acidities (0.64 mmol/g) of the present MOR sample, the number of the acid sites with mid-strong acidities in the 12 MRP channels of the MOR zeolite would be about 0.29 mmol/g, which were accessible for the isobutylene and ammonia molecules. From Table 2, we can see that, the amount of the mid-strong acid sites of EU-1, Beta, ZSM-5 and ZSM-11 were close to each other, from 0.29 mmol/g to 0.34 mmol/g, which also approached to that in the 12 MRP channels of the MOR zeolite. The main difference of those mid-strong acid sites between EU-1, Beta, ZSM-5 and ZSM-11 and MOR was in their acid strength. In order to further reveal the correlation between catalysts' activity and acid strength, the HT peak temperature and isobutylene conversion variation were plotted with the above zeolites with similar amount of mid-strong acid sites, as shown in Fig. 3. The highest conversion of isobutylene was obtained on EU-1, the peak of which centered around 678 K. It could be considered that the mid-strong acid sites of EU-1 had the most suitable acid strength for the amination of isobutylene under the studied mild reaction conditions; also, from Fig. 3, we can see that the larger difference (no matter positive or negative) between the value of HT desorption peaks temperature of other samples and that of EU-1 (678 K), the lower conversion of isobutylene in its amination reaction, and on MOR zeolite sample with the largest difference (about 836 K), the lowest isobutylene conversion (about 2.94%) was gained. This is the first time elucidating the relationship between the strength of the zeolite acid sites with the isobutylene amination performance, especially clarifying the reason why the MOR with strong acidity give rather poor activity in the amination process. The very good regularity presenting in Fig. 3 provided scientific guidance for the improvement and optimization of isobutylene amination catalyst under mild reaction condition in future.

Furthermore, from Table 2(b) and Fig. 1(b), we find that the HT desorption peaks of EU-1, MCM-22 and MCM-49 nearly centered at the same temperature, 678 K, which indicated that the strength of mid-strong acid sites of those three zeolites was similar. The only difference of those mid-strong acid sites among EU-1, MCM-22 and MCM-49 was their number. As mentioned above, EU-1, MCM-22

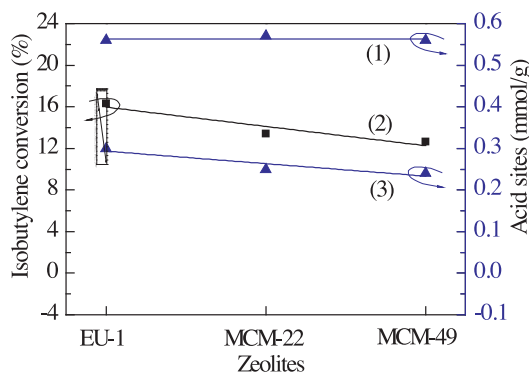


Fig. 4. Isobutylene conversion on zeolites with large pores. (1) Total acid sites (mmol/g), (2) isobutylene conversion (%), (3) mid-strong acid sites (mmol/g), (4) isobutylene conversion/mid-strong acid sites.

and MCM-49 had 10 MRP with similar large side pockets, the size of which was also close. For further revealing the relationship between mid-strong acid sites and amination activity, with the same structures and acid strength, the number of their mid-strong acid sites and their amination activity were related in Fig. 4. As shown in Fig. 4, with the similar zeolite structures and acid strength, the amination activity of the samples and the number of mid-strong acid sites showed very consistent regularity, viz. the larger the number of mid-strong acid sites (in this paper, the temperature of HT ammonia desorption peak was about 678 K) of zeolite sample was, the higher the amination activity was. The conversion of isobutylene had a significant linear correlation with the number of mid-strong acid sites of samples, which gave clear acidity-activity relationship and would also give guidance to the development of high active catalysts for isobutylene amination under mild reaction conditions.

From the above results, we deduce that the pore structure and the acidities of zeolite catalysts played crucial roles in the isobutylene amination process, and suitable pore diameter (larger than 0.5 nm or with large side pockets/cups in the outside surface) and a certain number of mid-strong acid sites are indispensable to catalyze the amination reaction of isobutylene. For the samples, with similar pore structure and acid strength, the amination activity (isobutylene conversion) of them had a significant linear correlation with the amount of mid-strong acidity in them; On the other hand, if the samples contained similar amount of mid-strong acidity, the sample, the HT ammonia desorption peak of which was about 678 K, had appropriate acid strength and was the most conducive to the conversion of isobutylene to tert-butylamine under studied conditions. Too strong acid strength of acid sites in zeolites did not good for isobutylene amination reaction, because of the great adsorption strength between acid sites and alkaline substance. In a word, the large pore channels and/or void space favored the mass transfer of the reactants and products, while the high content of acid sites with proper acidity strength was beneficial to isobutylene convert.

3.2. Influences of the Si/Al₂ ratios of ZSM-5 zeolite on its isobutylene amination performance

As mentioned above, the zeolites with relative large-pore channels and suitable acidities exhibited good performances in isobutylene amination to tert-butylamine. Due to the good amination performance and the large adjustable Si/Al₂ ratio range, ZSM-5 was selected to further clarify the effect of acidity on the amination performance systematically under the mild amination reaction conditions in this section.

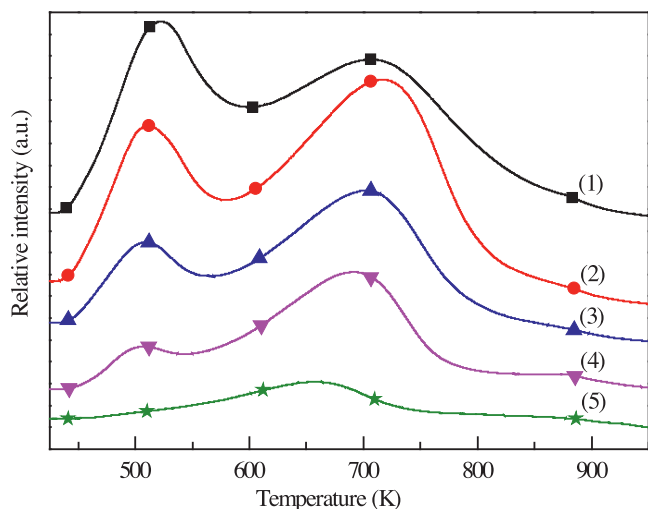


Fig. 5. TPD profiles of ZSM-5 zeolites with different Si/Al₂ ratios. (1) ZSM-5 (R33), (2) ZSM-5 (R50), (3) ZSM-5 (R75), (4) ZSM-5 (R111), (5) ZSM-5 (R412).

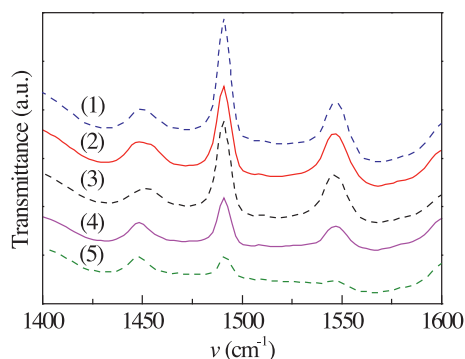


Fig. 6. IR spectra of pyridine adsorption on HZSM-5 zeolites. (1) ZSM-5 (R33), (2) ZSM-5 (R50), (3) ZSM-5 (R75), (4) ZSM-5 (R111), (5) ZSM-5 (R412).

3.2.1. Acidity of ZSM-5 zeolites with different Si/Al₂ ratios

The NH₃-TPD profiles of ZSM-5 zeolites with different Si/Al₂ ratios are represented in Fig. 5. There are two desorption peaks for the ZSM-5 zeolite, one centered in 505–525 K and the other in 730–740 K (except for R412, which centered at 675 K), corresponding to the weak acid sites and the mid-strong acid sites, respectively. Increasing the Si/Al₂ ratio of the zeolite, the number of both total and weak acid sites over the ZSM-5 showed an obvious decrease. The total acid densities of the five samples, of which the Si/Al₂ ratio was 33 to 412, were 0.55 mmol/g, 0.53 mmol/g, 0.31 mmol/g, 0.26 mmol/g and 0.07 mmol/g, respectively, as measured by the NH₃-TPD technique. However, the number of mid-strong acid sites over the ZSM-5 (R50) was the most, 0.33 mmol/g. The mid-strong acid densities of the others from Si/Al₂ ratio 33 to 412 were 0.27 mmol/g, 0.21 mmol/g, 0.19 mmol/g and 0.07 mmol/g, respectively. Moreover, the desorption peaks shifted to a lower temperature with the Si/Al₂ ratio increase. That meant the acid strength of the samples also decreased with increasing of the Si/Al₂ ratio of the ZSM-5 zeolite. But overall, except for R412, the acid strength of the samples was similar, and the gap of their desorption peaks was less than 10 K.

The Brönsted and Lewis acidities of the samples were determined by pyridine adsorption using FT-IR spectroscopy. The results of the ZSM-5 catalysts with different Si/Al₂ ratios are shown in Fig. 6. The pyridine band at 1547 cm⁻¹ could be assigned to pyridinium ions, and the band at 1454 cm⁻¹ to Lewis acid-coordinated pyridine, respectively [36,37]. The band at 1491 cm⁻¹ consisted of

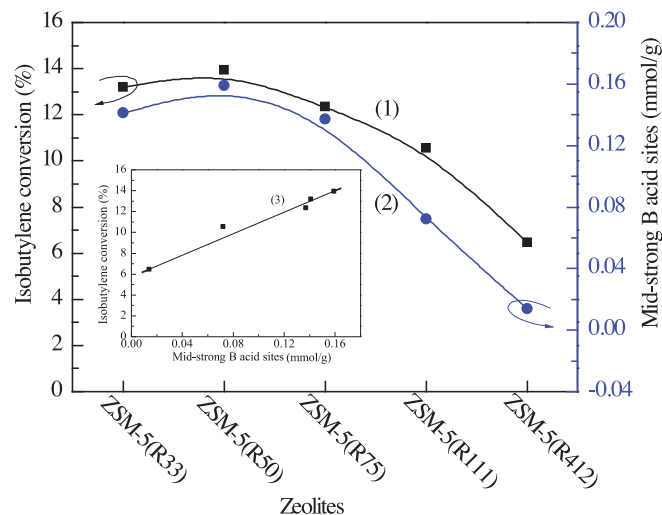


Fig. 7. Isobutylene conversion on ZSM-5 zeolites with different Si/Al₂ ratios. (1) Isobutylene conversion (%), (2) mid-strong B acid sites (mmol/g), (3) isobutylene conversion/mid-strong B acid sites.

bands due to the Brönsted and Lewis sites. In this paper, the mid-strong Brönsted (mid-strong B) acid sites belonged to the acid sites that the pyridine desorption temperature was above 573 K. From Fig. 6, we can see that zeolite ZSM-5 (R50) showed the most mid-strong B acid sites. With the increase of the Si/Al₂ ratio of the ZSM-5 samples from 50 to 412, the numbers of the Brönsted acid sites and the Lewis acid sites were gradually decreased. The mid-strong B acid sites of the ZSM-5 samples with Si/Al₂ ratio from 30 to 412 were 0.141 mmol/g, 0.159 mmol/g, 0.137 mmol/g, 0.072 mmol/g and 0.014 mmol/g respectively, corresponding to the results of mid-strong acid sites from NH₃-TPD. The reason why the mid-strong B acid sites of ZSM-5 (R33) were lower than those of ZSM-5 (R50) might be that part of aluminum existed in the form of extra-framework aluminum in ZSM-5 (R33) [38]. As a result, although the total acidity was high in ZSM-5 (R33), but the number of Brönsted acid sites corresponding to the framework aluminum was lower than that of ZSM-5 (R50).

3.2.2. Influence of the Si/Al₂ ratio of ZSM-5 on its amination performance

The effects of variation in Si/Al₂ ratio of ZSM-5 on isobutylene conversion under the reaction conditions of 523 K, 5.0 MPa, *n*(NH₃)/*n*(*i*-C₄H₈) molar ratio of 4 and WHSV of isobutylene 0.5 h⁻¹ are shown in Fig. 7. It can be seen that, on the ZSM-5 (R50) zeolite catalyst, isobutylene conversion obtained a maximum of 13.94%. With the increase of the Si/Al₂ ratio from 50 to 75, 111 and further to 412, isobutylene conversions decreased to 12.36%, 10.57% and further to 6.45%, respectively. Obviously, with increasing the Si/Al₂ ratio from 50 to 412, isobutylene conversion decreased steadily due to the decreasing acidity of the catalyst. Compared with ZSM-5 (R50), the lower isobutylene conversion on ZSM-5 (R33) owed to its relatively few mid-strong B acid sites. From Fig. 7, we can see that the amount of B acid sites of mid-strong strength and isobutylene conversion showed a consistent trend with the change of the Si/Al₂ ratio. To further clarify the relationship between the mid-strong B acidity of ZSM-5 and its amination activity, the isobutylene conversion was plotted with the amount of acid sites of mid-strong strength of ZSM-5 in Fig. 7. It was amazing that the isobutylene conversion, on ZSM-5 (R412), with which the amount of mid-strong B acid sites of mid-strong strength is only 0.01 mmol/g, was about 6.45%, which was much higher than those of ZSM-35 and ZSM-23, 0.01% and 0.94% respectively. As can be seen from Table 2 and Fig. 5, ZSM-35 and ZSM-23 had much more mid-

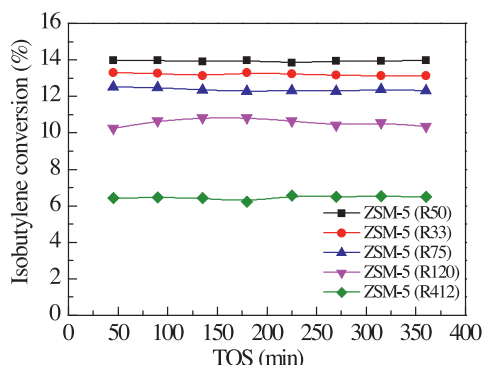


Fig. 8. Stability of ZSM-5 zeolites.

strong acid sites than those of ZSM-5 (R412), which further proved that the relative narrow pore size of them restrained the formation of intermediates and then the formation of tert-butylamine in isobutylene amination process. Further improving the amount of acid sites of mid-strong strength in ZSM-5, the isobutylene conversion increased nearly linearly (the inset in Fig. 7), which tallied with the relationship between the mid-strong acidity amount of different zeolite catalysts and their amination activity discussed in Section 3.1.2.

All the results suggested that the strength and number of the Brönsted acid sites were the factors controlling the isobutylene amination reaction under the mild reaction conditions studied.

As mentioned above, the alkaline molecules ammonia preferentially absorbed in the acid sites of catalysts, which would inhibit the polymerization of isobutylene and coking or carbon deposition on the surface of the catalysts to make the catalysts deactivated. Therefore, zeolite catalysts showed better reaction stability in isobutylene amination reaction. Under the studied reaction conditions, the isobutylene conversion changed little with TOS over ZSM-5 zeolites with different Si/Al₂ ratios, which also presented good amination stability. The result of reaction stability with TOS over ZSM-5 zeolites was shown in Fig. 8. It can be seen that, within TOS studied, the isobutylene conversion did not change significantly. Besides, after reaction, the crystalline structures of ZSM-5 (R50) and ZSM-11 zeolites were maintained according to the XRD results, and the relative crystallinity of the reacted sample has no obvious change compared with the corresponding fresh sample, showing that the structure of the zeolite samples were stable enough under the experiment conditions studied. All the studied zeolite catalysts had similar structural stability.

4. Conclusions

The relationship between the zeolite structures and acidities and the catalytic performance of direct amination of isobutylene to tert-butylamine, an atomically economic and green chemical reaction, especially under the mild reaction conditions, was disclosed. And the results show that zeolites suitable pore diameter (larger than 0.5 nm or with large side pockets/cups in the outside surface) and a certain number of mid-strong acid sites of the zeolites exhibited good amination performance (>46.4% of the equilibrium conversion, and >99.0% of tert-butylamine selectivity), while ZSM-35 (narrow pore diameter), ZSM-23 (narrow pore diameter), SAPO-11 (weak acidity) and MOR (too high strong acidity) zeolites had rather poor isobutylene amination activity.

Also the results shown that, for zeolite samples with similar pore structure and acid strength, the amination activity had a linear correlation with the amount of mid-strong acidity under the

conditions; Among the samples contained similar amount of mid-strong acidity, EU-1, the HT NH₃ desorption peak of which was about 678 K, had appropriate acid strength and gave the highest conversion of isobutylene to tert-butylamine under the studied conditions. And the larger difference between the values of HT desorption peaks temperature of the samples and 678 K was, the lower conversion of isobutylene in its amination reaction gained. For the first time the relationship between the strength of the zeolite acid sites with the isobutylene amination performance was elucidated, especially the reason why the MOR with strong acidity gave rather poor activity in the amination process was clarified.

Moreover, the effect of acidity on the amination performance of ZSM-5 with different Si/Al₂ ratios further verified the linear relationship between the amination activity and the amount of B acid sites with mid-strong strength. All the above can provide good guidance for further developing high-efficient amination catalyst under mild reaction conditions available for future industrial use.

Acknowledgments

We are grateful for the financial support of K.C. Wong Education Foundation and Dalian Eminent Young Scientist Program (2015R009).

References

- [1] M. Beller, C. Breindl, M. Eichberger, C.G. Hartung, J. Seayad, O.R. Thiel, A. Tillack, H. Trauthwein, *Synlett* 34 (2003) 1579–1594.
- [2] J.F. Hartwig, *Synlett* 1997 (1997) 329–340.
- [3] D.M. Roundhill, *Chem. Rev.* 23 (1992) 1–27.
- [4] V.E. Antipanova, *Khimst (Moscow)* 12 (1988) 720–722.
- [5] T.R. Felthouse, P.L. Mills, *Appl. Catal. A: Gen.* 106 (1993) 213–237.
- [6] T.E. Mueller, M. Beller, *Chem. Rev.* 98 (1998) 675–704.
- [7] E. Haak, S. Doye, *Chem. Unserer Z.* 33 (1999) 297–303.
- [8] J.J. Brunet, D. Neibecker, F. Niederborn, *J. Mol. Catal.* 49 (1989) 235–259.
- [9] Y. Ono, *Catal. Rev.* 34 (1992) 179–226.
- [10] M. Misono, N. Nojiri, *Appl. Catal.* 64 (1990) 1–30.
- [11] K. Tanabe, W.F. Hölderich, *Appl. Catal. A: Gen.* 181 (1999) 399–434.
- [12] B. Yilmaz, U. Müller, *Top. Catal.* 52 (2009) 888–895.
- [13] X. Jin, Y. Ma, S. Guo, X. Shu, X. He, *Petrochem. Technol.* 34 (2005) 948–953.
- [14] M. Deeba, M.E. Ford, *J. Org. Chem.* 53 (1988) 4594–4596.
- [15] M. Deeba, W.K. Hall, *J. Phys. Chem.* 144 (1985) 85–103.
- [16] U. Dingerdissen, R. Kummer, P. Stops, U. Müller, J. Herrmann, K.D. Eller, US Patent 6 143934, 2000.
- [17] S.Y. Gao, X.X. Zhu, X.J. Li, Y.Z. Wang, Y. Zhang, S.J. Xie, J. An, F.C. Chen, S.L. Liu, L.Y. Xu, *Chin. J. Catal.* 38 (2017) 106–114.
- [18] C.A. Emeis, *J. Catal.* 141 (1993) 347–354.
- [19] Y. Ma, X. Jin, S. Guo, X. Shu, S. Yi, *Petrochem. Technol.* 35 (2006) 720–724.
- [20] N.A. Briscoe, D.W. Johnson, M.D. Shannon, G.T. Kokotailo, L.B. McCusker, N.A. Briscoe, D.W. Johnson, M.D. Shannon, G.T. Kokotailo, L.B. McCusker, *Zeolites* 8 (1988) 74–76.
- [21] M.E. Leonowicz, J.A. Lawton, S.L. Lawton, M.K. Rubin, *Science* 264 (1994) 1910–1913.
- [22] L. Li, H.F. Pan, W.B. Li, *Chin. J. Catal.* 23 (2002) 65–68.
- [23] G.J. Gainsford, C.F. Hosie, R.J. Weston, *Appl. Catal. A: Gen.* 209 (2001) 269–277.
- [24] X. Zhu, S. Liu, Y. Song, L. Xu, *Appl. Catal. A: Gen.* 288 (2005) 134–142.
- [25] P. Wang, L. Huang, J. Li, M. Dong, J. Wang, T. Tatsumi, W. Fan, *RSC. Adv.* 5 (2015) 28794–28802.
- [26] W.S. Zhang, S.Y. Gao, S.J. Xie, H. Liu, X.X. Zhu, Y.C. Shang, S.L. Liu, L.Y. Xu, Y. Zhang, *Chin. J. Catal.* 38 (2017) 168–175.
- [27] P.C. Mihindou-Koumba, J.D. Comparot, S. Laforge, P. Magnoux, *J. Catal.* 255 (2008) 324–334.
- [28] X. Li, R. Prins, J.A.V. Bokhoven, *J. Catal.* 262 (2009) 257–265.
- [29] S. Zhang, S.L. Chen, P. Dong, Z. Ji, J. Zhao, K. Xu, *Catal. Lett.* 118 (2007) 109–117.
- [30] J. Martins, E. Birot, E. Guillon, F. Lemos, F.R. Ribeiro, P. Magnoux, S. Laforge, *Microporous Mesoporous Mater.* 171 (2013) 238–245.
- [31] J. Cejka, B. Wichterlova, *Cat. Rev.* 44 (2002) 375–421.
- [32] N. Mizuno, M. Tabata, T. Uematsu, M. Iwamoto, *J. Catal.* 146 (1994) 249–256.
- [33] R.B. Borade, A. Clearfield, *Zeolites* 14 (1994) 458–461.
- [34] A. Bhan, A.D. Allian, G.J. Sunley, D.J. Law, E. Iglesia, *J. Am. Chem. Soc.* 129 (2007) 4919–4924.
- [35] P. Atkins, J. Paula, *Physical Chemistry*, eighth ed., Oxford University Press, London, 2006, pp. 928–929.
- [36] G. Poncelet, M.L. Dubru, *J. Catal.* 52 (1978) 321–331.
- [37] J.S. Lee, M. Boudart, *Catal. Lett.* 20 (1993) 97–106.
- [38] J. Zhuang, D. Ma, G. Yang, Z. Yan, X. Liu, X. Liu, X. Han, X. Bao, P. Xie, Z. Liu, *J. Catal.* 228 (2004) 234–242.