Difference of ZSM-5 zeolites synthesized with various templates

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Abstract

ZSM-5 zeolites with similar Si/Al ratio were synthesized successfully using various templates (*n*-butylamine (BTA), ethylamine (ETA), isopropylamine (IPA), ethylenediamine (EDA), ethanol (ETL), ethanol–ammonium (ETL–AM) and no template (NT)) under hydrothermal conditions. The samples were characterized by XRD, SEM, XRF, NH_3-TPD and BET surface area measurements in order to understand the template effects and the differences of the ZSM-5 samples. The synthesis of ZSM-5 with organic templates was relatively easier than those with inorganic templates and without template. SEM results revealed that ZSM-5 synthesized with different templates had different morphology and particle size. The Si/Al ratio and BET specific surface area of the sample with ethanol as template was the lowest. NH_3-TPD results showed that the sample synthesized without template had fewer strong acid sites than others. *n*-Hexane cracking reaction was carried out over the samples to evaluate the catalytic properties. All ZSM-5 zeolites were effective in *n*-hexane cracking reaction, especially for the sample synthesized without template.
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Keywords: ZSM-5 zeolite; Synthesis; Template

1. Introduction

ZSM-5, first made by Argauer and Landolt in 1972 [1], is a medium pore (~6 Å) zeolite with three-dimensional channels defined by 10-membered rings. Due to its unique channel structure, thermal stability, acidity, shape-selective property, ZSM-5 has been used as sorbents and catalysts, and applied to petrochemical processing, fine chemical production, liquid and gas separation [2,3]. Increasing attention has been devoted to the synthesis, the properties and applications of ZSM-5 zeolites. Many templates [2–9] have been reported for the synthesis of ZSM-5 zeolites, such as tetrapropylamine bromide. The physicochemical properties of ZSM-5 zeolites are influenced by the compound used as template, the gel composition, the nature of the reagents and other factors. It is of great importance to clarify whether or not ZSM-5 synthesized with different template show different properties. Comparative data on the influences of templates on ZSM-5 can be found in some reports. Shiralkar and Clearfield [10] reported the synthesis of ZSM-5 with or without template and found only slight difference in the sorption properties among these samples. However, the structural stability of ZSM-5 synthesized using no template was lower as compared with that synthesized using template. Sankarasubbier et al. [11] compared the acidity and other physicochemical properties of templated and non-templated ZSM-5 zeolites. They found that non-templated zeolites with SiO_2/Al_2O_3 greater than 50, contained α-quartz along with ZSM-5 and the number of acid sites decreased almost linearly with the SiO_2/Al_2O_3 ratio of the zeolite. However, there are no systematic investigations reported in the open literature on the effect of templates on the physicochemical and catalytic properties of ZSM-5 zeolite. The present paper reports the synthesis of ZSM-5 with various templates and its catalytic performances for *n*-hexane cracking. The aim of this work is to provide some information about the effect of template on the physicochemical properties of ZSM-5 and is expected to throw further light on developing applied catalysts. We also would like to think about the question that how, so many templates differing in size and shape, can direct the same structure.

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2. Experimental

2.1. Synthesis

ZSM-5 was synthesized hydrothermally. Water glass and aluminum sulfate were used as Si source and Al source, respectively. Concentrated sulfuric acid was applied to adjusting gel pH. BTA, ETA, IPA, EDA, ETL, ETL–AM were used as template. The starting mixtures were formed using the following procedures: $Al_2(SO_4)_3 \cdot 18H_2O$ was first dissolved in water to get solution A, and then concentrated H_2SO_4 was added to solution A. Template, water and water-glass consist of solution B. Solution A was added to solution B while stirring. After the addition was completed, the gel was stirred for at least 30 min to get a homogenous gel, and then the gel was transferred to a stainless-steel autoclave and the sealed autoclave was placed in an air oven maintained at 448 K for hours. The products obtained were washed with deionized water until the pH value of the washing water reached 8, and then dried overnight at 373 K. The removal of organic template was carried out at 813 K for 3 h under air. Ion exchange were carried out four times with 0.5 M NH_4NO_3 solution at 353 K each for 1 h, followed by calcinations at 813 K in air for 3 h to give H-form products, from which 60–80 mesh catalysts were made by tableting, crushing and sieving.

2.2. Characterization

X-ray diffraction (XRD) patterns were measured on a D/max-rb type X-ray diffractometer using monochromatic Cu Kα radiation (30–40 kV and 40–50 mA), and the relative crystallinity of ZSM-5 was calculated based on the intensity of the peaks of angle $2\theta = 22$–25. The morphology and crystalline size of the samples were examined under a scan electron microscope (SEM, KYKY-AMRAY-1000B) using samples coated with an Au film. The surface area of the samples was measured by a single point BET method on NOVA 4000 physical adsorption series using nitrogen as adsorbate at 77 K. The samples were preheated at 623 K for 2 h before nitrogen absorption. The acidity was measured by ammonia adsorption–desorption technique using a chemical

adsorption instrument of AMERICAN micrometric 2910. The samples were outgassed at 873 K in a helium flow for 1 h, then cooled to 373 K and adsorbed NH_3 until saturation, the desorption began from 373 to 873 K by 20 K min^{-1}.

2.3. Reaction

n-Hexane cracking tests were carried out in a-quartz tubular pulse microreactor (3 mm i.d.) at 773 K. About 0.03–0.04 g catalyst was used and the volume of catalyst bed was 0.23 cm^3. The zeolite was sandwiched between two layers of acid washed quartz wool. All the catalysts were pre-treated by heating in N_2 flow at 10 K min^{-1} to 823 K and holding at 823 K for 1 h. Reaction products were analyzed by an on-line gas chromatograph (Varian CP-3800, PONA capillary: 100 m long, 0.25 i.d.). The distributions of products were analyzed by Detailed Hydrocarbon Analysis software of Varian Company.

3. Results and discussion

3.1. Physicochemical property

The gel compositions and crystallization conditions for ZSM-5 synthesis are listed in Table 1. The XRD pattern of ZSM-5(BTA) is given in Fig. 1, which agrees well with those reported in the literature [12]. All the as-synthesized samples give ZSM-5 XRD patterns, no other peak could be observed, indicating the high purity of the products. However, products from organic amine systems show higher crystallinity than other samples, indicating the strong directing function of amine for zeolite crystallization. At the same synthesis conditions, pure ZSM-5 samples with organic templates were easily formed. When ethanol or ethanol and ammonium or no template was used, α-quartz along with ZSM-5 was often produced. This may be due to high alkalinity and the weak directing function of inorganic templates. It has been reported in the literature [13] that at low alkalinity ($Na_2O = 3.5$ mol) pure ZSM-5 without template with $SiO_2/Al_2O_3 = 40$ is obtained. At low alkalinity less silica is dissolved and

Table 1
Synthesis condition of ZSM-5 zeolites with different templates and property of products

Sample	Gel compositions (mol)	Crystallization				Products	
	Al_2O_3:SiO_2:Na_2O:H_2O	Template	Seed	time (h)	Relative crystallinity (%)	Si/Al	BET area (m^2 g^{-1})
ZSM-5(BTA)	1.0:93.5:8.3:3880	18.3	No	26	100	24	293.6
ZSM-5(ETA)	1.0:93.5:8.3:3880	18.3	Yes	32	100.2	26	293.3
ZSM-5(IPA)	1.0:93.5:8.3:3880	12.2	Yes	30	96.9	27	312.4
ZSM-5(EDA)	1.0:100:8.3:3500	36	No	48	94.4	27	307.4
ZSM-5(ETL)	1.0:88.4:7.66:3500	34	No	48	85.0	18	264.0
ZSM-5(ETL-AM)	1.0:88.4:7.66:3640	34 + 36.8	Yes	50	81.3	24	284.3
ZSM-5(NT)	1.0:93:8.3:3870		No	60	84.0	25	312.1

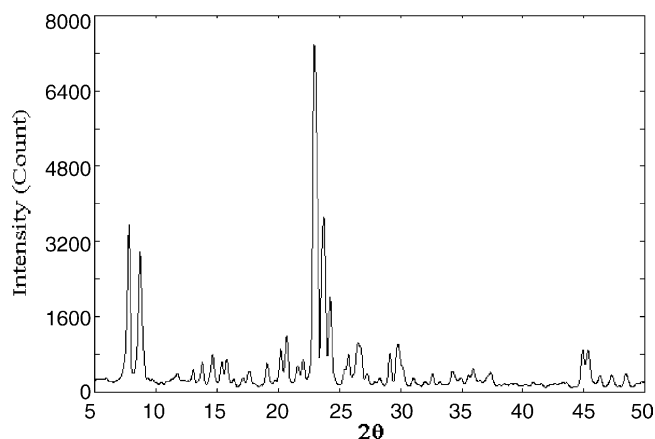Crystallization temperature: 448 K.

Fig. 1. XRD pattern of ZSM-5 (BTA) zeolites.

therefore, more silica becomes incorporated into a crystallized solid phase favoring crystallization of ZSM-5. By contrast, when the alkalinity increases, more and more silica is dissolved and remains in the liquid phase and therefore, less silica becomes incorporated into the crystalline solid phase, this favors crystallization of a mordenite phase which is more stable than ZSM-5. On further increasing the alkalinity ($Na_2O > 6$ mol), mordenite gradually transforms into the most stable α-quartz. This means that an alkalinity value higher than a certain limit inhibits the incorporation of Si and Al and thus favors crystallization of α-quartz. This result might be a proof for the hypothesis postulated by Ruren and coworkers [14] that organic amines are tetrahedrons and directly provide template centers for zeolite crystallization, which speeds up crystallization by contrast with other systems. For instance, tetrahedron centers must be formed in the gel without template agent before nucleation reaction begins. Pure ZSM-5 zeolites can be synthesized with various templates by carefully controlling the synthesis conditions.

As shown by SEM photographs in Fig. 2, templates affect the morphology, but have little effect on the particle size of ZSM-5. The as-synthesized samples consist of two different shaped crystals. Most of these crystals showed the MFI-typical hexagonal morphology. For ZSM-5(BTA) and ZSM-5(EDA), the morphology of crystals is cuboidal. The crystal shapes of ZSM-5(ETA) and ZSM-5(IPA) are similar: lath-shaped. The ZSM-5(ETL) crystals are of boat-liked, and the shape of ZSM-5(NT) is ellipsoidal. The different morphology was caused by the different size and geometric shape of templates we used. When templates of different sizes and geometric shapes were used, the filling manners of templates in the channel were different, so the growth orientation of crystals was also different, and the difference between morphology was produced. A small portion of spheroidal crystals exists in all the samples, made up of platelet-like units. This morphology could stem from a secondary nucleation yielding smaller crystallites which deposit onto the primarily formed larger individuals, still keeping the outline of their original form [15]. Zelimir [15] had re-

ported that in the system used Na^+ as cation, the morphology of as-synthesized ZSM-5 was like this. For the sample ZSM-5(ETL-AM), besides the MFI-typical morphology: lath-shaped, a small proportion of crystal clusters with a flaky habit shown in Fig. 2 was also observed. Francisco et al. [16] had reported this kind of morphology when ZSM-5 was synthesized without template. EPMA analysis of these unusual crystals showed that the Si/Al ratio of spheroidal crystals was 73, the Si/Al ratio of crystal clusters with a flaky habit was 17, whereas that of the typical hexagonal crystals was 36. The particle sizes of the as-synthesized products were also determined by laser particle size analyzer. The results are in close agreement with those from SEM. The particle sizes of the as-synthesized products were almost the same except the samples: ZSM-5(ETA), ZSM-5(IPA) and ZSM-5(ETL–AM), whose particle sizes were small because seeds were added into the gel of them. This has been reported by many authors [17].

As shown in Table 1, the products have lower BET surface area compared with literature value [18,19], but they are still in the reported region [10,20–22]. The samples synthesized by organic templates have higher BET surface than the samples synthesized by inorganic templates. The product from ethanol system has the lowest Si content and BET area as well as low crystallinity, which might be attributed to the physicochemical property in that ethanol neither provides with tetrahedron center for crystallization nor influences gel pH environment [23]. The reason for lower surface area of the ZSM-5(ETL) may be the presence of amorphous material. This situation has been improved by adding ammonium to the ethanol system. Clearly the Si/Al ratio and the BET area of the product (ZSM-5(ETL–AM), see Table 1) are increased. María et al. [24] also claimed that ZSM-5 cannot crystallize in the presence of ethanol at high SiO_2/Al_2O_3 ratios, showing a less templating effect of ethanol compared to TPA^+ cations. In the view of charge, organic amines are better templates than ethanol because they easily form H-bond complexes with the Si–OH terminal groups of the silicate anion [25].

3.2. Acidity of samples

NH_3-TPD profiles are shown in Fig. 3. All samples exhibit two well resolved desorption peaks: the low-temperature peak (LTP) at ca. 491–498 K and the high-temperature peak (HTP) at ca. 694–710 K, in good agreement with other previous reports [26]. Generally, LTP and HTP correspond to weak and strong acid sites respectively. In low-temperature region, peak temperature increases in the following order: ZSM-5(EDA) < ZSM-5(ETL–AM) < ZSM-5(NT) < ZSM-5(IPA) < ZSM-5(ETL) < *ZSM*-5(BTA) < ZSM-5 (ETA). Among high-temperature peaks, the peak position shifts toward higher temperature in the order: ZSM-5(NT) < ZSM-5(EDA) < ZSM-5(ETL–AM) < ZSM-5(ETL) < ZSM-5(IPA) < ZSM-5(ETA) < ZSM-5(BTA). Several authors reported [27] that the total acid sites of ZSM-5
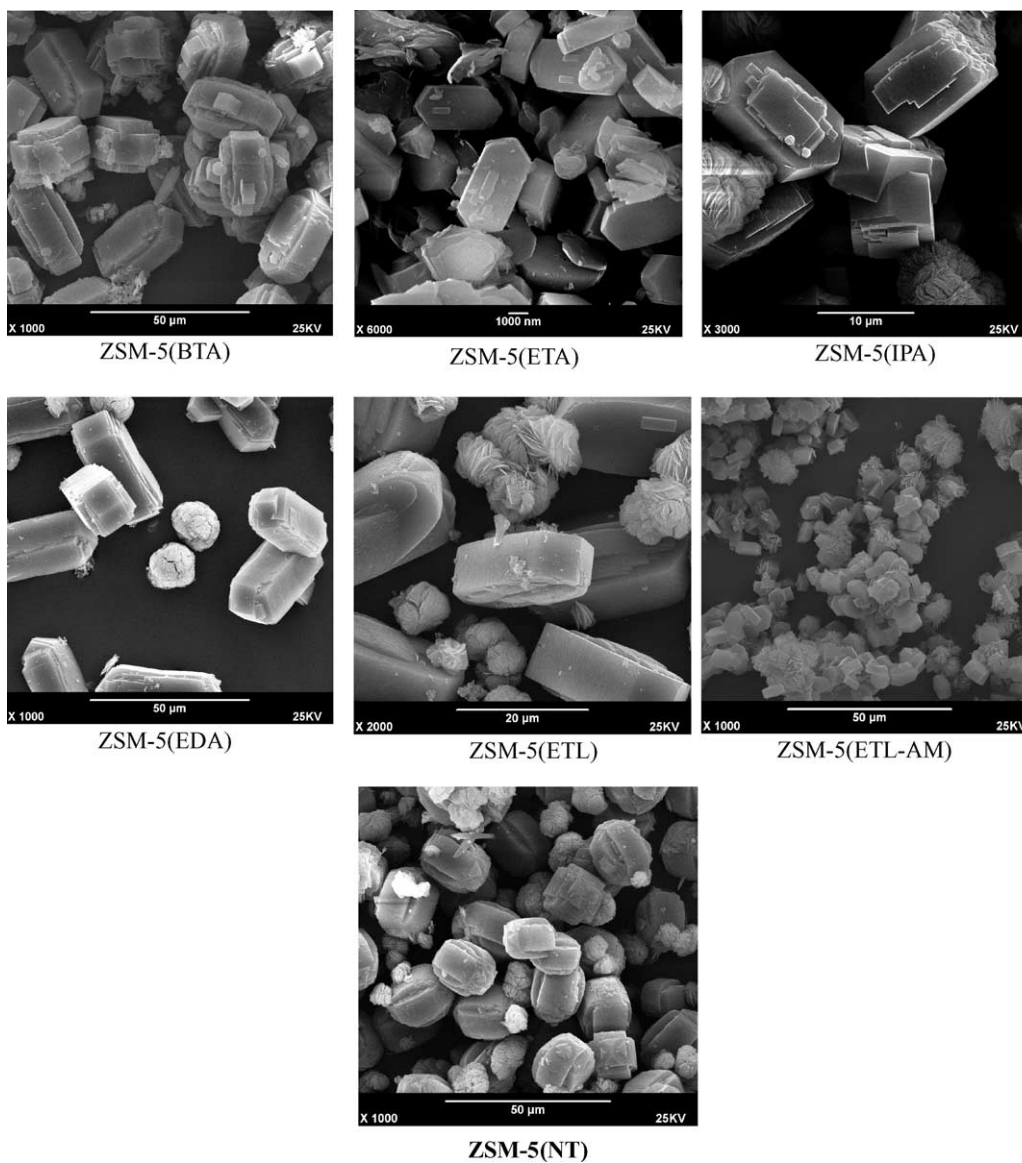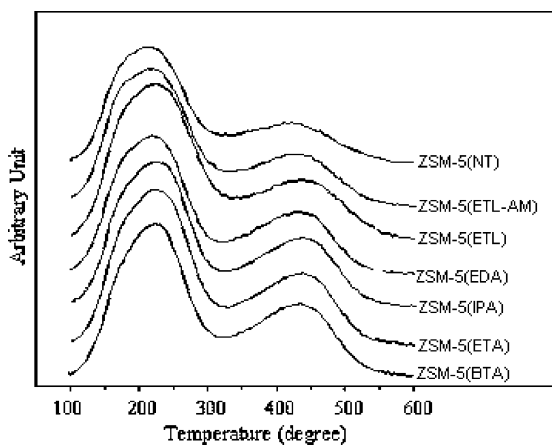
Fig. 2. SEM photographs of ZSM-5 samples.

Fig. 3. NH$_3$-TPD profiles of ZSM-5 samples.

decrease with the increasing of Si/Al ratio, so it would then be expected that the peak area should be similar because of the close Si/Al of samples except ZSM-5 (ETL). Nevertheless, this is not the case in Fig. 3. The sample ZSM-5(ETL) should have the most acid sites because of its smallest Si/Al ratio. The fact is the sample ZSM-5(NT) synthesized by no template had fewer strong acid sites. This means that there are factors other than the Si/Al ratio that lead to different acidity in ZSM-5 samples [28]. Because the samples were synthesized at the same synthesis condition except the variety of template, the difference between acidity may be caused by the different templates we used. It has been shown [29] that the number of acid sites that corresponds to the high-temperature desorption peak of NH$_3$-TPD corresponds to the framework Al atoms of fresh HZSM-5 zeolites. Although the Si/Al ratios of the as-synthesized

Table 2
The conversion and distributions of products of *n*-hexane cracking

Product	ZSM-5 (BTA)	ZSM-5 (ETA)	ZSM-5 (IPA)	ZSM-5 (EDA)	ZSM-5 (ETL)	ZSM-5 (ETL–AM)	ZSM-5 (NT)
Conversion(%)	40.16	40.2	47.4	40.6	57.9	47.3	69.2
Selectivity(%)							
Methane	0.60	0.54	0.58	0.66	0.73	0.53	0.81
Ethylene	5.60	5.58	5.39	6.52	6.49	5.60	5.81
Ethane	5.54	3.79	4.37	5.95	5.22	5.19	6.15
Propylene	10.94	12.59	10.7	13.49	9.35	10.24	7.1
Propane	36.72	33.55	36.2	35.26	39.0	38.24	41.2
Ethylene/ethane	1.01	1.47	1.23	1.10	1.24	1.08	0.94
Propane/propylene	3.36	2.66	3.38	2.61	4.17	3.73	5.8
Benzene	1.17	0.86	1.0	1.22	1.22	1.05	1.64
C2–C4 olefin	26.77	28.33	25.52	30.78	24.49	24.97	20.31
$\geq$C4	40.6	43.95	42.76	38.42	39.21	39.90	38.33
Total	100	100	100	100	100	100	100

The cracking of *n*-hexane was performed on a pulse reaction device at 773 K with an on-line GC for product analysis.

samples are close except the sample ZSM-5(ETL), because of the weak direction of inorganic template, some species of extra framework Al(EXFAL) may exist in the samples synthesized by inorganic templates and without template, these phase had a low capability of absorbing ammonia compared to the framework Al(FAL) species, so they had fewer strong acid sites.

3.3. Catalytic properties

The catalytic performances and products distribution of as-synthesized ZSM-5 products in the cracking of *n*-hexane are listed in Table 2. All samples were effective in the reaction of *n*-hexane cracking. The sample synthesized without template showed the highest activity. The ZSM-5 samples with organic template exhibited the lowest activity. Post and van Hooff [28] reported that for *n*-hexane cracking it is mainly the number of strong acid sites, which is important, and not the strength. It has been shown [16] that the catalytic activity for *n*-hexane cracking is proportional to the framework aluminum. But in our tests, the result of conversion is not like this. The sample synthesized without template shows the highest activity, although it had fewer strong acid sites. The samples synthesized without template and with inorganic templates showed higher activity, this may be due to easy accessibility of the reactants to acid sites. Masuda et al. [30] had reported that accessibility to acid sites instead of acid strength is the major influencing factor on the catalytic activity. The coexistence of intra- and extra framework aluminum can enhance the catalytic activity as has been shown [31–33]. The weak template effect of inorganic templates may cause the coexistence of intra- and extra framework aluminum in the samples, which may be the reason for higher catalytic activity of the samples ZSM-5 with inorganic templates.

The product distributions are shown in Table 2. Compared with other samples, ZSM-5(NT) exhibits a relatively low selectivity for propylene and a high selectivity for the formation of propane and benzene. The existence of benzene and low olefin/alkane value of product shows that severe hydrogen transfer occurred in *n*-hexane cracking for sample ZSM-5 (NT). Furthermore, with the order of NT, ETL, ETL–AM, organic amine, the olefin content of the product molecules decreases. This is probably due to the same channel structure caused by different templates.

4. Conclusions

At the same synthesis conditions, ZSM-5 zeolites with various templates have been synthesized with high crystallinity. Pure ZSM-5 zeolites were easily obtained with organic templates. Scanning electron microscopy revealed that morphologies of products were cuboidal to ellipsoidal, a small proportion of spheroidal crystals made up of platelet-like units was also observed. In the sample of ZSM-5(ETL–AM), the crystal clusters with a flaky habit were also observed. The BET specific surface area of the sample synthesized by ethanol was the smallest, and then the sample synthesized by ethanol and ammonium, and the largest was the samples synthesized by isopropylamine and no template. NH$_3$-TPD showed that various templates had a little effect on surface acidity of samples. The samples synthesized by inorganic templates and without template had fewer strong acid sites. They all exhibited good catalytic properties for cracking of *n*-hexane. The sample synthesized by no template presented the highest activity.

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