



Catalysis, Kinetics and Reaction Engineering

Influence of the post-treatment of HZSM-5 zeolite on catalytic performance for alkylation of benzene with methanol[☆]

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ABSTRACT

The porous material HZSM-5 zeolite with micro-mesopore hierarchical porosity was prepared by post-treatment (combined alkali treatment and acid leaching) of parent zeolite and its catalytic performance for benzene alkylation with methanol was investigated. The effect of post-treatment on the textural properties was characterized by various techniques (including ICP-AES, XRD, nitrogen sorption isotherms, SEM, NH_3 -TPD, Py-IR and TG). The results indicated that the post-treatment could modify the structural and acidic properties of HZSM-5 zeolite. In this procedure, not only additional mesopores were created by selective extraction of silicon but also the acidity was tuned. Consequently, the modified HZSM-5 zeolite showed larger external surface area with less acid sites as compared to the parent zeolite. It was found out that the modified zeolite exhibited a higher benzene conversion and xylene selectivity for alkylation of benzene with methanol as well as excellent life span of the catalyst than conventional ones. This can be explained by the facts that the presence of additional mesopores improved the diffusion property in the reactions. Furthermore, the modified zeolite showed an appropriate Brønsted acidity for effective suppression of the side reaction of methanol to olefins, thus reduced the accumulation of coke on the HZSM-5 zeolite, which was favorable for the catalyst stability. In comparison with the parent HZSM-5 zeolite, the modified zeolite by alkali treatment and acid leaching showed better performance for the benzene alkylation with methanol.

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1. Introduction

Toluene and xylene (TX) are important raw materials for commodity production in chemical industry [1]. Traditionally, they are produced from catalytic reforming or naphtha pyrolysis; however, the process is now limited by the shortage of petroleum resources [2]. Compared with toluene and xylene, benzene has been produced in excess [3]. Therefore, the conversion of the surplus benzene to the more valuable toluene and xylene is a potential way to balance the demand for aromatic production. Currently, alkylation of benzene is receiving increased attentions in petrochemical industry due to its possible nature as the promising alternative for the synthesis of toluene and xylene from natural gas and coal industry [4].

Alkylation of benzene with methanol, as a well-known acid catalyzed reaction, can produce a mixture of aromatics and the selectivity for productions highly depends on the characteristics of the catalyst. ZSM-5 zeolite catalysts were believed to be optimal catalysts for

alkylation reaction because of their high thermal stability, tunable acidity and remarkable shape-selectivity within the uniform micropores [5,6]. However, the intrinsic micropores structures in conventional ZSM-5 inhibit the diffusion of bulky substrates, which resulted in low conversion of benzene and low selectivity of xylene in the alkylation of benzene [7]. Hierarchical ZSM-5 zeolite, which possess the porosity and channel structure with the coexistence of micropore and mesopore, can observably improve the diffusion property and exhibit excellent catalytic performance in different reactions [8,9]. Recently, Lu *et al.* [10] synthesized hierarchical ZSM-5 catalyst using solid-phase hydrothermal method and found that the hierarchical ZSM-5 showed an enhanced performance compared with conventional ZSM-5: the conversion of benzene increased by 8%, the selectivity of toluene and xylene increased by 5% and 10% respectively. Hu *et al.* [11] pointed out that the excellent catalytic activity and high xylene selectivity was mainly due to the presence of mesopores, which promoted the diffusion of the reactants and products and provided easier access to the active sites in micropores. Catalytic tests in the alkylation of benzene with methanol show that selectivity of TX is improved over hierarchical ZSM-5, which is potentially important for the selective formation of TX chemicals in the future. However, the traditional template method for synthesizing hierarchical ZSM-5 zeolite is considered to be expensive and environmental unfriendly which would limit its commercial

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application on a large scale [12,13]. Fortunately, it has been demonstrated that post-treatment of zeolites is a facile and cost-effective route to obtain hierarchical materials [14,15].

Recently, a wide variety of post-treatment ways for hierarchically porous structures have been reported, exemplified by the desilication and dealumination of MCM-22, ZSM-5, beta, mordenite, etc. in relevant basic and acidic conditions [16,17]. Ogura *et al.* [18] pointed out that alkali treatment by sodium hydroxide solution created mesopores without changing the microporous structures of zeolite, and resulted in an enhanced catalytic activity for cumene cracking. Groen *et al.* [19] reported the detailed investigation on the formation of mesopores in ZSM-5 crystals by NaOH treatment, they found that mesoporosity was originated from selective removal of framework Si and the framework aluminum played an important role in regulating mesopore formation. According to the pioneering work on controlled desilication of ZSM-5 zeolites, a specific threshold of the framework Si/Al ratio has been proven available, being in the range of 25–50, in which the desilicated ZSM-5 zeolites exhibited optimal structure properties, especially for the hierarchical pore development [20,21]. The desilication has been proven to be an effective method to generate mesoporosity. However, some extra-framework aluminum species are often observed under the base treatment due to the realumination [17]. Therefore, an additional acid treatment step is needed to remove the species for opening the micropores and mesopores. On the other hand, dealumination is also a well-known process to modify pore structure which has been widely applied in industry [22,23]. Many researchers [24,25] declared that mesoporosity was generated from the loss of aluminum from the zeolite framework. Steaming and acid leaching are facile and the most common methods for dealumination. Steaming is generally performed at high temperature above 500 °C in the presence of steam, mesopores established under these circumstances are mostly connected to the surface of the crystals by bottle-necks [26]. During the treatment extra-framework aluminum species (EFAl) are generally formed, which may cause a negative effect, so acid-leaching is always employed to remove the undesired amorphous species, and secondary mesoporosity might be created [27].

The above findings inspired us to investigate the effect of post-treatment method on the catalytic performance of ZSM-5 zeolite for the alkylation of benzene with methanol. Compared with conventional ones, this study focused on post-synthesis modification with treatment in alkaline and/or acid media to the zeolite crystals. The structural changes and the alteration in the catalytic performance have been thoroughly examined. The catalysts were characterized by various techniques (including ICP-AES, XRD, nitrogen sorption isotherms, SEM, NH₃-TPD, Py-IR and TG). We observed that the hierarchical structure was well formed in ZSM-5 zeolite by means of post-treatment and the modified ZSM-5 zeolite showed an excellent catalytic performance in the alkylation of benzene with methanol.

2. Experimental

2.1. Catalyst preparation

A commercial ZSM-5 with Si/Al ratio of 42 (supplied by Nankai Chemical Plant, NH₄-form) was used in this study. HZSM-5 catalyst was prepared as follows: the zeolite powder was tableted, crushed and screened to 0.45–0.90 mm successively, then calcined in air at 550 °C for 7 h to obtain HZSM-5, denoted as ZSM-5-P.

2.1.1. Alkaline treatment

Alkali-treatment of the ZSM-5 zeolite was carried out based on method described in literatures [19,28]. In brief, appropriate amount of parent NH₄-ZSM-5 was suspended in 0.5 mol·L⁻¹ NaOH solution at 353 K for 2 h under stirring and refluxing to produce a mixture. Then the mixture was cooled down immediately, followed by washing with deionized water. Finally, the as-prepared zeolite samples were dried at 383 K overnight, followed by three consecutive exchanges

in 0.5 mol·L⁻¹ NH₄Cl solution and calcined in air at 823 K for 7 h to produce ZSM-5-AT.

2.1.2. Acid treatment

Acid treatment of the zeolites was performed in a reflux-attached round bottom flask, containing 10 ml of oxalic acid solution and 1 g of the zeolite solid, stirring at 363 K for 2 h. Then, the solid was filtered and washed with distilled water repeatedly until complete elimination of the acid. Lastly, the sample was dried at 383 K and calcined at 823 K for 7 h to obtain the pretreated zeolite, labeled as ZSM-5-OT. Zeolites treated by successive alkaline and acid was denoted as ZSM-5-AT-OT.

2.2. Catalyst characterization

The morphology of the catalyst was observed by using a scanning electron microscopy (SEM) (Hitachi S-4700(II)). The crystallography of the catalysts was characterized by X-ray diffraction (XRD) (SCINTAG X" TRA), using CuK_α (154.2 nm) at 30 mA and 40 kV with scanning angle (2θ) from 5° to 80°. The nitrogen sorption isotherms were measured by using a Micromeritics ASAP-2020 system. Chemical Al and Si analyses of the materials were obtained by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Winlab Optima 3300 DV ICP spectrometer from Perkin-Elmer. NH₃ temperature-programmed desorption (TPD) of the catalysts was carried out using a Tianjin XQ TP-5076 chemisorption instrument equipped with a thermal conductivity detector (TCD). Fourier transform infrared (FT-IR) spectra were measured on a VERTEX 70 FT-IR spectrometer. The concentrations of Brønsted acid (B) and Lewis acid (L) were calculated from the peak areas of adsorbed pyridine at around 1545⁻¹ and 1454 cm⁻¹, and the extinction coefficients of ε(B) and ε(L) were 1.88 and 1.42 cm·mmol⁻¹, respectively [29].

2.3. Catalytic performances evaluation

All the catalytic performance evaluations were carried out in a continuous-flow fixed-bed reactor with a stainless steel tube (8-mm i.d.) at atmospheric pressure. 0.5 g catalyst diluted with 5.0 g inert quartz sand was loaded in the reactor. The catalyst was *in-situ* heated from room temperature to 400 °C at 10 °C·min⁻¹ and maintained for 1 h in N₂ flow with a space velocity of 2400 h⁻¹. Benzene and methanol mixture (B/M molar ratio = 1:1) was then fed into the reactor (WHSV = 2.0 h⁻¹) with a co-feed N₂ flow of 120 ml·min⁻¹. The product was directly analyzed online by the gas chromatography (Fuli GC9790) equipped with a DB-1 capillary column (30 m × 0.25 mm × 1.00 μm) and a flame ionization detector.

Conversion of benzene and selectivity to toluene, xylene and ethylbenzene were defined as follows respectively:

$$\text{Conversion of benzene} = \frac{\text{benzene in feed} - \text{benzene in product}}{\text{benzene in feed}} \times 100\%$$

$$\text{Selectivity of toluene} = \frac{n(\text{toluene})}{n(\text{conversion of benzene})} \times 100\%$$

$$\text{Selectivity of xylene} = \frac{n(\text{xylene})}{n(\text{conversion of benzene})} \times 100\%$$

$$\text{Selectivity of ethylbenzene} = \frac{n(\text{ethylbenzene})}{n(\text{conversion of benzene})} \times 100\%$$

3. Results and Discussion

3.1. Catalyst characterization

Representative SEM micrographs for the parent and the treated ZSM-5 zeolites are shown in Fig. 1. As observed, the ZSM-5-P sample

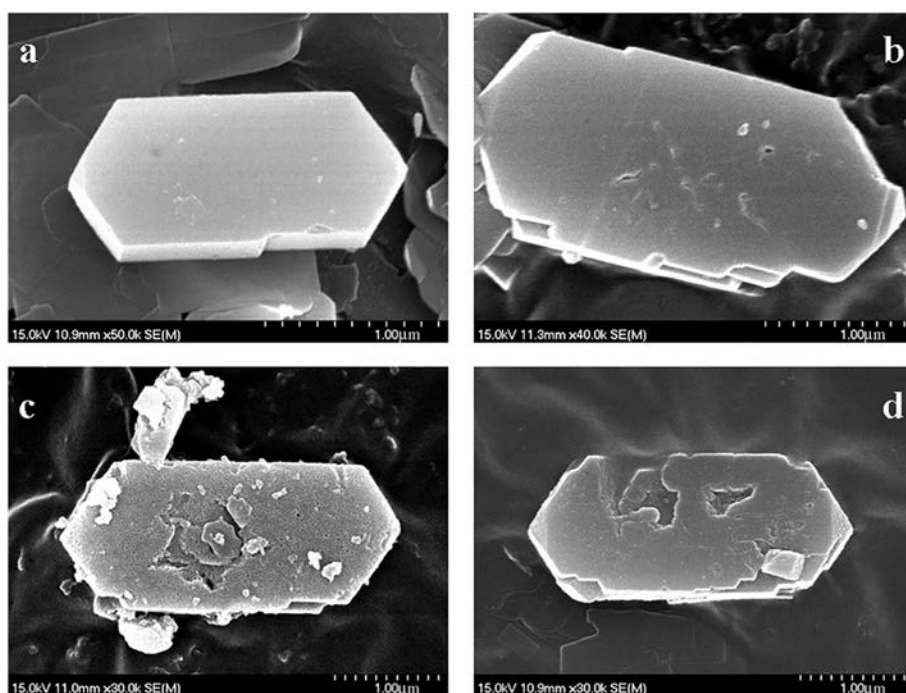


Fig. 1. SEM images of parent and treated zeolites: a. ZSM-5-P b. ZSM-5-OT c. ZSM-5-AT d. ZSM-5-OT-AT.

is typical twin hexahedrons with smooth morphological surface and highly ordered structures, demonstrating the high crystallinity of the parent zeolites (Fig. 1a). The ZSM-5-OT maintains the cubic morphology after acid treatment except sporadic defects (Fig. 1b). In contrast, the morphology of the zeolite was obviously changed after alkali treatment. Many faults and voids on the surface of the zeolite can be found. A portion of the framework has collapsed, suggesting that desilication happened under the alkaline conditions (Fig. 1c). As for ZSM-5-AT-OT (Fig. 1d), irregular solid particles and amorphous debris which deposited on external surface almost disappeared upon the sequential acid leaching treatment. V. Mavrodinova *et al.* [30] suggest that extra-lattice can be expelled from the zeolite structure upon the acid reflux which could improve the accessibility to the intrinsic micropores in the zeolite.

XRD characterization was performed to determine the possible changes in the relative crystallinity and the framework structure of ZSM-5 with the modification (Fig. 2). As indicated by the intensity of the peaks in the XRD patterns, all samples exhibit the same peaks, which are exclusively

corresponded to the structure of MFI topology [31]. It can be concluded that the alkali treatment or/and the followed oxalic acid leaching did not destroy the structure of the ZSM-5 zeolite. However, the crystallizations of the samples changed. Due to the formation of the amorphous phase, the crystallinity of ZSM-5-AT decreased [32]. This indicates the desilication happened under the alkali treatment. While upon acid washing the crystallinity increased slightly (ZSM-5-OT), suggests that dealuminization in the zeolite framework is negligible. According to Cambor *et al.* [33], the enhance intensity of these reflections can be due to the removal of EFAl from lattice positions. Particularly, owing to the removal of the amorphous phase, the crystallizations of ZSM-5-AT-OT were recovered which is consistent with the observation from SEM images.

The elemental analysis results decided by ICP-AES are listed in Table 1. The Si/Al ratio of ZSM-5(P) zeolite is 42.5 (the nominal Si/Al ratio is 42), which increased to 44.9 after a moderate acid treatment (ZSM-5-OT). The similarity in the Si/Al ratio suggests that dealuminization in the zeolite framework is negligible during the acid leaching post-treatment, which is in agreement with the XRD characterization and scanning electron microscopy measurement. While for the alkali-treated samples (ZSM-5-AT), a distinct decline of the Si/Al ratio is presented. Such variation demonstrates that the process of alkali treatment affects the environment of the framework and leads to the dissolution of the siliceous species, which agrees with prior studies [8,9]. However, the acid treatment performed upon desilication sample (ZSM-5-AT-OT) leads to a more significantly change of the Si/Al ratio (from 29.1 to 87.4), indicating that a part of aluminum species has been removed. On the basis of previous study [17,24], some extra-framework aluminum species are generally produced simultaneously

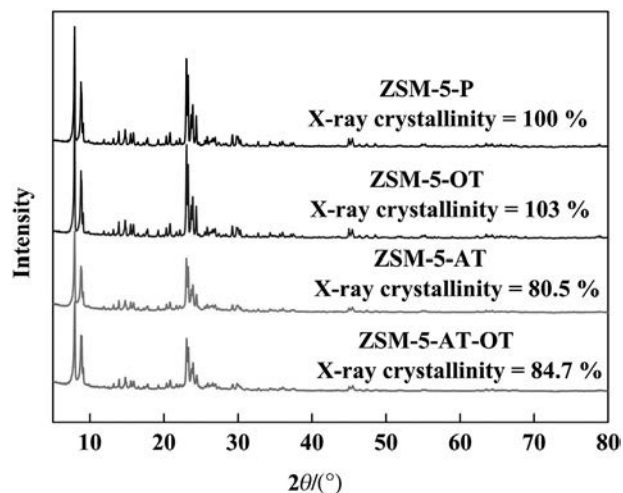


Fig. 2. XRD patterns of HZSM-5 zeolites before and after treatment.

Table 1

The different treatment methods and the characteristics of the resulting zeolites

Samples	Treatment methods	Composition (ICP-AES)		
		Si/mg·kg ⁻¹	Al/mg·kg ⁻¹	Si/Al
ZSM-5-P	Parent	1412763	31912	42.5
ZSM-5-OT	Acid treatment	1366176	29210	44.9
ZSM-5-AT	Alkali treatment	1247758	41163	29.1
ZSM-5-AT-OT	Alkali-acid treatment	1459358	16029	87.4

with the removal of Si atoms (Si–OH–Si) from the ZSM-5 lattice. Combined with these results, we can attribute the increase in the Si/Al ratio to be consequences of the removal of the amorphous phase, which formed during the alkali treatment. The result will be discussed in detail together with the following physicochemical analysis.

Fig. 3 displays the N_2 adsorption isotherms and pore size distributions of parent and treated ZSM-5 zeolites. As observed, the parent zeolites gave a typical Langmuir type I nitrogen adsorption isotherm, which represented a microporous material. According to isotherms of ZSM-5-OT, the adsorption isotherm did not change dramatically which indicates negligible leaching of framework Al at the conditions applied here [34]. Comparatively, the isothermal curves of ZSM-5-AT and ZSM-5-AT-OT zeolites exhibited the behavior of type IV with a type-H3 hysteresis loop, which was typically associated with the filling and emptying of mesopores [35], suggesting these two samples possessed mesopore structures. Comparing the isothermal curves in Fig. 3, the sequent treatments (alkaline plus acid leaching) over the ZSM-5 samples lead to a progressive increase of the N_2 adsorbed amount at high relative pressures, which was indicative of the additional mesoporosity. The results are consistent with SEM micrographs that more defects emerged upon the sequent acid treatments. The textural parameters derived from N_2 adsorption were listed in Table 2. After the alkali treatment, the total pore volume of the sample increased from 0.19 to 0.33 $\text{cm}^3 \cdot \text{g}^{-1}$, while the micropore volume slightly decreased from 0.11 to 0.09 $\text{cm}^3 \cdot \text{g}^{-1}$. It indicates that the alkali treatment has created mesopore system in ZSM-5-P sample, while the micropore systems did not dramatically affected. As to the sample of ZSM-5-AT-OT, the specific surface area and pore volumes increased further, which as consequence of the removal of the extra-framework species formed during the desilication treatment. In brief, the results presented above show that hierarchical zeolites have formed during post-treatments.

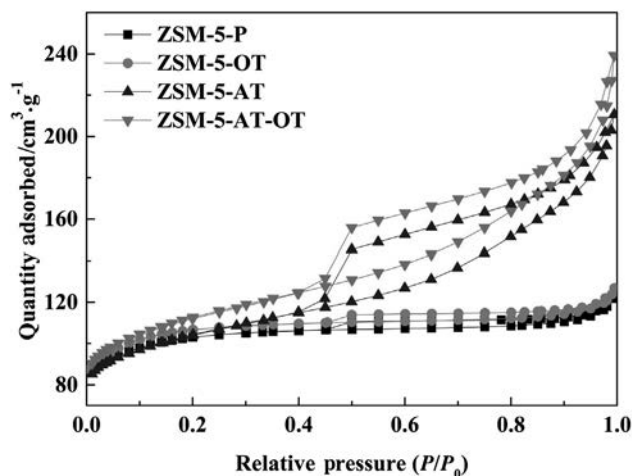


Fig. 3. Nitrogen adsorption-desorption isotherms of ZSM-5 zeolites.

Table 2

The porosity properties for ZSM-5 zeolites before and after treatment

Samples	Surface area/ $\text{m}^2 \cdot \text{g}^{-1}$			Pore volume/ $\text{cm}^3 \cdot \text{g}^{-1}$	
	BET	Micropore	External	Micropore	Total
ZSM-5-P	317.7	229.4	88.3	0.11	0.19
ZSM-5-OT	327.7	225.9	101.8	0.11	0.20
ZSM-5-AT	354.6	204.5	150.1	0.09	0.33
ZSM-5-AT-OT	372.1	192.8	179.3	0.10	0.37

Micropore volume is estimated using the t -plot method. Mesopore macropore volume is calculated by a subtraction of total pore volume at a relative pressure of $P/P_0 = 0.99$ from the micropore volume obtained from the t -plot method.

As mentioned above, the zeolites structure has changed during the post-treatment. The acidity of zeolites is an important factor in determining the catalytic activity and product selectivity for alkylation reaction. The acid site properties were studied using NH_3 -TPD and the profiles are displayed in Fig. 4. As well known the amounts of ammonia desorbed from the catalyst surface could be estimated via TPD peak areas and the acid strength attributes to the peak temperature. It is observed that different degrees of change in the number and strength of acid sites occurred for the treated samples when compared to the untreated ZSM-5 (ZSM-5-P). Table 3 summarizes the acidic properties of these zeolites. As compared with the parent ZSM-5, the peak of desorption temperatures and the corresponding peak area of the ZSM-5-OT sample changed very little in Peak I and Peak II, indicating that only small changes in the acid properties occurred after the oxalic acid treatment steps. On the other hand, a noticeable decrease of the amount of acid sites is produced by the alkali treatment that attributes to desilicification. According to previous study [36], these phenomena are owing to the selectively leaching of siliceous species during alkali-treatment, the leaching of the framework resulting in a loss of acid sites. Furthermore, the spectrum of sample ZSM-5-AT-OT, prepared by alkali treatment subsequent with acid washing, exhibits minimal peak area and the lowest temperature ammonia desorption peak with respect to the other samples which indicative of minimal amount of acid sites and the weakest acid strength. According to literatures, the function of acid leaching for the zeolite is the removal of extraframework species [23,27]. Therefore, this result demonstrates that the extra-framework species which generated by alkali treatment is removed by the subsequent oxalic acid washing procedure. This result is in agreement with the proposed mechanism for alkali desilicification [19,20], in which the destruction of silanol groups (Si–OH–Si) could lead to the presence of extraframework species. From the research above, we conclude that alkali and/or acid treatment does not only improve the pore accessibility (according to the nitrogen adsorption analysis) but also further adjust the acid properties of ZSM-5 zeolites.

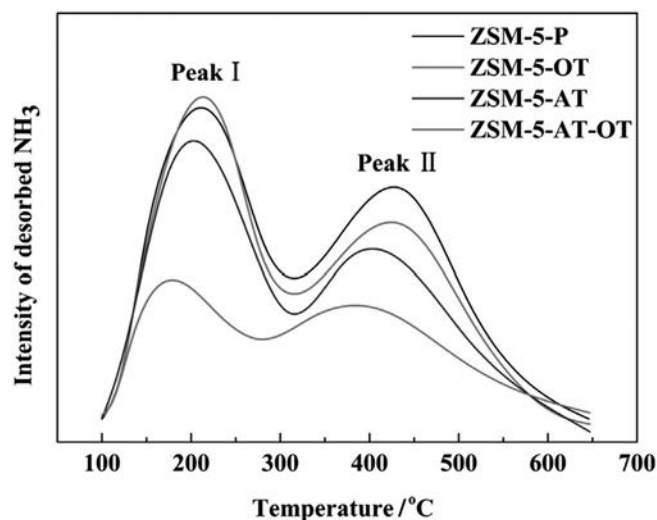


Fig. 4. NH_3 -TPD profiles of parent and modified ZSM-5.

Table 3

The deconvolution results of NH_3 -TPD profiles of the parent and modified ZSM-5

Samples	Peak I		Peak II	
	Temperature/ $^{\circ}\text{C}$	Area	Temperature/ $^{\circ}\text{C}$	Area
ZSM-5-P	207	972	438	934
ZSM-5-OT	209	965	440	831
ZSM-5-AT	198	847	403	670
ZSM-5-AT-OT	172	413	395	550

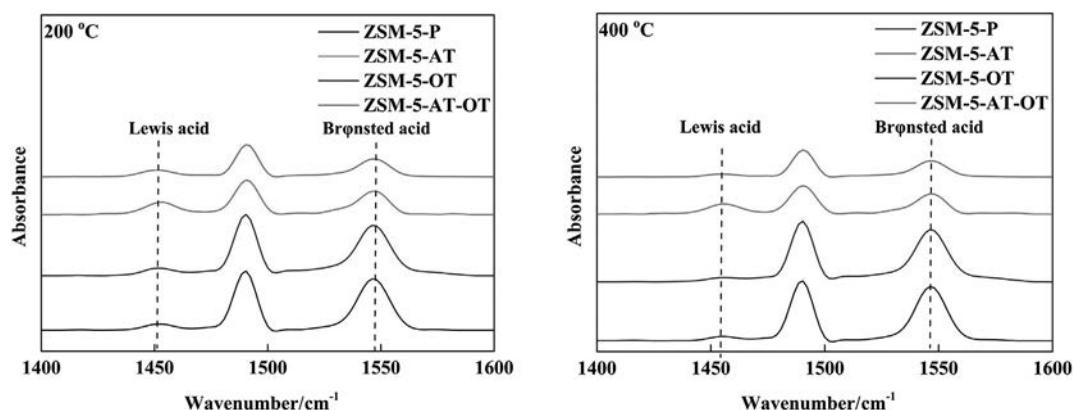


Fig. 5. FT-IR spectra of pyridine adsorption on parent and modified ZSM-5 catalysts.

Further acidity characterization was done by FTIR spectroscopy of adsorbed pyridine. As shown in Fig. 5, the absorption peak at 1454 cm^{-1} is assigned to the C–C stretching of coordinately bonded pyridine on the Lewis acid sites while the peak at 1545 cm^{-1} is attributed to the C–C stretching vibration of pyridinium ion by interaction with Brønsted acid sites. The amount of both Brønsted and Lewis acid sites calculated with respect to the integrated area of the absorption bands is given in Table 4. It is obvious that the quantity of Brønsted acid sites in the NaOH treated zeolites ZSM-5-AT is much lower than parent samples, which owing to the removal of a few Al atoms (Si–OH–Al) that occurs simultaneously with the preferential removal of Si atoms (Si–OH–Si) from the HZSM-5 framework [36,37]. Based on the previous research [38], the alkali treatment inevitably produced partially extra-framework Al species, which was associated with the Lewis acidity. Hence, the presence of EFAl species that resulted from alkali treatment should be responsible of the enhancement of Lewis acid sites. As for ZSM-5-AT-OT samples, sequential acid leaching treatment has no remarkable effect on the amount of Brønsted acid sites over ZSM-5-AT [26]. However, the intensity of the Lewis acid decreased because of the removal of the amorphous phase (SiO_2 and Al_2O_3) in the acid washing step [24]. This is consistent with the observation from N_2 physical adsorption and SEM images.

Table 4
Brønsted acid sites and Lewis acid sites of zeolites by IR spectra of adsorbed pyridine

Samples	Brønsted acid site/ $\text{mmol} \cdot \text{g}^{-1}$		Lewis acid/ $\text{mmol} \cdot \text{g}^{-1}$	
	200 °C	400 °C	200 °C	400 °C
ZSM-5-P	0.0422	0.0412	0.0032	0.0016
ZSM-5-OT	0.0410	0.0402	0.0020	0.0011
ZSM-5-AT	0.0179	0.0148	0.0080	0.0064
ZSM-5-AT-OT	0.0172	0.0145	0.0037	0.0017

3.2. Catalytic performance

The parent and treated ZSM-5 samples were evaluated in alkylation of benzene with methanol, the catalytic performance and product distribution are listed in Table 5. As data indicated, methanol was not observed in the products, which could lead us to the conclusion that all catalysts showed efficient performance of the methanol conversion. Meanwhile, alkene and alkane were observed in the reaction products which indicated that the side reaction of methanol to olefins had occurred, which was attributed to the effect of strong acid sites on ZSM-5 [35]. In the MTO process, methanol is first dehydrated to dimethyl ether (DME) and then converted to light olefins, which can further react to form paraffin, aromatics, and oligomer through hydrogen transfer, alkylation, or polycondensation (Fig. 6) [39]. The key step in the

Table 5
Products content of benzene alkylation with methanol over different HZSM-5

Components	Content/wt%	
	ZSM-5-P	ZSM-5-AT-OT
Methane	0.51	0.24
Ethylene	0.97	0.09
Ethane	0.44	0.20
C3	1.99	1.57
C4	0.21	0.23
C5	0.08	0.07
Benzene	53.23	42.39
Toulene	21.51	25.78
Ethylbenzene	3.96	0.50
Xylene	11.85	20.75
Trimethylbenzene	2.32	6.02
Others	2.93	2.16

Reaction condition: 400 °C, N_2 , 0.1 MPa, 2 h^{-1} , methanol to benzene molar ratio = 1:1.



Fig. 6. Reaction path of methanol during the MTO process.

conversion of methanol is to control the reaction during olefin formation, where the acidity of the catalyst plays an essential role. According to the literatures, although the alkylation of benzene with methanol and the side reaction of methanol to olefins were both catalyzed by the Brønsted acid, acid strength was different. MTO process prefers stronger Brønsted acid than alkylation reaction [17]. Therefore, the Brønsted acidity of ZSM-5 catalyst was closely related to the product distribution. Compared the performance of the three catalysts, the percentage composition of alkene and alkane was in the order ZSM-5-P > ZSM-5-AT-OT, which implied that the amount of strong acid sites on the ZSM-5 was also in the order ZSM-5-P > ZSM-5-AT-OT. The decreasing trend of alkene and alkane indicates the reduction of strong Brønsted acid sites. The experimental results are in good agreement with Py-IR results (Table 4 and Fig. 5).

As shown in Fig. 7, the treated ZSM-5 presented a much higher benzene conversion compared with the parent ZSM-5 catalyst, which was due to the channels in treated ZSM-5 catalyst that provide larger reaction volume for reactant to access active site. Furthermore, the ZSM-5-AT-OT showed a better activity than ZSM-5-AT, which was attributed to the effect of acid leaching resulting in more active sites exposed and the accessibility to the zeolite internal porosity improved. This is supported by the N_2 physical adsorption, both the pore volume and surface area of the samples increased after treatment. On the other hand, the selectivity of xylene is also enhanced, suggesting that the existence of mesopores could promote the diffusion of bulky aromatics in the

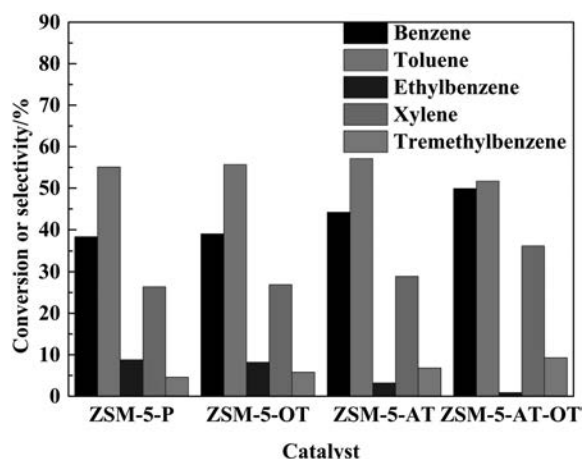


Fig. 7. Catalytic performance of different zeolites in benzene alkylation with methanol.

reactions [7]. In conclusion, the hierarchical pores ZSM-5 modified by alkali and the sequential acid treatment improved the catalytic activity and product selectivity for the alkylation of benzene with methanol.

According to the literatures [40], alkylation of benzene with methanol and methanol to olefins were both catalyzed by the Brønsted acid, while ethylbenzene was formed by benzene alkylation with ethylene that was converted from methanol to olefins over ZSM-5 catalyst. Moreover, several excellent reviews have proven that suppressing the side reaction of methanol would help to reduce the formation of ethylbenzene. As seen in Fig. 7, the ethylbenzene selectivity of the alkylation of benzene with methanol over different ZSM-5 zeolites was compared. It was found that the selectivity to ethylbenzene was decreased over treated ZSM-5 catalysts (8.8% for ZSM-5-P and 0.9% for ZSM-5-AT-OT). This result suggested that the modified ZSM-5 zeolite could inhibit the side reaction of methanol to olefins, thus improved the utilization rate of methanol in the alkylation reactions. This result was in accordance with the Py-IR results and previous researches [17,41].

The long-term stability of the catalyst is vital for industrial application. Thus, it is necessary to investigate the effect of the modified catalysts on the stability for the alkylation of benzene with methanol, as shown in Fig. 8. Compared to parent ZSM-5, the ZSM-5-AT-OT catalyst exhibited remarkably high resistance to deactivation with over 250 h times on stream. As pointed out by many researchers, accumulation of coke deposits blocks the micropores of the catalyst and physically restricts the access of reactants towards the catalytic centers causing rapid deactivation [42]. Furthermore, alkenes are primary precursors

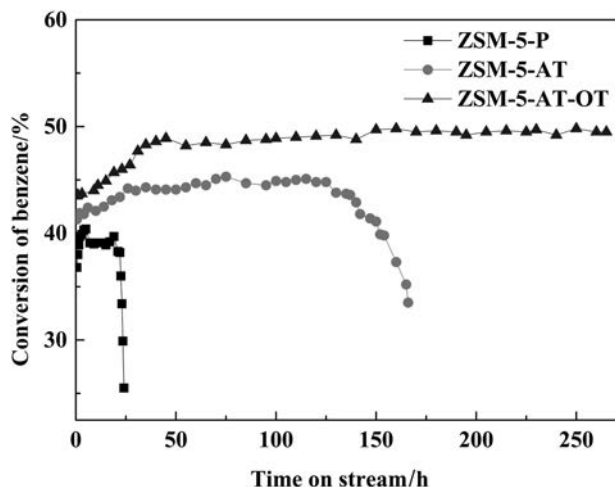


Fig. 8. Stability of different zeolite in benzene alkylation with methanol.

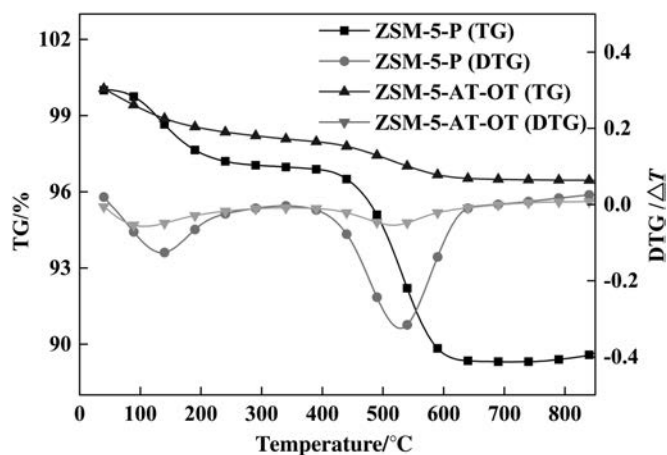


Fig. 9. TG-DTA profiles of the catalysts after successive reaction time (24 h).

of the mechanism of coke formation [43,44]. Hence, the decrease of alkenes could reduce the coke deposit rate and prolong the lifetime of the catalyst. TG-DTA was performed to evaluate the coke content of the catalysts after 24 h usage (Fig. 9). Depending on the analysis, a less amount of coke was observed over ZSM-5-AT-OT. As mentioned above, the modified ZSM-5 zeolite (ZSM-5-AT-OT) could decrease the acidity of the HZSM-5 zeolite and inhibit the side reaction of methanol to olefins, thus decreased precursors of the mechanism of coke formation. In addition, the ZSM-5-AT-OT catalyst possesses a larger pore volume and surface area to bear the coke than conventional microporous zeolite. Consequently, hierarchically structured zeolites synthesized by post-treatment are not only beneficial in enhancing the catalytic performance, but also prolonged the catalytic lifetime.

4. Conclusions

In this work, we successfully prepared hierarchical ZSM-5 zeolite by combining alkali treatment with acid leaching under mild conditions. After the suitable treatment, not only the mesopores introduced into the structure of ZSM-5 zeolite by selective extraction of silicon, but also amorphous particles and crystal splinters within the ZSM-5 zeolites were cleared. The hierarchical ZSM-5 zeolite presented appropriate properties in terms of acidity and accessibility for promoting the conversion of benzene, a higher selectivity to toluene and xylene as well as a higher anti-coking performance than conventional microporous zeolites in the alkylation of benzene with methanol was achieved. Most importantly, as compared to the template method to synthesize hierarchical ZSM-5 zeolite, the method adopted here was technically feasible and economically reasonable which would help to improve the commercial viability for the alkylation of benzene with methanol in industrial production.

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