

Shape-selective amination of EO over HZSM-5 for MEA and DEA

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ABSTRACT

Shape-selective amination of ethylene oxide over HZSM-5 was thoroughly investigated. TPD, FTIR and catalytic performance showed that HZSM-5 was more active than the sodium form. Relative selectivity of product was mainly controlled by the crystal size of ZSM-5. Surface modification such as silylation was effective for enhancing the shape selectivity. Among the catalysts tested in this study, HZSM-5 with SiO₂/Al₂O₃ ratio being 76.7 exhibited the best performance. At 353 K and total pressure of 8.0 MPa the total selectivity of MEA and DEA was 97.6%, the yield reached 96.6%, the best performance achieved so far among EO amination.

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1. Introduction

Ethanolamine (EA) is widely used in surfactant, intermediate, fabric softeners, gas purification and pharmaceutical industry etc. and the demand for monoethanolamine (MEA) and diethanolamine (DEA) is especially great [1,2]. Thus the selective synthesis of MEA and DEA is attracting more attention. Traditionally EA is synthesized by the reaction of ethylene oxide (EO) and ammonia (NH₃) in aqueous environment [3–6]. But such a process has three drawbacks: high energy cost for separation, serious side reactions and equilibrium product distribution [7–10]. So it is very necessary to selectively prepare EA on heterogeneous catalysts in liquid phase [11–15]. However, the reaction conditions are so harsh that few reports were published. Weibull et al. [16,17] thoroughly studied cation-exchange-resin as catalyst in anhydrous system but it was thermally unstable. Johnson [18] and Grice [19] respectively reported the results on SiO₂-Al₂O₃ and acid activated clays, but the total conversion was less than 90% and the highest selectivity obtained at 84.6% NH₃/EO ratio was as high as 15.0. Synthesis of EA via shape-selective zeolites catalyzed amination of EO has attracted much attention. This interest is caused by the special properties of zeolite which is able to produce preferentially linear molecules [20,21]. Though recently, shape-selective synthesis of DEA over ZSM-5 zeolite has been studied [10,11,22,23], there are still several points needed to be addressed. For example, the influences on the activity and selectivity are still unclear. In this paper, a detailed and thorough investigation on the shape-selective amination of EO over ZSM-5 is reported in detail, including

the effects on the active site, the influences of crystal size, surface modification and SiO₂/Al₂O₃ ratio.

2. Experimental

2.1. Catalyst preparation

Small crystal sized NaZSM-5 zeolite used in this study was synthesized using the recipe developed by Wang [24,25]. In brief, the followings were subsequent treatments on NaZSM-5 zeolite. The resulted HZSM-5 was prepared through NaZSM-5 exchanged with NH₄NO₃ solution, followed by drying and calcination at 823 K. The treatment of HZSM-5 in ethylenediamine tetraacetic acid (EDTA) solution led to HZSM-5 (Al), while HZSM-5 (Si) was obtained by impregnation of HZSM-5 in tetraethyl orthosilicate (TEOS) solution. Samples with different SiO₂/Al₂O₃ ratio were obtained by adjusting the ratio of source. The as-prepared sample was named HZSM-5 (n), where 'n' in the bracket indicated SiO₂/Al₂O₃ molar ratio. To compare the effect of crystal size, HZSM-5 (C) with large crystal size was prepared according to these papers [26,27].

Before characterization and performance evaluation, all of the samples were subject to activation. In addition, before evaluation it was pressed into pellets, crushed, sieved (30–40 mesh). The sample was heated from room temperature to 723 K at a rate of 5 K/min in flowing nitrogen ambient, and was kept at this temperature for 4 h.

2.2. Catalyst evaluation

The 6.0-g catalyst (10.0 mL) was evaluated for amination of EO to EA in a fixed-bed micro-reactor with a continuous reactant down-flow. The feed composition was NH₃/EO = 7.2 (molar ratio) and

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balanced with nitrogen, but during the reaction period nitrogen didn't pass through the reactor any more. Liquid hourly space velocity (LHSV) was in the range of 1.0–6.0 mL reactant/mL cat h⁻¹. Reaction temperature was in the range of 343–373 K and system pressure was kept at about 8.0 MPa. All the reactants and products were kept in liquid phase during the whole process. And products at outlet were analyzed by GC-Agilent 7890. The carbon balance was over 95.5% based on EO during the whole experiment.

2.3. Characterization

Powder X-ray diffraction (XRD) was conducted using a Bruker D8 Advance diffractometer with monochromatized Cu-K α radiation ($\lambda = 0.1541$ nm) and X-ray energy of 30 kV. The element composition of the zeolite was characterized by X-ray fluorescence (XRF) method. Brunauer–Emmet–Teller (BET) method surface area was measured by means of tristar-3000 equipment. Scanning electron microscope (SEM) images were taken by an XL30E scanning electron microscope. Temperature-programmed desorption (TPD) was carried out in the temperature range of 300–873 K with a ramp rate of 10 K/min. Infrared (IR) spectrum was carried out in the range of 1300–4000 cm⁻¹ while pyridine was used as probe molecule. The measurement of relative adsorption capacity of MEA, DEA and TEA on ZSM-5 zeolite was carried on Micromeritics Autochem II instrument.

3. Results and discussion

3.1. BET, XRD and SEM

The physico-chemical properties of all as-prepared zeolite samples are listed in Table 1. Microporous surface area of listed samples is all in the range of 220–280 m²/g which indicates the surface area is mainly attributed to the microporous surface area. From Table 1, it has been established that HZSM-5 (C) has a smaller external surface area than HZSM-5. Furthermore SEM pictures (Fig. 1) show that the crystal size of HZSM-5 (C) is about 8 μ m while HZSM-5 is smaller than 0.4 μ m. As to the crystalline structure of listed samples in Table 1, Fig. 2 well indicates that all the as-prepared samples have typical MFI structure. HZSM-5 (C) sample shows stronger XRD intensity than others. When HZSM-5 is silylated by TEOS, the diffraction peak becomes partially widen. The possible reason is amorphous SiO₂ phase formed on the surface of HZSM-5 (Si). And HZSM-5 (Al) sample shows shaper diffraction peaks than before. This may result from the removal of amorphous Al₂O₃ phase. Based on Table 1 and Fig. 2, it can be concluded that these treatments are effective and do not change the structure much.

3.2. TPD and FTIR

The (M + D)/T ratio in Table 1 shows the relative adsorptive capacity of MEA/DEA and TEA molecules over ZSM-5 zeolites. MEA and DEA are both linear molecules which can diffuse into micropore

Table 1

Physico-chemical properties of as-prepared ZSM-5 zeolite samples.

Catalyst	SiO ₂ /Al ₂ O ₃ Molar ratio	In area m ² /g	Ex area m ² /g	(M + D)/T wt.%/wt.%
NaZSM-5	76.5	256	81	4.5
HZSM-5	76.7	262	80	11.3
HZSM-5 (Al)	77.8	258	82	22.0
HZSM-5 (Si)	78.8	251	84	44.5
HZSM-5 (C)	76.0	225	22	16.3
HZSM-5 (50)	40.8	247	82	13.2
HZSM-5 (100)	97.0	244	85	8.5
HZSM-5 (300)	306	277	84	7.5

Note: The number in the bracket indicates the ratio of SiO₂/Al₂O₃. In area indicates microporous surface area, Ex area indicates external surface area, (M + D)/T indicates the weight ratio of (MEA + DEA)/TEA.

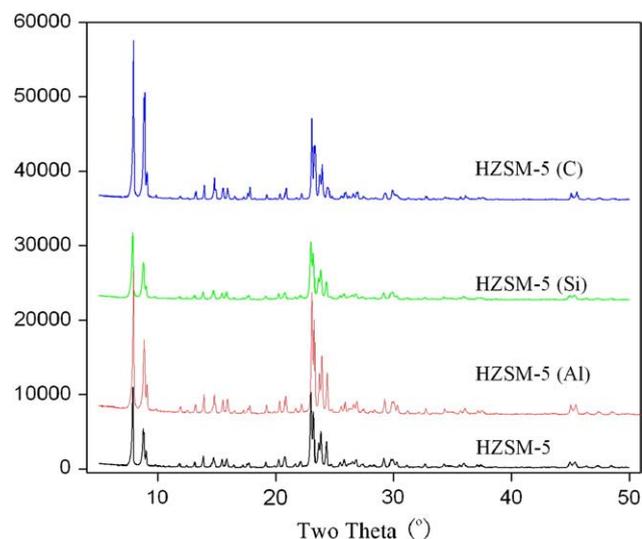


Fig. 1. XRD patterns of as-prepared HZSM-5 with different treatments.

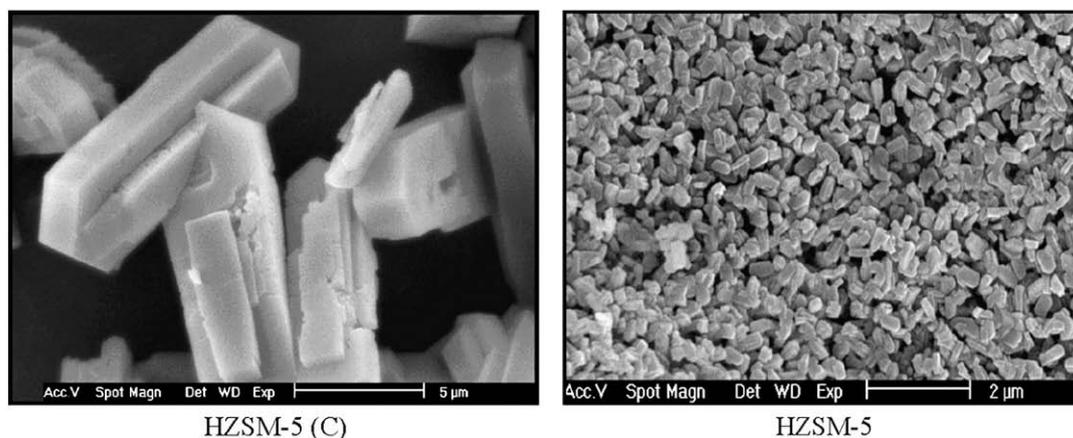
while it is difficult for TEA. It partially explains why all samples show high (M + D)/T ratio except NaZSM-5. As to NaZSM-5, the low ratio mainly results from the lower acid concentration which is evidenced in NH₃-TPD spectrum (Fig. 3). For HZSM-5 (Si) sample which is silylated by TEOS reagent shows the highest (M + D)/T value. This further confirms that most of acid sites are located in micropore. For the HZSM-5 (Al) sample, although the acid concentration is decreased, it still shows higher (M + D)/T ratio than pre-treatment, because the extra-framework alumina which probably blocks the micropore is removed, and more MEA and DEA molecules can diffuse into micropore. Due to high external surface area HZSM-5 shows lower (M + D)/T ratio than HZSM-5 (C). With the increase of SiO₂/Al₂O₃ ratio the (M + D)/T ratio of HZSM-5 (n) slowly decreases, on one hand it is the different ratio of the microporous area to external area, and on the other it is the decrease of acid concentration which is depicted in NH₃-TPD spectrum (Fig. 3).

As there are two typical ammonia-desorption peaks which indicate at least two types of acid sites for as-prepared ZSM-5 zeolite samples from Fig. 3, to distinguish acid type of the sample FTIR measurement is employed. Fig. 4 shows that there is no obvious peak in 1545 cm⁻¹ for NaZSM-5 which indicates that there is no Brönsted acid site. And also no peak in 1454 cm⁻¹ for HZSM-5 (Al) indicates no Lewis acid site [28]. It appears that both HZSM-5 (Al) and HZSM-5 (Si) show partly acid concentration decrease of poor/strong acid sites after treatment. As to HZSM-5 (n) zeolite with different SiO₂/Al₂O₃ ratio, it is deduced from Figs. 3 and 4 that Brönsted acid concentration decreases with the increase of SiO₂/Al₂O₃ ratio. The calculated Brönsted acid concentration is used for depicting the relationship between acid and catalytic activity in Fig. 5.

3.3. Catalytic performance

3.3.1. Comparative study on NaZSM-5, HZSM-5 and HZSM-5 (Al)

EO can easily react with aqueous ammonia at room temperature while it is difficult to react in anhydrous system [10,29–31]. Reports on the amination of EO suggest that proton acid can effectively accelerate this reaction. However few data of the amination on zeolites were published. Table 2 describes the catalytic results on NaZSM-5, HZSM-5 and HZSM-5 (Al). When NaZSM-5 is used as catalyst, T_{100%}, the temperature of 100% conversion of EO, decreases by 10 degree to 383 K. When HZSM-5 and HZSM-5 (Al) are tested, the corresponding T_{100%} further decreases to 353 K. That indicates protonic form of ZSM-5 has higher activity than sodium form. NH₃-TPD spectrum (Fig. 3) together with Py-FTIR (Fig. 4) spectrum shows



HZSM-5 (C)

HZSM-5

Fig. 2. SEM pictures of as-prepared HZSM-5 with different crystal size.

that there is a negligible amount of Brønsted acid sites on NaZSM-5, which means that ZSM-5 zeolite only have Lewis acid sites have poor catalytic effect on EO amination. Although acid concentration of HZSM-5 (Al) is less than HZSM-5 from Fig. 3, the Brønsted acid concentration is quite similarly from Fig. 4. In Table 2 the $T_{100\%}$ value of HZSM-5 (Al) is in good agreement with HZSM-5, which further

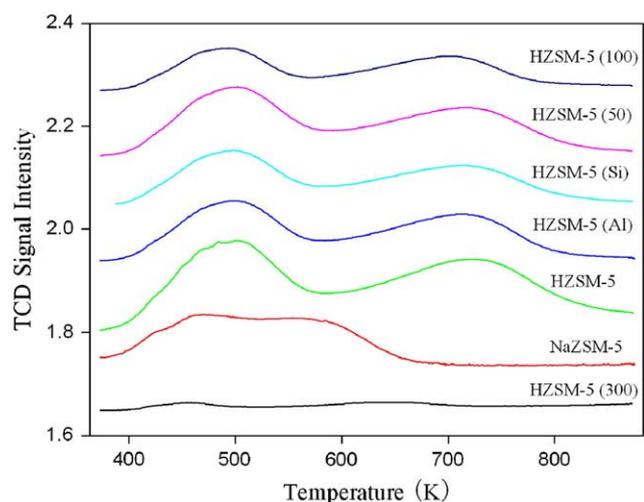
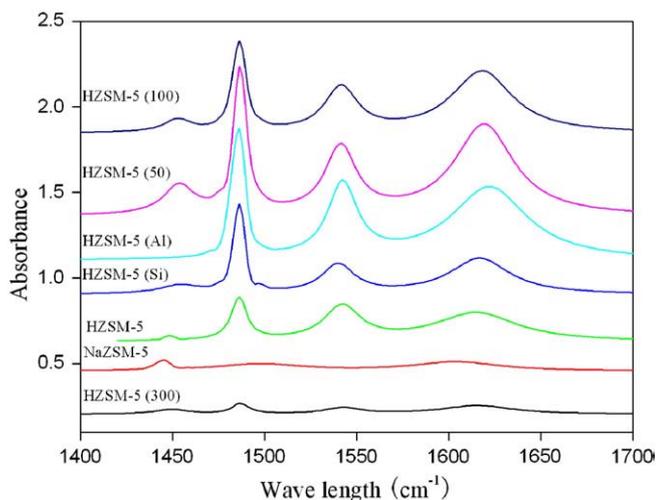
Fig. 3. NH_3 -TPD spectra of as-prepared ZSM-5 zeolite samples.

Fig. 4. Py-FTIR spectra of as-prepared ZSM-5 zeolite samples.

proves that Brønsted acid plays a major role in the amination of EO. Similar report was also published in the amination of methanol [32].

To further quantify the relationship between Brønsted acid and catalytic activity experiments were carried out on HZSM-5 (n) with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. Fig. 5 depicts the relationship between Brønsted acid concentration and catalytic activity. It easily can be found that the activity increases with the increase of Brønsted acid concentration. As to HZSM-5 (25) its activity is not higher than HZSM-5 although its Brønsted acid concentration is higher. This may result from the acid intensity, but the real reason is still unclear. In the amination of iso-butylene similar phenomena was also found [33].

3.3.2. Improved selectivity of MEA and DEA

In general, large crystal size of zeolite is preferentially to shape selectivity. Because more active sites are distributed in the micropore

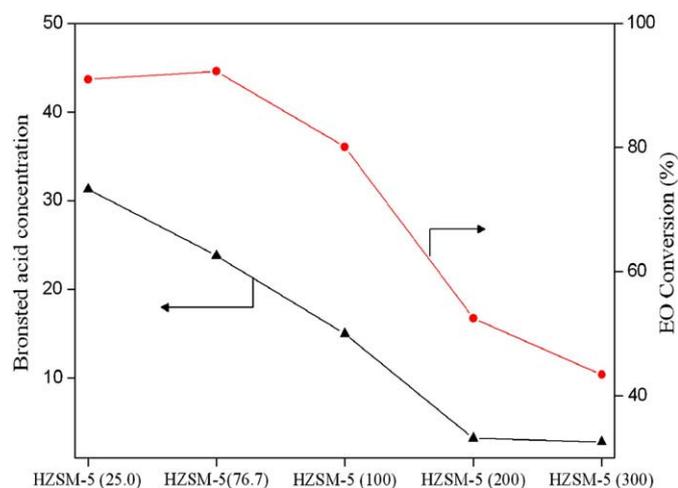
Fig. 5. Brønsted acid concentration and catalytic activity of HZSM-5 with different $\text{SiO}_2/\text{Al}_2\text{O}_3$.

Table 2

Catalytic performance of EO amination on as-prepared zeolite samples.

Catalyst	$T_{100\%}$	P	NH_3/EO	LHSV	Sel. (%)	
	/K				/MPa	/h ⁻¹
None	393	12.0	6.0	1.0	98.9	1.1
NaZSM-5	383	12.0	6.0	1.0	99.6	0.4
HZSM-5	353	9.0	6.0	2.0	100.0	0
HZSM-5 (Al)	353	9.0	6.0	2.0	100.0	0

Note $T_{100\%}$: temperature when EO conversion is 100%, EA: ethanolamine, EA-EG: ethoxylated ethanolamine, NH_3/EO : molar ratio of NH_3/EO .

Table 3
Influences of crystal size and surface modification on catalytic performance.

Catalyst	Temp.	Press.	NH ₃ / EO	LHSV /h ⁻¹	Conv. (%)	Selectivity (%)	
	/K	/MPa				MEA + DEA	TEA
HZSM-5	353	8.0	8.0	6.0	90.5	97.1	2.9
HZSM-5 (C)	353	8.0	8.0	6.0	65.9	99.2	0.8
HZSM-5 (Si)	353	8.0	8.0	6.0	88.2	98.7	1.3

Table 4
Influences of NH₃/EO ratio on relative selectivity of MEA/DEA on HZSM-5 zeolite.

NH ₃ / EO	Conv. (%)	Selectivity (%)		
		MEA	DEA	TEA
4.0	95.6	47.7	42.4	9.9
5.0	96.7	53.6	40.6	5.8
6.5	98.1	58.2	36.9	4.9
8.0	99.3	69.6	27.8	2.6
9.0	99.3	72.7	25.8	1.5

Reaction conditions: temperature 353 K, pressure 8.0 MPa, LHSV 4.0 h⁻¹.

compared to the small crystal size of zeolite. It is convinced in Table 3 which shows that the selectivity of MEA and DEA on HZSM-5 (C) is higher than that on HZSM-5. As the reaction mainly occurs in the micropore, then the formed product diffuses out of the micropore to the external surface which lowers the mass transfer efficiency of reactant and product. While regarding to the small crystalline zeolite, it has shortened pore passages and enriched pore mouths which are very useful to the catalytic performance. Although the shape effect is weakened, the catalytic activity is largely improved, which is convinced in Table 3. To further improve the shape selectivity, surface modification becomes necessary and important. Lercher [34] reported the silylation of mordenite which would improve the mono- and dimethylamine selectivity. The catalytic result listed in the following Table 3 shows that the silylation method is also valid for EO shape-selective amination.

As MEA and DEA are both linear molecules, it is very difficult to obtain high selectivity towards MEA or DEA on HZSM-5 at a constant NH₃/EO ratio, thus the adjusting of the NH₃/EO ratio is necessary. Table 4 lists the influence of NH₃/EO ratio on the relative selectivity of MEA and DEA. From Table 4 it can be seen that the selectivity of DEA increases with lowering the NH₃/EO ratio. That is due to the increasing EO concentration is beneficial to the secondary amine formation in micropores. And it is also found that DEA selectivity reaches maximum according to the NH₃/EO ratio, but TEA selectivity increases much as the NH₃/EO ratio is further lowered. It mainly comes from the self-catalytic effect. Remained EO leaving the catalyst can react with MEA and/or DEA to TEA in homogeneous system containing ethanolamine, which explains why there is so much TEA in the product. Hideaki [10] further developed this work, but the selectivity of DEA scarcely reached 50% when the TEA content was restricted to below 5%. And attempts have been carried out very recently [35].

Highly selective preparing DEA is still a great challenge and will become an important target.

4. Conclusion

Shape-selective catalysis amination of EO based on HZSM-5 was studied. This work reveals that Brønsted acid site plays a major role in this reaction. To improve the selectivity of MEA and DEA, deactivation external surface active site is an effective method. Shortened pore passages and enriched pore mouths are beneficial to the diffusion of reactant and product, which can largely improve the yields of MEA and DEA.

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