



Study on optimum base-treatment of mordenite for catalytic alkylbenzene transalkylation



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ABSTRACT

The effect of base-treatment by single-cycle or multiple-cycle protocol on the textural and catalytic properties of mordenite was studied. According to BET (Brunauer, Emmett and Teller) isotherm and temperature programmed desorption of hexane isomers, mordenite after single-cycle base-treatment generated disordered mesopores in the size of 8 nm regardless of base-treating time, and multiple-cycle treatment generated 8–14 nm mesopores interconnected with silica-blocked 12-MR micropore. The latter treatment was more effective for enhancing both of the catalytic activity and stability of mordenite than the former. Study on optimum base-treatment condition by varying cycle number and base-treating time in each cycle was conducted. The improved catalytic performance is attributed to the mesopore formation with enhanced diffusivity.

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1. Introduction

In modern petrochemical industry, benzene and xylene ($A_6 + A_8$) are produced from either the disproportionation of toluene or transalkylation of alkylbenzenes [1–3]. Since heavy alkylbenzenes being used as a blending stock of gasoline is gradually restricted by more stringent law and is in large excess, transalkylation of heavy alkylbenzenes could be an efficient way for reducing the production cost of $A_6 + A_8$. Unfortunately, as the content of heavy alkylbenzenes in transalkylation feed increases, zeolite catalysts imposing strong diffusional resistances to large organic molecules suffer inevitably fast deactivation rate. In tackling with the deactivation problem in processing heavy alkylbenzenes, increasing numbers of industrialized transalkylation processes use metal incorporating zeolite (metal/zeolite) catalysts to enhance catalyst stability by hydrogenating coke precursors [4]. Because of the formation of benzene co-boilers from benzene hydrogenation side reactions, delicate catalyst systems are required, i.e., pre-conditioned metal/zeolite catalyst [4,5], dual bed catalyst system [6], to meet benzene product purity specification. Some other useful approaches have been proposed, such as mesoporous zeolite for improving catalytic stability [7]. The base-modified H-mordenite

showed comparable catalytic stability to Pt/mordenite with a much better benzene product purity. The improved stability is attributed to an enhanced diffusion behavior in the meso-micro hierarchical structure. Referring to the current Pt/zeolite catalysts, the hierarchical zeolite is an environmental benign solution with extremely high benzene product purity at minimal hydrogen consumption and no concern of reactor temperature run.

In a recent review, Valtchev et al. [8] noted the unattended modification in mesoporosity through generation of structural defects from leaching of framework T atoms during general post-treatments such as thermal activation (drying and calcination), chemical activation (template removal processes), functionalization (surface modification), metal deposition and incorporation (ion exchange and impregnation). Mesoporosity could be created on zeolite by means of selective removal of skeletal alumina or silica from zeolite framework by means of acid or base post treatment respectively [9]. Base post treatment could be more effective in mesoporosity generation than acid post treatment [7,9]. In reference to the direct synthesis methods which generate well crystalline structures, post treatment always generate versatile changes of zeolite morphology and meso-structures which is dedicated to the specific post treatment procedure. The effect of alkaline treatment varies with zeolite structure [10], composition of parent zeolite [7,11,12], concentration of treating solution, treating temperature and time [13,14], and binder [15]. The present paper studies the optimum desilication procedure of mordenite for the

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catalysis of heavy alkylbenzene transalkylation. The effect of textural property of mordenite prepared from different post treatment procedures is examined.

2. Experimental

Zeolon 100 (denoted as M7) with SiO₂/Al₂O₃ ratio of 6.8 supplied by Norton Chemicals, was used as the parent mordenite sample. M7 sample was subjected to post treatment with various procedures. Referring to the designation code in Table 1, by “single-cycle protocol”, the base-treated sample *dm*M7 was prepared by heating M7 sample in 0.1N NaOH solution at solution-to-solid weight ratio of 20 at 333 K for “*m*” minutes. By “multiple-cycle protocol”, the sample denoted as *d15*×*n*M7 was prepared from M7 sample treated with the “single-cycle protocol” procedure for 15 min in each cycle and for “*n*” treating cycles. After the base-treatment, the solid sample was then filtered and further ion exchanged with 1N NH₄NO₃ solution at 333 K for 6 h. Then the solid sample was filtrated and calcined in air at 540 °C for 8 h.

The framework structure of solid powder was measured with a Rigaku Multiflex X-ray Diffractometer using Cu Kα radiation. Nitrogen adsorption–desorption isotherms and BET (Brunauer, Emmett and Teller) surface area measurements were conducted using Micromeritics ASAP2020 at 77 K. The samples of 0.1–0.15 g were first degassed in vacuum at a ramp rate of 10 °C/min up to 623 K for 8 h. The BET method was used to calculate the specific surface areas. The pore volumes and pore size distributions were derived from the desorption isotherms using the Barrett–Joyner–Halenda (BJH) method. Temperature programmed desorption (TPD) of hexane isomers were conducted in a HP5890 Gas Chromatography equipped with flame ionization detector using a column packed with a zeolite sample of interests following the reported experimental procedure [16].

Transalkylation reaction tests were conducted in a continuous flow fixed-bed reactor. A typical reaction condition was feed composition as toluene: 1,2,4-trimethylbenzene (124TMB) at 50:50 wt/wt; reaction temperature: 553 K; WHSV: 3.0 h⁻¹; pressure: 2068 kPa; H₂/feed ratio of 3.0 mol/mol. The reactor effluent was analyzed with gas chromatography using a methylsilicone high resolution HP-1 capillary column in accordance with the ASTM D5134 DHA (detailed hydrocarbon analysis) from which the conversion and product benzene purity were determined. “Benzene purity” was determined from the compositions of reactor effluents by the following equation:

$$\text{Benzene purity (\%)} = \frac{100 \times Y_{A6}}{(Y_{A6} + 0.1 \times Y_{C6P} + 0.7 \times Y_{MCP} + Y_{CH} + Y_{C7N})}$$

Table 1
Base-treated mordenite samples with various treating conditions and their sample numbers.

Sample	Treating condition			
	NaOH conc'n	Temperature (K)	Time (min)	Cycle
M7	–	–	–	None
Single-cycle treatment				
d15M7	0.1N	333	15	1
d30M7	0.1N	333	30	1
d480M7	0.1N	333	480	1
d2230M7	0.1N	333	2230	1
d6780M7	0.1N	333	6780	1
Multiple-cycle treatment				
d15 × 2M7	0.1N	333	15	2
d15 × 3M7	0.1N	333	15	3
d15 × 4M7	0.1N	333	15	4

where Y_{A6} , Y_{C6P} , Y_{MCP} , Y_{CH} , and Y_{C7N} represent the product yields of benzene, hexane isomers, MCP, CH and N₇ (sum of MCH and DMCP), respectively.

3. Results

Two desilication protocols with single-cycle or multiple-cycle base-treatment were devised. The X-ray diffraction spectra of the parent M7 and base-treated M7 samples using single-cycle protocol and multiple-cycle treatments are shown in Fig. 1(A) and (B), respectively. The desilicated mordenite samples kept MOR framework integrity after being subjected to base-treatment with 0.1N NaOH solution at 333 K with single-cycle even for 110 h (denoted as d6780M7) or multiple-cycle protocols. With the single-cycle protocol, the MOR crystallinity of M7 reduced after long time treatment in basic solution beyond 480 min at 333 K (for d480-, d2230- and d6780-M7). With the multiple-cycle protocol, the MOR crystallinity remained the same after the treatment for four cycles (d15×4M7).

The textural properties of various mordenite samples were determined with nitrogen adsorption isotherms. As shown in Figs. 2 and 3, the adsorption isotherms of the base-modified mordenite samples changed dramatically in variance with base-treatment protocol and base-treating time. The single-cycle base-treated mordenite samples exhibited Type IV isotherms (Fig. 2(A)) with type H4 hysteresis similar to that of the parent mordenite sample M7. Adsorption branch was used for the determination of the pore size distribution to get rid of “tensile strength effect” (Fig. 2(b)) [17–19]. The textural properties of these samples are summarized in Table 2. By extending base-treating time (*m*), the micropore surface areas and micropore volumes of the single-cycle desilicated samples *dm*M7 decreased, which was in agreement with the decreasing crystallinity. On the other hand,

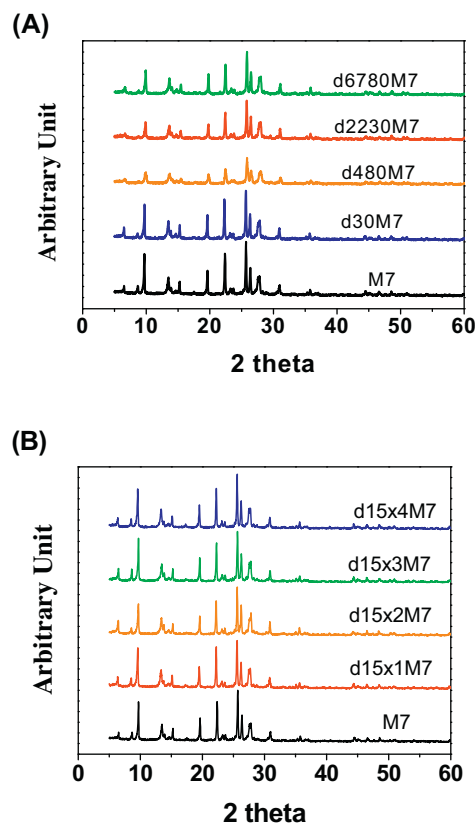


Fig. 1. X-ray diffraction spectra of (A) parent M7 and single-cycle base-treated M7; and (B) multiple-cycle base-treated M7 samples.

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