



Energy, Resources and Environmental Technology

Synthesis of ZSM-5 with the silica source from industrial hexafluorosilicic acid as transalkylation catalyst☆

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ABSTRACT

A new effective process to improve the utilization of industrial fluorosilicic acid of phosphate fertilizer by-product has been investigated to comprehensive application of the silicon and fluorine source. Two-step ammoniation was applied to recover high-quality silica. The recovered silica can be used to hydrothermal synthesize ZSM-5 zeolite without impurity phase contamination, which was confirmed by XRD, TG, SEM, BET and EDS characteristic techniques. It was found that with the increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and the extension of reaction time, the crystal type transform from the orthorhombic to the monoclinic phase. The impurity fluorine content of the recovered SiO_2 from H_2SiF_6 has great influence on the hydrothermal process for ZSM-5 crystal structure formation. Moreover, the increase of fluorine ions content in the hydrothermal process can control the crystal morphology and size of synthesized ZSM-5. Catalytic properties of synthesized HZSM-5 with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in transalkylation of toluene and 1,2,4-trimethylbenzene show good and stable catalytic performance. The ZSM-5 synthesized with recovered silica source exhibits similar catalyst life as the performance of small particle size HZSM-5, because the ZSM-5 synthesized with the silica source from industrial hexafluorosilicic acid prefers a thin disk crystal along the *b* axis direction, which shortens the diffusion distance of generated products.

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1. Introduction

Phosphate fertilizer industries have produced mass of gaseous silicon tetrafluoride (SiF_4) and it was absorbed by water to form hexafluorosilicic acid [1,2]. Hexafluorosilicic acids are naturally hazardous for the human and creature living in the water, soil and even the air [3]. However, the by-product hexafluorosilicic acid of phosphate fertilizer industry is regarded as a major fluorine and silicon-containing source [4]. Hexafluorosilicic acid has many applications by different industrial processes [5–7]. Hexafluorosilicic acid has been reported to produce fluorine–silicate, such as sodium fluorosilicate, potassium fluorosilicate, magnesium fluorosilicate and zinc fluorosilicate for many years [8]. However, the market share of these salts is very small, that is why the applications of hexafluorosilicic acid are greatly limited. Another product from hexafluorosilicic acid is siliceous reinforcing

agent, white carbon black [9–11]. However, the economic value-added of this product is very low.

ZSM-5 zeolite with the characteristics of three-dimensional straight channel and acidity modification has been widely used in petrochemical industry as catalysts, adsorbents and others [12,13]. Zeolite has been widely synthesized with silicon source of water glass, silica sol, tetraethyl orthosilicate, fumed silica *etc.* [14]. The high cost of the silica source blocks the further industrial application of ZSM-5. If the hexafluorosilicic acid can be used as silicon source for zeolite synthesis, this new method can greatly improve the economic value-added and solve the environmental problem of the phosphorus chemical industry by-product hexafluorosilicic acid and reduce the cost of ZSM-5 production.

Industrial C9 components from oil reforming or pyrolysis process contain trimethylbenzene, ethyl benzene, propylbenzene, indan and other aromatic components. The majority of content in C9 aromatic is trimethylbenzene. If the trimethylbenzene can be efficiently transferred to benzene, toluene and xylene (BTX), this method can achieve the rational utilization of resources and benefit maximization of the resource. The hydrodealkylation and transalkylation of trimethylbenzene to produce high value-added products BTX have aroused the attention in the domestic and foreign researchers [15].

Here, a systemic method for ZSM-5 synthesis with the crude industrial hexafluorosilicic acid as silicon and fluorine resources is reported.

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The ZSM-5 zeolite with a different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio can be synthesized successfully under the optimal synthesis conditions. The obtained MFI zeolite from the process is applied as catalyst for toluene and 1,2,4-trimethylbenzene transalkylation and disproportionation.

2. Experimental

2.1. Preparation of materials

Industrial hexafluorosilicic acid (10%–25%) was provided by a phosphate fertilizer factory from the phosphoric acid of wet process. Tetrapropyl ammoniumbromide (98%) comes from Aladdin Industrial Corporation; aluminum hydroxide brought from Sinopharm Chemical Reagent Co., Ltd.; nano fumed silica (99.8%) comes from Aladdin Industrial Corporation; ammonium hydroxide (25%–28%), ammonium nitrate (99%) and toluene (99.5%) are commercial products from Xilong Chemical Co., Ltd.; 1,2,4-trimethylbenzene (98%) comes from Aladdin Industrial Corporation. Commercial Products ZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio = 38) comes from Sinopec Jinling Petrochemical Corporation South Refined Institute.

2.2. Procedure and methods

Two-step ammoniation method was applied to recover high-quality silica and produce ammonium fluoride from hexafluorosilicic acid reported in [1]. The recovered SiO_2 and NH_4F are applied as silicon and fluorine source for hydrothermal synthesis ZSM-5 zeolites. The compositions were the following molar ratio: $\text{SiO}_2:\text{NH}_4\text{F}:\text{Al}(\text{OH})_3:\text{TPABr}:\text{H}_2\text{O} = 10:x:y:z:330(x = 0 \text{ or } 9; y = 0.83, 0.33, 0.16 \text{ or } 0.08; z = 2.5, 1.25, 0.625 \text{ or } 0.5)$. The reagents were mixed in the following order: NH_4F solid was added to distilled water, then tetrapropyl ammonium bromide (TPABr), $\text{Al}(\text{OH})_3$ and SiO_2 hydrogel from the second step of the two-step ammoniation method are added sequentially with the constant stirring in 4 h. Then the stirred mixture was transferred to a hydrothermal crystallization kettle and crystallization for 1–7 d at 443 K. Then the crystallized products are filtered, washed with 1000 ml D.I. water and dried at 333 K overnight to obtain ZSM-5 precursor. The precursor is calcined at 823 K for 7 h in the Muffle furnace to obtain ZSM-5 zeolite that indicated as $x\text{-ZSM-5}$ (x stand for molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$). To comparison with the $x\text{-ZSM-5}$ synthesized from recovered SiO_2 , the commercial fumed pure silica was used to synthesize ZSM-5 with the same procedure under the condition of NH_4F or not, the synthesized samples are indicated as $x\text{-ZSM-5(f)}$. The parent $x\text{-ZSM-5}$ zeolite was exchanged with $1.0 \text{ mol} \cdot \text{L}^{-1} \text{ NH}_4\text{NO}_3$ solution at reflux for 3 times (8 h), fully washed, then dried at 393 K for 12 h and calcinated at 823 K in air, at last the H-form $x\text{-HZSM-5}$ zeolites were obtained. After calcinations, the commercial ZSM-5 zeolite is indicated as 38-ZSM-5(S).

2.3. Catalysts characterization

Powder X-ray diffraction (XRD) was performed using a Panalytical X'Pert automatic diffractometer. The light source is Cu target K_α radiation (X-ray wavelength 0.1541874 nm), tube current is 40 mA, tube voltage is 45 kV, the diffraction pattern is recorded in 2θ of 5° – 50° . Phase and relative crystallinities of zeolite samples were judged by JADE5 software. Apparent morphology and crystal size of the zeolite were observed with S-4800 type cold field emission scanning electron microscope (SEM). FALCON type Energy Dispersive Spectrometer (EDS) produced by EDAX company of America is applied to measure the elemental composition of the sample. The machine is rated at 4 kW, with cathode maximum current 160 mA. The thermogravimetric (TG) analysis is carried out at 473 K with 30 mg sample of particle sizes 0.18–0.28 mm at atmospheric pressure. The system was quenched at 823 K for 2 h in a flow of He at $20 \text{ ml} \cdot \text{min}^{-1}$ (STP), then it was performed under the same He flow with a ramp of $10 \text{ K} \cdot \text{min}^{-1}$ to

1073 K. N_2 adsorption–desorption measurements were carried out on Micromeritics VII2390 apparatus at 77 K. Prior to the analysis, the samples were degassed at 373 K under nitrogen purging for 1 h, then at 573 K under nitrogen purging for 1 h. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method in the 0.05–0.25 P/P_0 range. The pore volumes and their size distributions were derived from the desorption branch of the N_2 isotherms using the Barrett–Joyner–Halenda (BJH) method.

2.4. Catalytic reaction experiments

Toluene and 1,2,4-trimethylbenzene (3:1 ratio mixed by weight) transalkylation was carried out in a fixed-bed flow reactor under 3 MPa pressure with N_2 as carrier gas. The catalyst was activated in a gas flow at 773 K for 1 h and cooled down to the reaction temperature of 723 K. The WHSV was 3 h^{-1} . Reaction products were analyzed by GC using capillary column FL-INNOWAX capillary column. The toluene and 1,2,4-trimethylbenzene conversion and product selectivities are calculated by the following equations.

$$\text{Conversion of reactants} = \frac{\text{Consumed amount of the reactant in mol}}{\text{Initial amount of the reactant in mol}} \times 100\%$$

$$\text{Selectivity of products} = \frac{\text{Specific product in mol/All products in mol}}{\times 100\%}$$

3. Results and Discussion

3.1. Hydrothermal synthesis of ZSM-5 zeolite

3.1.1. The two-step ammoniation method for high purity SiO_2 recover from hexafluorosilicic acid

The results of the two-step ammoniation with different allocation proportion of ammonia usage in the first and second ammoniation steps are shown in Table 1. According to the report of Yu *et al.* [1], the high-grade amorphous silica can be obtained in the second step with the two-step hexafluorosilicic acid ammoniation method. With the increasing amount of $\text{NH}_3 \cdot \text{H}_2\text{O}$ in the first step, most of the impurities, such as Fe, Mg, Ca, and Na, in the fluorosilicic acid can be deposited in the first step. Although the amount of rest produced SiO_2 in the second step is decreased, it is getting purer. The obtained silica of the second step is more suitable for the preparation of the zeolite. According to the yield and purity of SiO_2 generated in the second step, the most important condition for preparing silica hydrogel is that the molar ratio of ammonia and fluorosilicic acid in the first step and the second step is 3 and 4.2, respectively. Under this condition, the yield of amorphous silica is 42.6% and 52.5% in the first and second ammoniation steps, respectively. Moreover, the produced SiO_2 purity in the second step is 97.5% according to EDS analysis results. It can be seen from

Table 1
Effect of ammonia addition on the two-step ammoniation

First step	Molar ratio of $\text{NH}_3 \cdot \text{H}_2\text{O}/\text{H}_2\text{SiF}_6$	2	3	4	5	6
	25% $\text{NH}_3 \cdot \text{H}_2\text{O}$ volume/ml	18	27	36	45	54
	Final pH	5	6	7	8	8
	Recovery silica yield/%	27.0	42.6	76.2	89.6	83.2
Second step	Molar ratio of $\text{NH}_3 \cdot \text{H}_2\text{O}/\text{H}_2\text{SiF}_6$	5.2	4.2	3.2	2.2	1.2
	25% $\text{NH}_3 \cdot \text{H}_2\text{O}$ volume/ml	47	38	29	20	11
	Final pH	9	9	9	9	9
	Recovery silica yield ^① /%	51.9	52.5	22.8	0.2	0.05
	Recovery silica purity ^② /%	95.2	97.5	97.4	97.8	98.1
	Total mass of produced silica/g	8.68	10.47	10.89	10.08	9.20

Note: The EDS analysis the purity of SiO_2 in second step.

$$\text{① Silica yield} = \frac{\text{mass of } \text{SiO}_2 \text{ in each step}}{\text{theoretical value of total mass } \text{SiO}_2} \times 100\%$$

$$\text{② Silica purity} = \frac{\text{the mass of pure } \text{SiO}_2 \text{ in second step}}{\text{recovery mass of } \text{SiO}_2 \text{ in second step}} \times 100\%$$

Appendix A (Table A1). The element composition of this SiO_2 is Al 0.71 wt%, Si 49.12 wt%, Mg 0.56 wt%, F 1.81 wt% and does not detect other impurities.

3.1.2. Influence of silica to alumina molar ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) on the synthesis of ZSM-5

To investigate the influence of $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio on the zeolite synthesis, the ZSM-5 zeolite is hydrothermally synthesized with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio from 12 to 125 under the same reaction condition, such as reaction time stirring 4 d; $\text{SiO}_2/\text{TPABr} = 8$; $\text{SiO}_2/\text{NH}_4\text{F} = 1.11$; $\text{H}_2\text{O}/\text{SiO}_2 = 33$. The EDS analysis results of the produced ZSM-5 are illustrated in Table 2, in which the relative crystallinity is calculated based on the XRD patterns as shown in Fig. 1.

The XRD pattern of the zeolite samples with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is shown in Fig. 1, which only contains the characterized (1 0 1), (2 0 0), (0 2 0), (3 0 1) and (5 0 3) diffraction peaks of ZSM-5. The peaks at $2\theta = 23.2^\circ$ (5 0 1) and $2\theta = 24.2^\circ$ (3 1 3) indicate that the ZSM-5 is orthogonal phase [16]. The results in Fig. 1 show that with the increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, the peaks in the region of $2\theta = 7.5^\circ$ – 9.5° and $2\theta = 22.5^\circ$ – 24.5° changed obviously. In order to describe the change of these two regions more clearly, the partial enlarged detail of these two diffraction regions are shown in Fig. 1(B) & (C). From Fig. 1(B), it can be seen that the single diffraction peak at the (2 0 0) of $2\theta = 8.5^\circ$ has become bimodal as the growth of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. At the same time, the two diffraction peaks at the (3 3 2) and (5 0 1) crystal planes merged to form one peak at the $2\theta = 23.08^\circ$ in Fig. 1(C). These results show that the crystal phase of ZSM-5 transfers from the orthogonal crystal phase to monoclinic phase [17].

The EDS analysis of this sample indicates that the element compositions of the ZSM-5 are Al 1.62 wt%, Si 35.17 wt%, O 63.21 wt% and do not detect other impurities. Although the silica gel from the second ammoniation step of the industrial hexafluorosilicic acid contains the impurities of Mg ions, the metal ions are actually hard to be incorporated into the structure skeleton of ZSM-5 to replace silicon atoms. This result indicates that the impurity of Mg ions in the silica gel is hard to influent the synthesized zeolite. The elemental analysis results show that with the presence of the Al elements in the ZSM-5, the actual $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the zeolite is a little smaller than the theoretical ratio of

hydrothermal solution as shown in Table 2. It can be deduced that the impurity Al of the silica gel can also be incorporated into the zeolite. Finally, the success of the synthesis of the ZSM-5 with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is confirmed.

Table 2

Influence of $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio and crystallization time on the synthesis of ZSM-5 zeolite

$\text{SiO}_2/\text{Al}_2\text{O}_3$ of samples ^①	Condition on variables		Relative crystallinity ^② /%
	Stirring	Time/d	
32	Yes	1	97.02
32	Yes	2	96.11
32	Yes	3	95.52
23	Yes	4	96.04
26	Yes	4	96.23
32	Yes	4	100
45	Yes	4	94.97
32	Yes	7	94.12
32	NO	1	80.67

^① The EDS analysis results of the produced $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of ZSM-5.

^② Calculated according to the intensity of peak of (1 0 1), (2 0 0), (0 2 0), (3 0 1) and (5 0 3) from XRD spectra.

3.1.3. Influence of crystallization time on the synthesis of ZSM-5

Under the same molar ratio of $\text{SiO}_2:\text{NH}_4\text{F}:\text{TPABr}:\text{Al}(\text{OH})_3:\text{H}_2\text{O} = 10:9:1.25:0.16:330$, the XRD patterns of synthesized ZSM-5 zeolites with different crystallization time are shown in Table 2. The XRD patterns in Fig. 2 show the influence of crystallization time on the synthesis of ZSM-5 zeolite. They have only the characteristic structure peaks of ZSM-5 zeolite as (1 0 1), (2 0 0), (0 2 0), (3 0 1) and (5 0 3). These results indicate that only MFI zeolite crystals are formed during the hydrothermal synthesis. There are separate (5 0 1) and (3 1 3) peaks in the $2\theta = 23.2^\circ$ and 24.2° , which are corresponding to the orthogonal phase. With the increase of hydrothermal time, the diffraction peak in the $2\theta = 22.5^\circ$ – 24.5° has great change. From the enlargement of partial

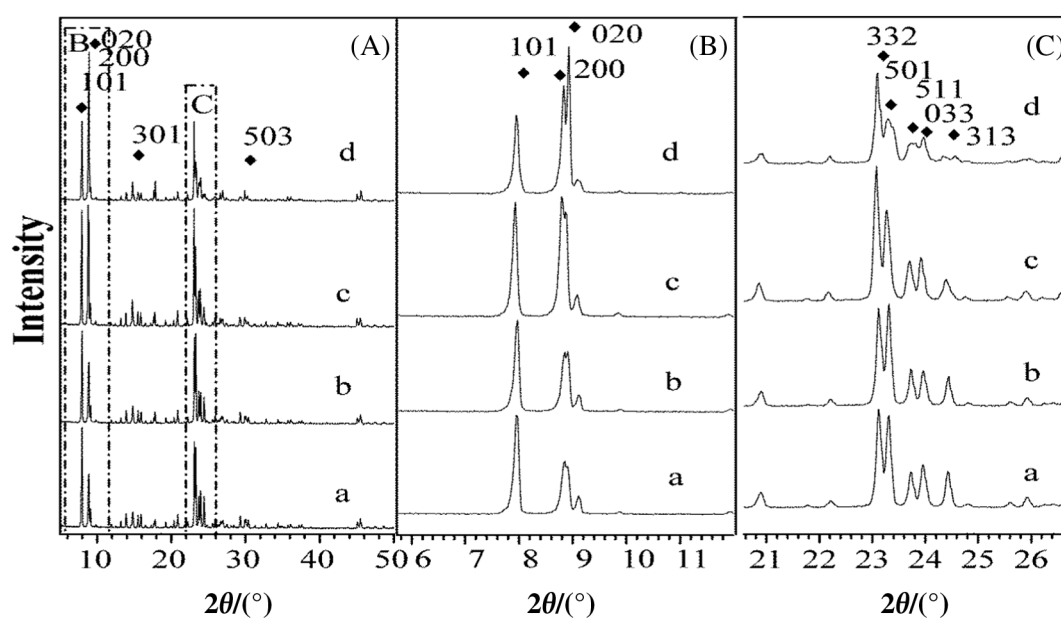


Fig. 1. XRD patterns of synthesized ZSM-5 zeolite with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio (a) 23-ZSM-5, (b) 26-ZSM-5, (c) 32-ZSM-5 and (d) 45-ZSM-5. ($\text{SiO}_2/\text{NH}_4\text{F} = 1.11$; $\text{SiO}_2/\text{TPABr} = 8$; reaction time (stirring 4 d); $\text{H}_2\text{O}/\text{SiO}_2 = 33$).

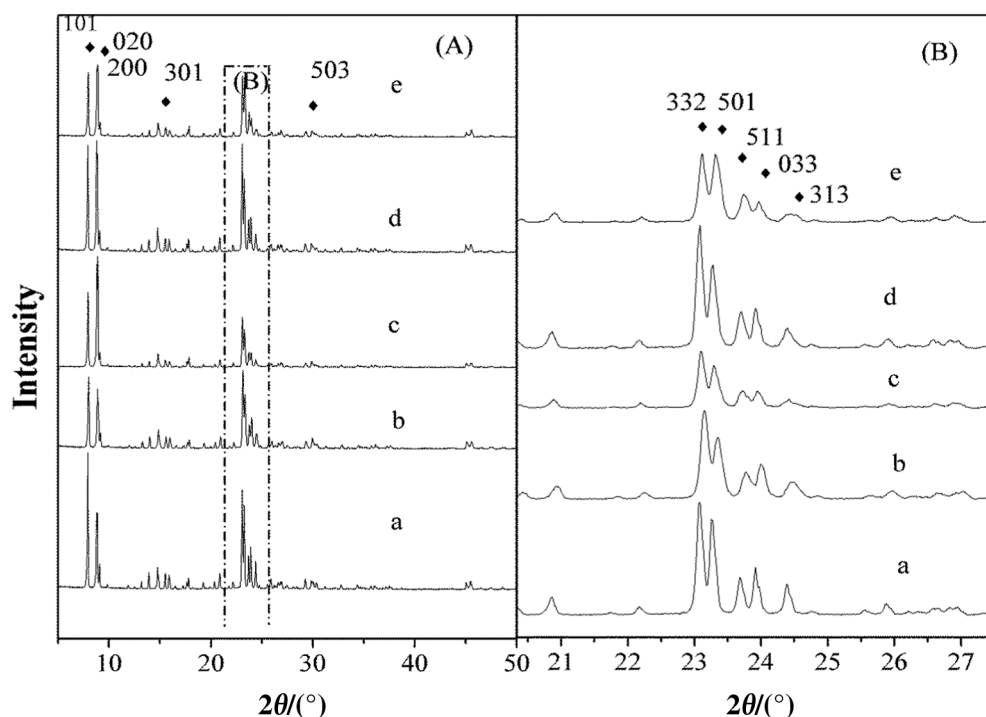


Fig. 2. XRD patterns of synthesized 32-ZSM-5 zeolite under dynamic condition with different hydrothermal time (a) dynamic 1 d, (b) dynamic 2 d, (c) dynamic 3 d, (d) dynamic 4 d, (e) dynamic 7 d. ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 32$; $\text{SiO}_2/\text{TPABr} = 8$; $\text{SiO}_2/\text{NH}_4\text{F} = 1.11$; $\text{H}_2\text{O}/\text{SiO}_2 = 33$).

diffraction of Fig. 2(A) & (B), it can be seen that the intensity of the separate diffraction peak at the (5 1 1) crystal plane in $2\theta = 23.8^\circ$ and (3 1 3) crystal plane in $2\theta = 24.2^\circ$ decreased and merged with the increase of crystallization time. This phenomenon is corresponding to the transfer of orthogonal crystal system to monoclinic system [17].

3.1.4. The influence of dynamic and static hydrothermal condition on the ZSM-5 zeolite synthesis

The XRD patterns of the ZSM-5 zeolite with dynamic or static reaction are shown in Fig. 3. The zeolites synthesized both in the dynamic and static methods exhibit the ZSM-5 characteristic diffraction peaks. The intensity of the peak indicates that the ZSM-5 synthesized

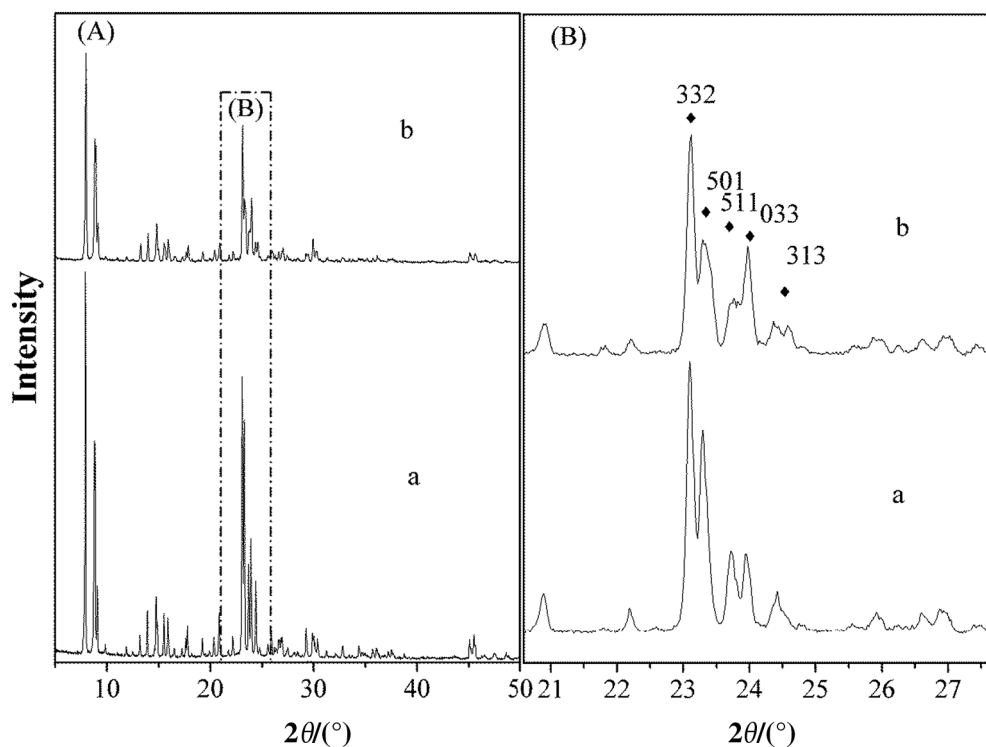


Fig. 3. XRD patterns of synthesized ZSM-5 zeolite under different hydrothermal condition (a) dynamic 1 d and (b) static 1 d. ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 32$; $\text{SiO}_2/\text{TPABr} = 8$; $\text{SiO}_2/\text{NH}_4\text{F} = 1.11$; $\text{H}_2\text{O}/\text{SiO}_2 = 33$).

with dynamic method under 1 d hydrothermal treatment possesses higher crystallinity than that synthesized with static method under the same time. The detailed topography information shown in Fig. 3(B) indicates that the ZSM-5 synthesized in the dynamic condition has two diffraction peaks at around $2\theta = 23.2^\circ$ and 24.2° for the (5 0 1) and (3 1 3) crystal planes, which is corresponding to a typical orthogonal crystal system. However, these two peaks merge to a single peak at $2\theta = 23.5^\circ$ – 24° for ZSM-5 synthesized under the static reaction, which is the characteristic of the monoclinic phase [17].

3.1.5. Influence of the molar ratio of silica to TPABr ($\text{SiO}_2/\text{TPABr}$) on the synthesis of ZSM-5

The synthesized ZSM-5 with the composition of $\text{SiO}_2:\text{NH}_4\text{F}:\text{TPABr}:\text{Al}(\text{OH})_3:\text{H}_2\text{O} = 10:9:x:0.16:330$ and different ratio of $\text{SiO}_2/\text{TPABr}$ is characterized by the thermogravimetric analysis (DTG/TG) and N_2 de/adsorption and shown in Table 3. The DTG/TG curves of ZSM-5 zeolite precursor with different $\text{SiO}_2/\text{TPABr}$ ratio are shown in Fig. 4. There is no mass loss with the temperature lower than 373 K, which suggests that there is no adsorption water retained in the sample, because the ZSM-5 zeolite samples have been dried in the 333 K of oven for 12 h before test. The total mass loss is about 12% from 333 K to 1073 K, the organic templates are burned out between 673 and 773 K [18]. The samples with the $\text{SiO}_2/\text{TPABr}$ ratio lower than 8 have almost the same mass loss for the removing surfactant during TG test. These phenomena show that the surfactant incorporated to the samples does not increase with the increase of TPABr contents in the hydrothermal solution, when the $\text{SiO}_2/\text{TPABr}$ ratio is up to 8. The maximum amount of TPABr incorporated in the sample is about 12% in the synthesized ZSM-5 precursor [19]. The nitrogen sorption isotherm in Appendix Fig. A1 is typical type I isotherm and depicts that the adsorption curve

rapidly rising before the relative pressure is 0.1, which is attributed to typical of microporous nature.

3.1.6. Influence of the molar ratio of silica to NH_4F ($\text{SiO}_2/\text{NH}_4\text{F}$) on the synthesis of ZSM-5

The XRD patterns of synthesized ZSM-5 by the silica source from industrial hexafluorosilicic acid are shown in Fig. 5. All the 32-ZSM-5 samples with NH_4F and without NH_4F as mining agent during hydrothermal process only contain the ZSM-5 character peaks. The detailed topography information shown in Fig. 5(C) indicates that the ZSM-5 synthesized with NH_4F and without NH_4F has two diffraction peaks at $2\theta = 23.2^\circ$ and 24.2° for the (5 0 1) and (3 1 3) crystal planes, which are corresponding to a typical orthogonal crystal system. However, the relative intensity of the peaks (1 0 1), (2 0 0) and (0 2 0) between $2\theta = 7.5^\circ$ and 9.5° is different for the samples 32-ZSM-5 with NH_4F and without NH_4F . The increased relative intensity of peak (2 0 0) and (0 2 0) to (1 0 1) for 32-ZSM-5 with NH_4F compared with the 32-ZSM-5 without NH_4F indicates that the 32-ZSM-5 with NH_4F has longer order structure along b or a axis direction. These phenomena are further confirmed by SEM characterization as shown in Fig. 6. The crystal structure of synthesized 32-ZSM-5 with or without fluorine as mining agent during hydrothermal process is almost the same [13]. It can be seen that the crystal size of the 32-ZSM-5 with fluorine ions in the hydrothermal process is about $50\text{ }\mu\text{m} \times 10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$. While the crystal size of the ZSM-5 without fluorine ions in the hydrothermal process is about $10\text{ }\mu\text{m} \times 1\text{ }\mu\text{m} \times 0.2\text{ }\mu\text{m}$. Therefore, the 32-ZSM-5 with NH_4F is thicker than that without NH_4F along the b axis direction.

To investigate the influence of fluorine ions on the synthesis of the ZSM-5, the synthesized samples of 32-ZSM-5(f) with NH_4F and without NH_4F from fumed pure SiO_2 are also characterized as the XRD pattern in Fig. 5 and SEM pictures in Fig. 6. The crystal size of ZSM-5(f) with fluorine ions is about $50\text{ }\mu\text{m} \times 10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$. It can be seen from Figs. 5 & 6 that under the fluorine ion hydrothermal condition the 32-ZSM-5(f) synthesized from fumed silica has almost the same SEM morphology and XRD pattern with 32-ZSM-5 synthesized from recovered silica. While the XRD pattern of sample (e) in Fig. 5 shows that without fluorine ion condition during the hydrothermal process, the ZSM-5 crystal structure cannot be synthesized with the pure fumed SiO_2 . Therefore, it can be deduced that the fluorine content of the recovered SiO_2 from H_2SiF_6 has great influence on the hydrothermal process for ZSM-5 crystal structure formation, while the small amount of fluorine ion content in the

Table 3
The effect of the $\text{SiO}_2/\text{TPABr}$ molar ratio on the synthesis of 32-ZSM-5 zeolite

No.	$\text{SiO}_2/\text{TPABr}$	TG mass loss percentage/%	$S_{\text{BET}}/\text{m}^2 \cdot \text{g}^{-1}$	$V_{\text{total}}/\text{cm}^3 \cdot \text{g}^{-1}$
1	8	12.20	441.65	0.192
2	16	11.98	425.93	0.198
3	20	11.35	377.99	0.194
4	40	7.84	374.37	0.193

Note: S_{BET} , BET surface area; V_{total} , total pore volume.

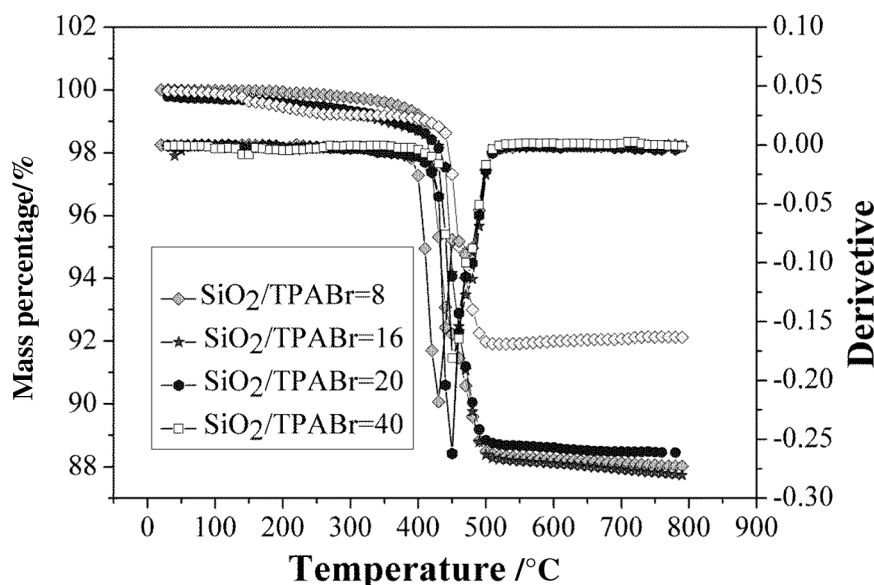


Fig. 4. The thermal gravimetric analysis results of the ZSM-5 with $\text{SiO}_2/\text{TPABr} = (8, 16, 20 \text{ or } 40)$. ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 32$; $\text{SiO}_2/\text{NH}_4\text{F} = 1.11$; reaction time (stirring 4 d); $\text{H}_2\text{O}/\text{SiO}_2 = 33$).

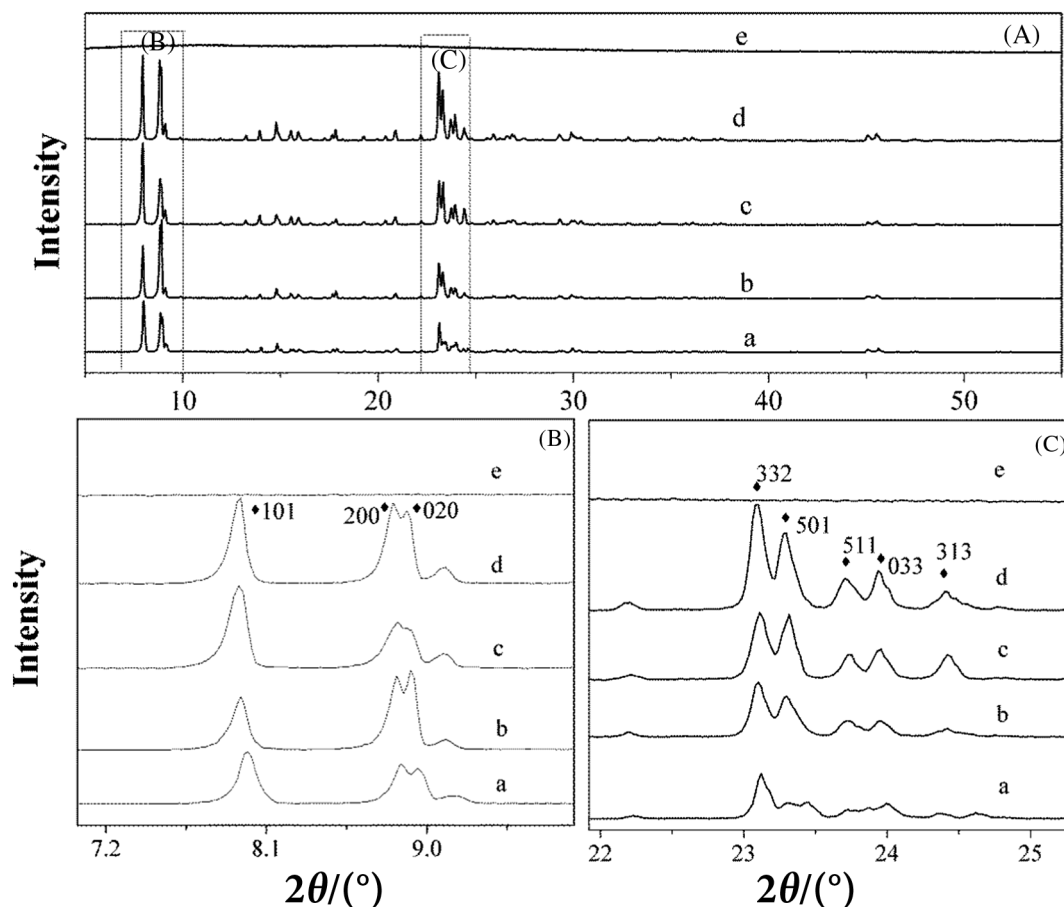


Fig. 5. XRD patterns of different zeolite (a) 38-ZSM-5(S), (b) 32-ZSM-5 with NH_4F and (c) 32-ZSM-5 without NH_4F . (d) 32-ZSM-5(f) with NH_4F , (e) 32-ZSM-5(f) without NH_4F . ($\text{SiO}_2/\text{TPABr} = 8$; $\text{SiO}_2/\text{Al}_2\text{O}_3 = 32$; reaction time (stirring 4 d); $\text{H}_2\text{O}/\text{SiO}_2 = 33$).

recovered SiO_2 causes the formation of the thin disk crystal along the b axis direction compared with 32-ZSM-5 synthesis with NH_4F addition. Moreover, the additional amount of fluorine ion content in the hydrothermal process can control the crystal morphology and size of synthesized ZSM-5.

For further comparison, the commercial 38-ZSM-5(S) with small particle size synthesized under the hydrothermal condition without fluorine ion content is also applied to XRD and SEM characterizations. It has small crystal particle size and uniform morphology in 3D direction compared with the sample 32-ZSM-5(f) hydrothermal synthesized under NH_4F addition. These results are consistent with the report of Aiello *et al.* [20] that the addition of fluorine ion can increase the growth of zeolite crystal, because the addition of fluoride ion can promote the solution of SiO_2 and $\text{Al}(\text{OH})_3$ to form the complex fluorides and speed up the crystallization rate and shorten the reaction time [21].

3.2. Catalytic properties of different $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio HZSM-5

The average results of the toluene and 1,2,4-trimethylbenzene conversion and product selectivities after 8 h reactions are shown in Table 4. According to the reaction products, the possible reaction elementary steps in the transalkylation process are as Fig. 7. Benzene is product from toluene disproportionation or dealkylation reaction [22]. Xylene isomers can be produced from the toluene disproportionation or transalkylation of toluene and trimethylbenzene or disproportionation of trimethylbenzene. Compared with the purposed product of xylene isomers from transalkylation reaction,

trimethylbenzene isomerization product selectivities are less than 10% in total product selectivity. For the synthesized x -HZSM-5 with the increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, the amount of acid sites should decrease and the acid strength raised [23,24]. At the same time, the toluene and 1,2,4-trimethylbenzene conversion have a clear decreasing trend with the decreased acid amount. While the sum of benzene and xylene selectivities decreases with the increase of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, the selectivities of trimethylbenzene isomerization reactions are increased, because the strength acid sites are more favorable for trimethylbenzene isomerization, which is consistent with the phenomena reported in the literature [25]. For the 23-ZSM-5, toluene and 1,2,4-trimethylbenzene conversion can reach 53% and 54%, respectively. The maximum of average p -xylene selectivity reaches 15% as shown in the Figs. 8 & 9.

3.3. Catalytic properties of different particle size and morphology of HZSM-5

Catalytic properties for toluene and 1,2,4-trimethylbenzene conversion of 38-HZSM-5(S) and the 32-HZSM-5 with or without NH_4F addition during hydrothermal process are compared and shown in Table 5. For the sample 32-HZSM-5 without NH_4F , the average toluene and 1,2,4-trimethylbenzene conversion reach 55% and 63%, while the total xylene selectivity and benzene selectivity is 62.5% and 28%, respectively. On the other hand, the average toluene conversion and the 1,2,4-trimethylbenzene conversion are 56% and 60%, respectively, and the total xylene selectivity and benzene selectivity are 61.5% and 27.5% for 38-HZSM-5(S), respectively. According to Figs. 10 & 11, the 32-HZSM-

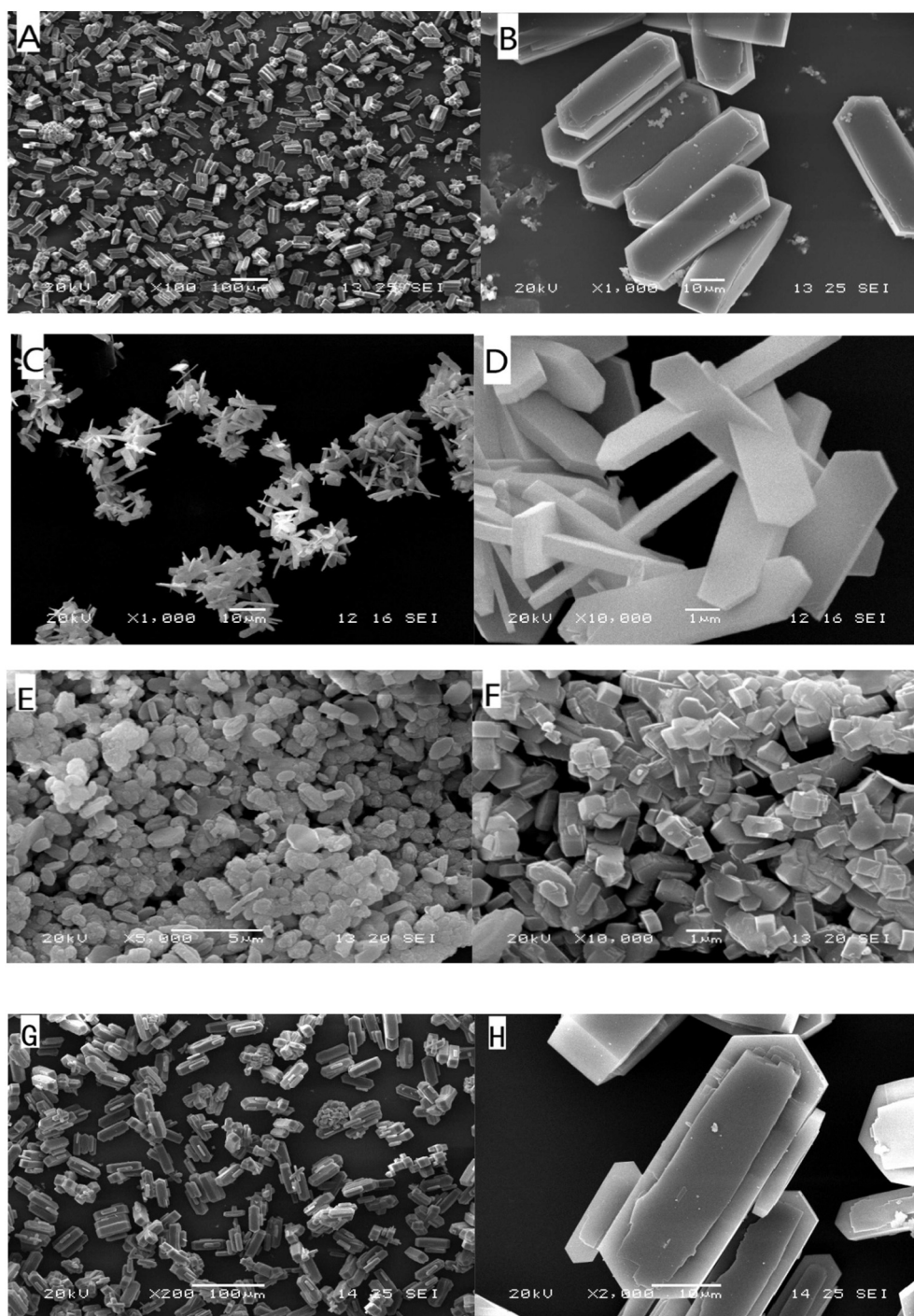


Fig. 6. SEM photographs of the different ZSM-5 zeolite: 32-ZSM-5 with NH_4F (A & B), 32-ZSM-5 without NH_4F (C & D), commercial 38-ZSM-5(S) (E & F); 32-ZSM-5(f) with NH_4F (G & H). ($\text{SiO}_2/\text{TPABr} = 8$, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 32$, reaction time (stirring 4 d); $\text{H}_2\text{O}/\text{SiO}_2 = 33$).

Table 4

The catalytic performance of different $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of HZSM-5 samples for transalkylation of toluene and trimethylbenzene

$\text{SiO}_2/\text{Al}_2\text{O}_3$ from EDS	Toluene conversion/%	1,2,4-trimethylbenzene conversion/%	$S_{\text{benzene}}/\%$	$S_{\text{xylene}}/\%$	Ratio for the $S_{\text{xylene}}/S_{\text{benzene}}$
23	53	54	27.8	63	2.27
26	48	45	28.2	60.6	2.15
32	45	44	23.0	62	2.70
45	34	35	29.8	52.7	1.77

Note: S_{benzene} , selectivity of benzene; S_{xylene} , selectivity of xylene.

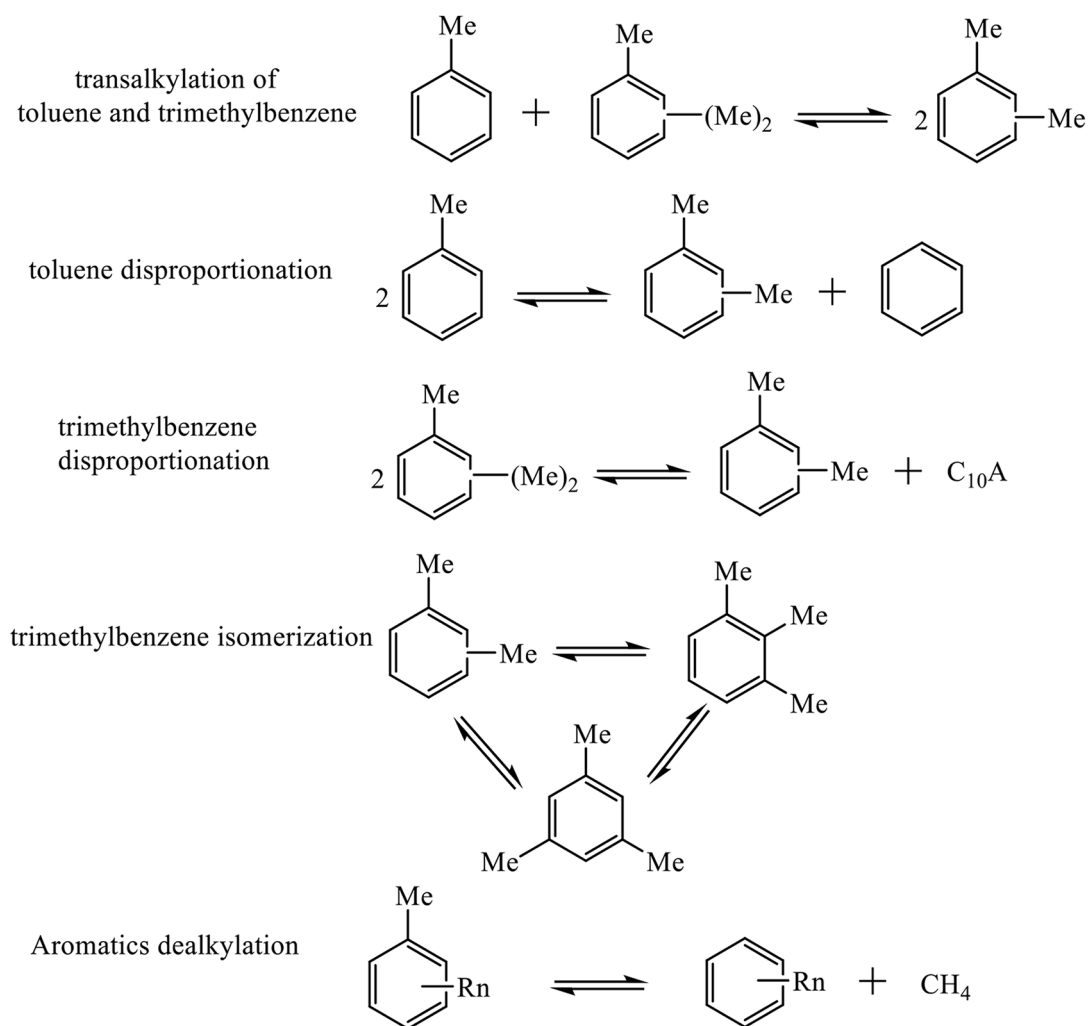


Fig. 7. Reaction elementary steps in transalkylation and disproportionation process of toluene and 1,2,4-trimethylbenzene.

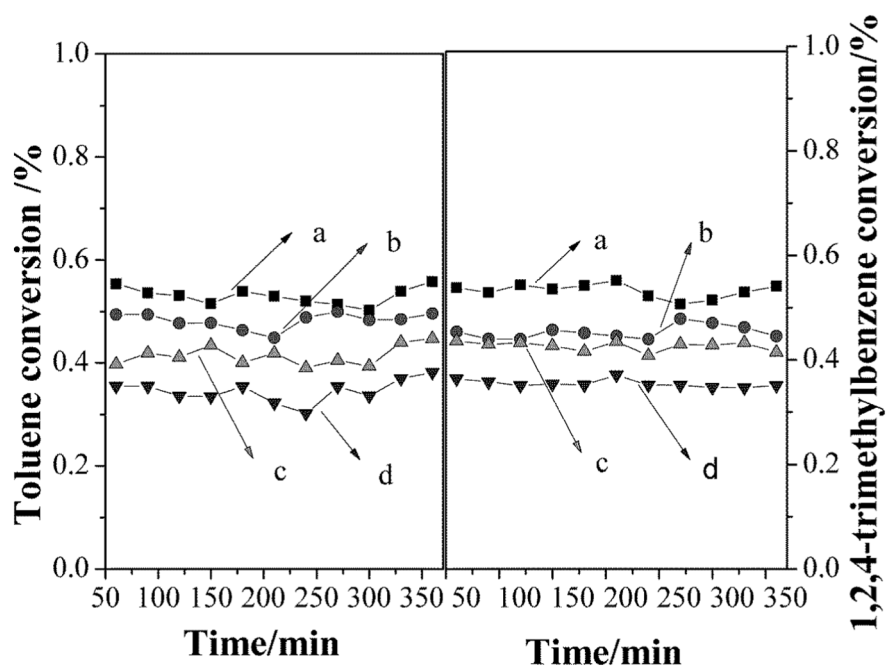


Fig. 8. Conversion as a function of the time on stream over HZSM-5 catalysts with various $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio (a) 23-HZSM-5, (b) 26-HZSM-5, (c) 32-HZSM-5 and (d) 45-HZSM-5 at 723 K with WHSV of 3 h^{-1} .

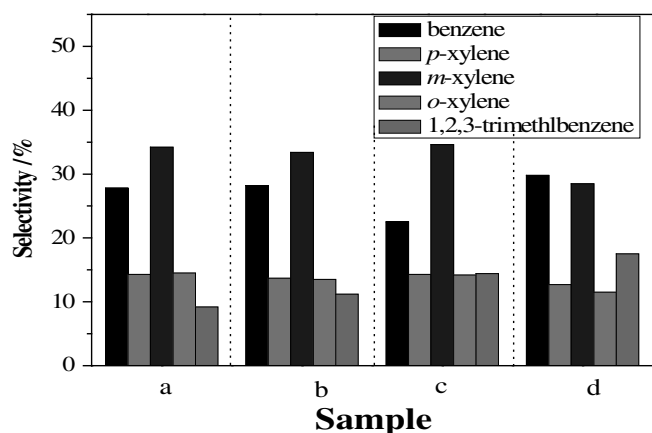


Fig. 9. The average product selectivity during 8 h reaction over HZSM-5 catalysts with various $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio (a) 23-HZSM-5, (b) 26-HZSM-5, (c) 32-HZSM-5 and (d) 45-HZSM-5 at 723 K with WHSV of 3 h^{-1} .

5 without NH_4F has a similar catalytic properties with 38-HZSM-5(S) for the 1,2,4-trimethylbenzene and toluene conversion.

ZSM-5 zeolite possesses a uniform pore size distribution without cage, which inhibits the generation of macromolecular coke precursor deposited in the zeolite [24]. Moreover, the commercial 38-HZSM-5(S) has smaller particle size but with a homogeneous 3D orientation of MFI zeolite crystals. Therefore, the 38-HZSM-5(S) processes a good catalytic stability. The synthesized 32-ZSM-5 without NH_4F is a thin circular disk along b axial direction with a bigger (0 1 0) crystal plane and a smaller section (1 0 0) crystal plane [26], as shown in Appendix Fig. A2. Therefore, it has relatively short straight channel along the b direction, which is more unblocked, particularly conducive to molecule diffusion. The pore distance along b axis of ZSM-5 is shortened, and the diffusion of the reaction molecules in it is easier during catalytic reaction. Although, the 32-ZSM-5 without NH_4F has a larger size than 38-HZSM-5(S), the short distance along b axial direction makes it a good service life as the 38-HZSM-5(S).

Although the crystal structure of synthesized ZSM-5 with or without NH_4F as mining agent during hydrothermal process has similar

Table 5

The average activity data of the samples 38-HZSM-5(S), 32-HZSM-5 with NH_4F or without NH_4F

Catalyst pretreatment	38-HZSM-5(S)	32-HZSM-5 with NH_4F	32-HZSM-5 without NH_4F	32-HZSM-5(f) with NH_4F
$\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio	38	32	31	30
Crystal size/ μm	$1 \times 0.5 \times 0.5$	$50 \times 10 \times 10$	$10 \times 1 \times 0.2$	$50 \times 10 \times 10$
$S_{\text{BET}}/\text{m}^2 \cdot \text{g}^{-1}$	401.7	425.9	406.3	415.3
$V_{\text{total}}/\text{cm}^3 \cdot \text{g}^{-1}$	0.21	0.20	0.38	0.18
Toluene conversion/%	56	45	55	Na
1,2,4-Trimethylbenzene conversion/%	60	44	63	Na
$S_{\text{benzene}}/\%$	27.5	23	28	Na
$S_{\text{xylene}}/\%$	61.5	62	62.5	Na
Ratio for the $S_{\text{xylene}}/S_{\text{benzene}}$	2.24	2.70	2.23	Na

Note: S_{benzene} , selectivity of benzene; S_{xylene} , selectivity of xylene.

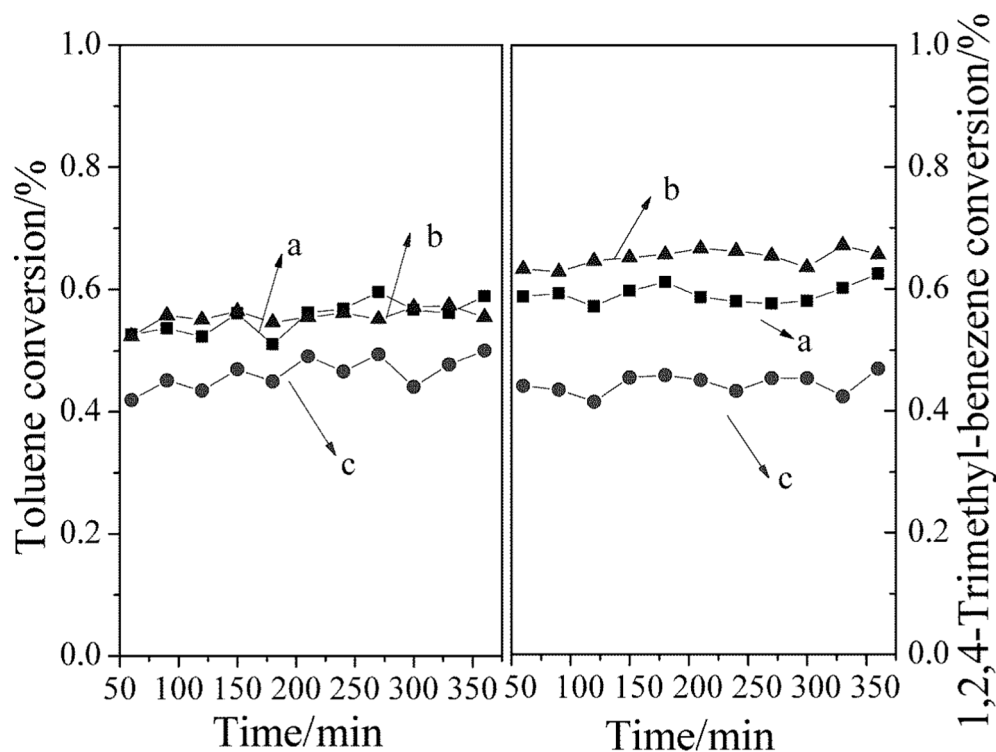


Fig. 10. Conversion as a function of the time on stream over (a) commercial 38-HZSM-5(S), (b) 32-HZSM-5 without NH_4F and (c) 32-HZSM-5 with NH_4F at 723 K with WHSV of 3 h^{-1} .

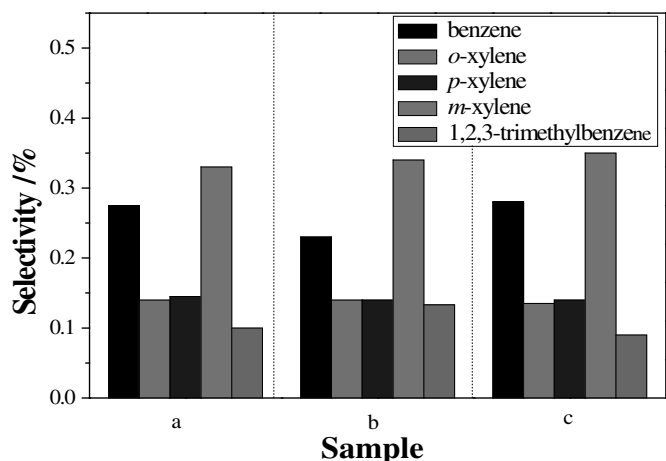


Fig. 11. Product selectivity as a function of the time on stream over (a) commercial 38-HZSM-5(S), (b) 32-HZSM-5 with NH_4F and (c) 32-HZSM-5 without NH_4F at 723 K with WHSV of 3 h^{-1} .

morphology of *ac* plan preferred orientation growth crystal. The crystal size of ZSM-5 with NH_4F is much bigger than the 32-HZSM-5 without NH_4F and commercial 38-HZSM-5(S) [27]. The larger size crystal particles own the smaller external surface area and less active center for large size molecule, *i.e.*, 1,2,4-trimethylbenzene reaction. The diameter of the corresponding aromatic molecules is shown in Appendix Table A2. Therefore, the 32-HZSM-5 with NH_4F has relatively lower catalytic properties than the other two samples [28]. But the 32-HZSM-5 with NH_4F has the highest ratio for the $S_{\text{xylene}}/S_{\text{benzene}}$, it is more conducive to transalkylation of toluene and 1,2,4-trimethylbenzene than other side reaction, such as disproportionation of toluene or 1,2,4-trimethylbenzene.

4. Conclusions

The two-steps ammoniation method recovered silica hydrogel from hexafluorosilicic acid can be directly used for ZSM-5 zeolite synthesis. The optimal hydrothermal conditions of ZSM-5 synthesis are investigated. It was found that with the increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and reaction time, the crystal type of ZSM-5 transforms from the orthorhombic to the monoclinic phase. The EDS analysis of these samples indicates that the element composition of ZSM-5 only contains Al, Si, and O without other impurities. The ZSM-5 synthesized with recovered SiO_2 has the morphology of *ac* plane preferred orientation growth crystal. It can be deduced that without the impurity fluorine content of the recovered SiO_2 from H_2SiF_6 the ZSM-5 crystal structure cannot be produced on the hydrothermal process for our synthesis procedure. The increased fluorine ion content by adding NH_4F during hydrothermal process can improve the growth of ZSM-5 crystal along *b* axis and get large size crystal, because the fluorine ions can promote the dissolution of the silica and aluminum source and shorten the hydrothermal reaction time. The catalytic performance of ZSM-5 in the transalkylation of toluene and 1,2,4-trimethylbenzene reaction indicates that with the increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of ZSM-5, the toluene and 1,2,4-trimethylbenzene conversions decrease, the sum of benzene and xylene selectivities decreases, and the 1,2,3-trimethylbenzene selectivity is on the rise. The morphology character of ZSM-5 produced from recovered SiO_2 has relatively short straight channel along the *b* direction, which shows similar catalytic activity and service life as the performance of small particle size commercial ZSM-5. The 32-HZSM-5 hydrothermal synthesized with NH_4F as mining agent has larger particle size and highest ratio for the $S_{\text{xylene}}/S_{\text{benzene}}$, which is more conducive to transalkylation of toluene and 1,2,4-trimethylbenzene than other side reaction, such as disproportionation of toluene or 1,2,4-trimethylbenzene.

Appendix

Table A1

The element content in high purity SiO_2 recovered from hexafluorosilicic acid

Elem	Molar fraction/%
O K	61.21
F K	1.95
Mg K	0.47
Al K	0.54
Si K	35.83
Total	100.00

Table A2

The diameter of the aromatic molecules

Aromatic hydrocarbon	Diameter/nm
Toluene	7.0
1,2,4-Trimethylbenzene	7.0
Benzene	7.0
<i>o</i> -Xylene	7.6
<i>p</i> -Xylene	7.6
<i>m</i> -Xylene	8.1
1,2,3-Trimethylbenzene	7.6
1,3,5-Trimethylbenzene	8.6

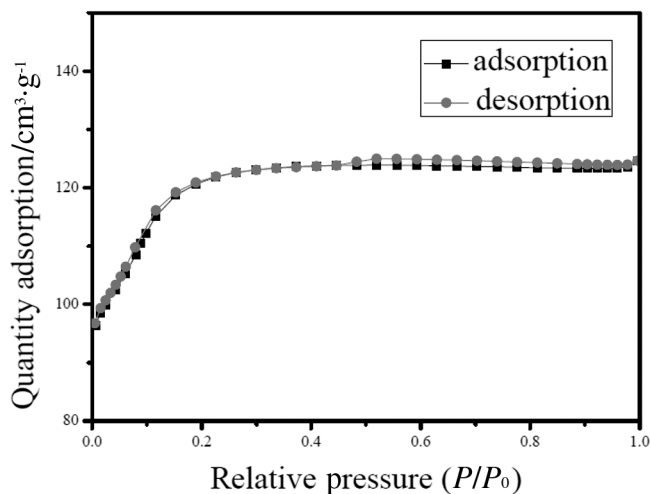


Fig. A1. N_2 ad/desorption spectra of 32-ZSM-5 zeolite. ($\text{SiO}_2/\text{TPABr} = 8$; $\text{SiO}_2/\text{Al}_2\text{O}_3 = 32$; reaction time (stirring 4d); $\text{H}_2\text{O}/\text{SiO}_2 = 33$).

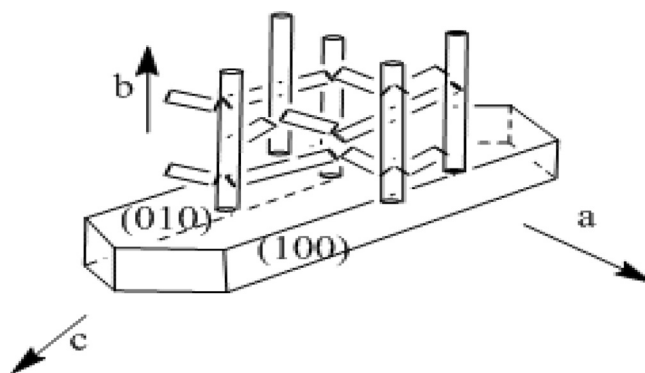


Fig. A2. Channel structure of ZSM-5 zeolite [24].

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