Effect of Alkali Treatment on the Structure and Catalytic Properties of ZSM-5 Zeolite

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Abstract: Catalytic properties of ZSM-5 zeolite samples pretreated with NaOH solution have been investigated. The samples are characterized by XRD, SEM, chemical analysis, and N_2 adsorption. The results indicate that mesopores are created in ZSM-5 crystals under alkali treatment without change the microporous structure and acidic strength of the zeolite, but the crystallinity is greatly decreased under severe treatment. IR indicates that the concentration of silanol is greatly enriched by alkali treatment. The etherification activities of ZSM-5 zeolites are greatly increased by alkali-treatment. The noticeably improved catalytic activity of treated samples is ascribed to the formation of mesopores and greatly enriched silanol group.

Keywords: Alkali treatment, ZSM-5, zeolite, ETBE, etherification.

Synthesis of MTBE and ETBE over zeolite instead of resin, which is commonly used in industry, has many advantages, such as high thermal stability, no corrosion to equipment and so on. Many papers have concerned about the synthesis of MTBE over zeolites catalyst, but synthesis of ETBE over zeolite is less reported. We[1] and F. Collignon *et al.*[2] studied the synthesis of ETBE over different zeolites and found that Beta is the most active one. ZSM-5 is much less active than Beta, but its selectivity is almost 100%. Hence ZSM-5 zeolite is an attractive catalyst for etherification. We systemically studied the synthesis of MTBE from methanol and *iso*-butene over ZSM-5 zeolite and found that this process is seriously kinetically-controlled[3]. The synthesis of ETBE over ZSM-5 zeolites is very similar with that of MTBE. Formation of mesopores in ZSM-5 crystal will help to improve the catalytic performance.

Tailoring micro- and meso-porous materials by development of bimodal pore size distributions is currently being subject of many publications[4-8]. Many researchers have found formation of secondary mesopores in the range 10~20 nm[9,10], which cause the catalytic improvement, when they study the relation between structure and catalytic performance of zeolite upon dealumination by hydrothermal and followed acid treatment. Alkali treatment is less documented due to the fragility of zeolite framework to alkali solutions. In contrast to acid leaching leading to removal of alumina, alkali treatments were found to selectively dissolve silica[11,12]. Recently, Ogura *et al.* found that alkali-treated ZSM-5 zeolites formed mesopores more uniform than that of MCM-41[13].

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Figure 1 SEM images for (a) as-received and (b) alkali-treated ZSM-5 (ZB1)
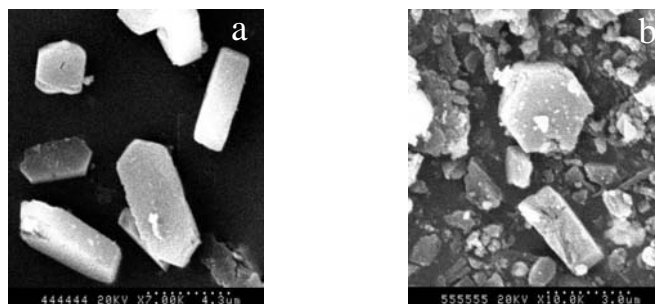
Table 1 Changes of SiO_2/Al_2O_3, acid amount and crystallinity for alkali-treated ZSM-5

Run.	SiO_2/Al_2O_3[a]		relative crystallinity /%	acid amount $(\mu mol/g)$[b]	B$(\mu mol/g)$[c]	L$(\mu mol/g)$[c]	B/L
	after alkali-treatment	after ion-exchange					
Parent	--	38.0	100	789	468	339	1.38
ZB1	31.6	37.9	79	754	324	306	1.06
ZB2	18.9	56.0	64	593	250	559	0.45

a: from chemical analysis.   b: from TPD results.   c: from Py-IR.

In this communication, we will show the changes of the textural and significant improvement of catalytic performance of ZSM-5 zeolite treated by alkali solutions.

Na-ZSM-5 zeolite with SiO_2/Al_2O_3 molar ratio of 38.0 was supplied by Catalyst Plant of Nankai University.   The as-received ZSM-5 crystals have uniform shape and particle size, as shown in **Figure 1a**.   Alkali treatment of ZSM-5 zeolite was performed with 0.2 mol/L aqueous NaOH solution for 2.5 h (designated as ZB1, sample treated with 0.4 mol/L NaOH solution for 1.0 h was designated as ZB2), as described elsewhere[13].   The solid was isolated by filtration, washed with distilled water and dried at 353K.   The resulting solids were ion-exchanged by 0.3 mol/L HCl at 363 K for 1 h 4 times.   The as-received ZSM-5 zeolite was also treated with 2 mol/L HCl aqueous solution at 363K for 2 h, and the resulted sample was designated as ZA.   Nano-sized HZSM-5 zeolite with size of 86 nm designated as ZNS was used as reference.

SEM (Hitachi X-650) shows (**Figure 1b**) most of the crystals were crashed into small crystals.   It was also observed that a large portion of the zeolites, *ca.* 35~65 %wt, was dissolved during alkali treatment.   This means that not only the extra-framework species, but also a large portion of framework silica and alumina was dissolved.   As shown in **Table 1**, after alkali treatment, the SiO_2/Al_2O_3 ratios decrease from 38 to 31.56 for ZB1, and 19.09 for ZB2. Lietz *et al.* described that the gradient of the Al distribution is remarkably reversed by alkali-treatment[12].   The surface was enriched of Al, but those Al species can be easy removed by acid treatment.   After ion-exchanged with HCl solutions, the SiO_2/Al_2O_3 was greatly increased (**Table 1**).

XRD (BD90 diffractometer) results indicate that ZSM-5 zeolites keep its topology after alkali-treatment, but the relative crystallinity is decreased obviously (**Figure 2**).

NH$_3$-TPD shows that alkali-treatment does not change the acid strength.   The acid amount decreased from 789 µmol/g to 754 (ZB1) and 593 (ZB2) µmol/g.   Py-IR shows that Brönsted acid amount of alkali-treated sample decrease while Lewis acid increase.

Figure 2   XRD patterns of parent and alkali-treated ZSM-5 samples
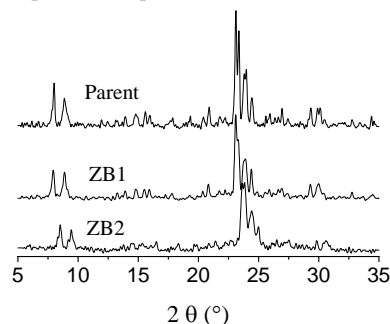

Liquid phase synthesis of ETBE from ethanol and *iso*-butene was carried out using a stainless-steel fix-bed reactor.   The conditions were as follows: weight of catalyst = 1.00 g; EtOH:IB=1.01 (molar ratio); P=1.3~1.8 MPa; WHSV=4.70 h^{-1}.   The samples in the form of 20~30 mesh-sized particles were placed in the reactor.   *Prior to* the reaction, the samples were saturated with ethanol.   The curves of etherification activities of the samples to temperature are shown in **Figure 3**.   Under the reaction conditions, all of the samples have the selectivities of almost 100% ETBE.

Noticeably improvement of etherification activity was found on alkali-treated samples.   ZB2 with highest activity was *ca.* 57.9 %.   It is comparable to that of Beta zeolites, which have the highest activity was about 62 %, and is the most active zeolite catalyst in the synthesis of MTBE and ETBE [2-4].

In our previous work, we have found that the acid amount and acid properties are not the controlling factors affecting the activity of synthesis of MTBE over ZSM-5 zeolite[4] in low temperature.   In this work, no clear relationship between activity and acid properties was found too.   Further characterizations were performed in order to find the reason of the higher activity of alkali-treated ZSM-5 zeolites.

Acid treatment also can remove extra-framework species hindering the diffusion of molecular, but acid-treated sample only shows a little increase of activity (as the results of ZA shown in **Figure 3**).   So the improvement of the activity can not be explained simply by remove of extra-framework species.   The crystals were crashed after alkali-treatment (**Figure 1b**), but it shows much greater activity than that of nano-sized ZSM-5 (ZNS). Its crystalline size was still larger than 1 μm, though.

The specific meso-pore area and volumes of as received and alkali-treated ZSM-5 were determined by use of N$_2$ adsorption at 77 k with ASAP 2010.   **Figure 4** illustrates the N$_2$ adsorption isotherms and pore distribution curves in the top-left of alkali-treated ZSM-5.   Both ZB1 and ZB2 appear a hysteresis loop during desorption measurement, strongly suggesting the formation of mesopores in ZSM-5 crystals.   The pore size distribution derived from BJH analysis of the N$_2$ desorption branch shows that sample ZB1 give a single peak at about 5.8 nm, while ZB2 give a single peak at about 9.1 nm, which indicates that more severe treatment enlarge the mesopores.   Alkali-treated samples also have larger mesoporous area (125.1 and 188.8 m^2/g for ZB1 and ZB2 respectively) and mesoporous volume (0.260 and 0.549 cm^3/g for ZB1 and ZB2 respectively) than those of the parent ZSM-5 zeolite.   There are only mesopores with size of 4.0 nm and 0.0639 cm^3/g of mesoporous volume in the parent ZSM-5.   Synthesis of ETBE over ZSM-5

Figure 3 Activities of alkali-treated, acid treated and nano-sized ZSM-5
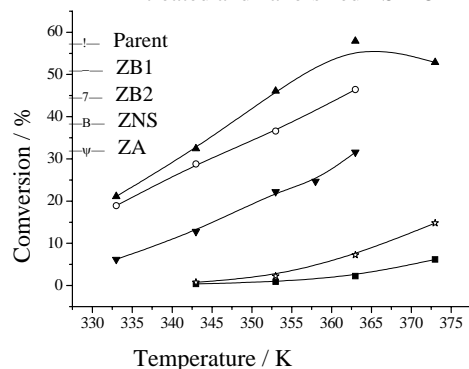
Figure 4 N$_2$ adsorption isotherms at 77K for sample ZB1 and ZB2
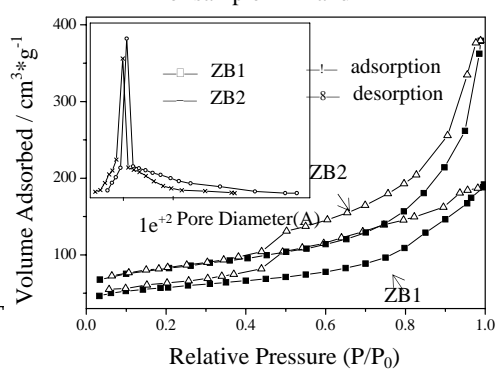
under low temperature is a diffusion-controlled reaction. The formation of mesopores facilitate the diffusion thereby improve the activity.

During the alkali-treatment, a quantity of silica was dissolved, which resulted in the breakage of Si-O-Si linkage and greatly enrichment of Si-OH. We studied the acid properties of alkali-treated samples by Py-IR, the OH-region of IR spectra. A clear peak appears at 3740cm^{-1} in IR assigned to silanoxyl group, suggesting the enrichment of Si-OH[14]. While this peak was not clear for parent sample. The enriched silanoxyl group can pre-adsorb ethanol molecular, and is thought to be helpful to improve the activity of etherification[15].

Acknowledgments

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