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Catalytic performance of MCM-22 zeolite for alkylation of toluene with methanol

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Abstract

MCM-22 zeolite with mid-strong acidity and openings of 10-membered ring channels may obtain a high catalytic activity and selectivity for alkylation of toluene with methanol. The acidic sites, for catalyzing alkylation of toluene with methanol, are weaker than that for catalyzing toluene disproportionation. Compared with silicon as a modifier, modification of MCM-22 with $La(NO_3)_3$ is a promising way to improve the catalytic selectivity of *para*-xylene. In addition, the experimental results also clearly indicate the characteristics of MCM-22 structure consisting of large intracrystalline cages, some of which may locate on surface of MCM-22.

Keywords: MCM-22 zeolite; Toluene alkylation with methanol; Toluene methylation; Catalytic performance of MCM-22

1. Introduction

The selective preparation of *p*-xylene by alkylation of toluene with methanol is an interesting way, as an alternative route to the conventional adsorption separation of xylene isomers or to toluene diproportionation. In general, alkylation of toluene with methanol, i.e. methylation of toluene, is carried out over acidic zeolites, such as ZSM-5, Mordenite, Y-Zeolite and SAPO-11, etc. [1–3]. Toluene disproportionation to benzene and xylene, as a main by-reaction, may also take place over acidic zeolites, which is directly related to acidity of zeolites. The acidity and structure of different zeolites varies greatly, so the selection of zeolites is the first step to get catalysts to be suitable for methylation of toluene. The modification of the acidity and structure of ZSM-5 as a common shape-selective zeolite, has widely been investigated to reduce by-reactions and improve the selectivity of methylation of toluene to *p*-xylene [4–6]. Zeolite MCM-22 was firstly synthesized in 1990, and its characterization shows two different intracrystalline pore systems, one consisting of a two-dimensional (i.e., interconnected) system of 10-membered ring channels, the other one consisting of large intracrystalline cages which are accessible only by 10-membered ring windows [7]. The catalytic properties of MCM-22 for alkylation of olefin, cracking of alkane and isomerization, etc., were also investigated, and its shape selectivity is intermediate between those of 10-membered ring medium pores and 12-membered ring large pores [8–10]. A new proprietary MCM-22 catalyst in a new Mobile process for alkylation of benzene with propylene, gives the high yield of cumene with a high purity, and has been commercialized successfully [11].

In this work, the effect of acidity and structure of MCM-22 zeolite on alkylation of toluene with methanol, including toluene disproportionation, has been investigated in detail. The modification of MCM-22 was also studied to improve the *para*-xylene selectivity of products.

2. Experimental

2.1. Catalyst preparation

Zeolite MCM-22 with Si/Al ratio of 25 was synthesized hydrothermally, using hexamethylenamine as the template, based on the procedure described elsewhere [12]. The as-synthesized zeolite was firstly calcined at 550 °C under dry air to remove the template, and the above sample was transformed into the NH_4-form by ion-exchange with NH_4NO_3 solution. The typed catalyst was prepared with

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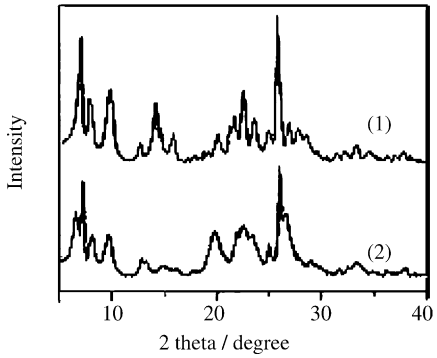

Fig. 1. XRD patterns of the as-synthesized MCM-22: (1) after calcination and (2) before calcination.

alumina as an adhesive, and was transformed into H-form by calcination at 550 °C and for 2 h. The modification of MCM-22 was performed by impregnating treatment of $La(NO_3)_3$ solution or silicone and following calcination at 550 °C. SAPO-11 zeolite, with the Si:Al:P molar ratios of 0.03:0.25:0.22, was synthesized by hydrothermal crystallization according to the reported method [13]. The acidic ZSM-5 zeolite and mordenite with the Si/Al ratios of 25 and 24 were supplied from Shanghai HuaKan catalyst plant. These typed catalysts of SAPO-11, ZSM-5 and mordenite were also prepared with alumina as an adhesive.

2.2. Characterization of catalysts

The as-synthesized zeolite was characterized by X-ray diffraction (XRD) (Rigaku D/max-RBX) and scanning electron microscope (SEM) (Pillips XL30E). The acidity of catalysts was determined by ammonia temperature programmed desorption (NH_3-TPD) (Altmira-100 Characterization System, Zeolton, USA) and pyridine-infrared spectrometry (py-IR) (Bruker IFS-88). N_2 adsorption was carried out using physical adsorption instrument (Digitsorb-2600, USA).

2.3. Alkylation procedure and apparatus

Alkylation of toluene with methanol was carried out in the fixed bed reactor at 420 °C, $2.0\,h^{-1}$ WHSV, with toluene/methanol molar ratio 2/1 using the continuous nitrogen flow at atmosphere pressure. The products were analyzed using on-line gas chromatography (Hp6890) with FFAP capillary column and FID.

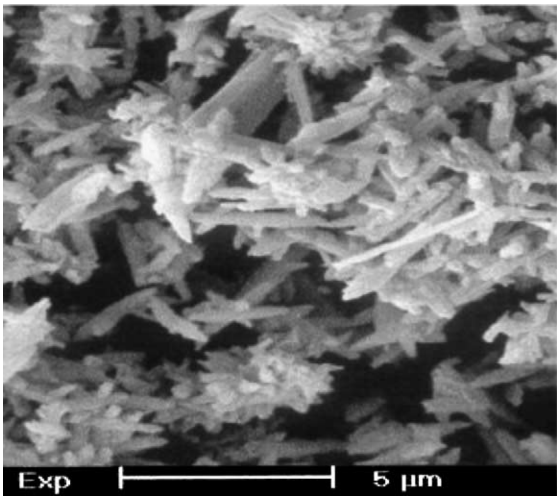

Fig. 2. SEM micrograph of MCM-22.

3. Results and discussion

3.1. Physicochemical properties of MCM-22

XRD pattern of the as-synthesized MCM-22 after calcination, seen in Fig. 1, clearly shows that its structure belongs to MWW and is in agreement with the literature [14,15]. XRD difference of the as-synthesized MCM-22 between before calcination and after calcination mainly results from the template being within intracrystallites. The SEM picture of the as-synthesized MCM-22, shown in Fig. 2, indicates that its crystals are needle-shaped particles with 0.5–1 µm diameter and 3–5 µm length.

The physical adsorption of some typical zeolites used in methylation of toluene was determined, shown in Table 1. The micropore volume of MCM-22 is much more than that of medium pore ZSM-5 or SAPO-11, nearly to that of large pore mordenite. The total BET surface area of MCM-22 is also more than ZSM-5 or SAPO-11, and is reduced

Table 1
The characterization of physical adsorption of zeolites

	Si/Al ratio	Specific surface area (m^2/g)	Micropore volume (ml/g)	Channel system size (nm)
Mordenite	24	522	0.24	0.67–0.7
SAPO-11[a]		216	0.10	0.40–0.65
ZSM-5	25	405	0.14	0.54–0.56, 0.51–0.55
MCM-22	25	479	0.21	0.40–0.59, 0.71–1.82 (0.40–0.54)
Si-MCM-22	25	253	0.13	
La-MCM-22	25	275	0.15	

[a] Si:Al:P molar ratios are 0.03:0.25:0.22.

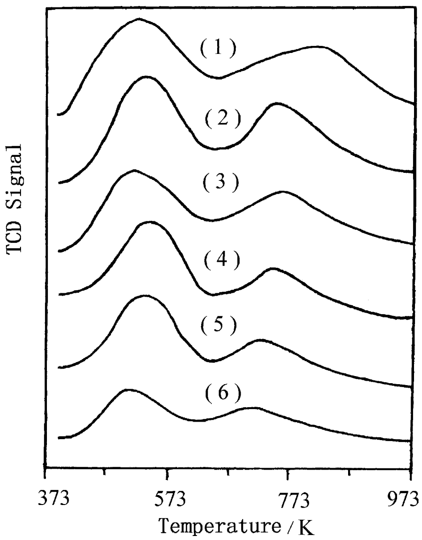

Fig. 3. The patterns of NH_3-TPD of zeolites: (1) mordenite, (2) MCM-22, (3) ZSM-5, (4) Si-MCM-22, (5) La-MCM-22, (6) SAPO-11.

greatly after modified with La or Si (i.e., La-MCM-22 or Si-MCM-22), due to partial coverage of surface and pores during modification of MCM-22.

NH_3-TPD of samples in Fig. 3 shows that all zeolites are of two peaks of NH_3 desorption, corresponding to strong acidic sites and weak acidic sites, respectively. Except for mordenite, the strength of acidic sites of these zeolites is at mid-strong level, and decreases with the following order: mordenite > ZSM-5 > MCM-22 ∼ SAPO-11 > Si-MCM-22 > La-MCM-22. However, with respect to the total amount of acidic sites, MCM-22 is the highest among these zeolites, especially the acidic sites whose NH_3 desorption takes place between 300 and 450 °C. Py-IR of MCM-22 before and after modification in Fig. 4 shows that modification with silicon results in decreasing Bronsted and Lewis acid sites simultaneously, due to the coverage of acid sites, but modification with La causes the slight increase of Lewis acid sites with decreasing Bronsted acid sites thank to metallic oxides on MCM-22 surface.

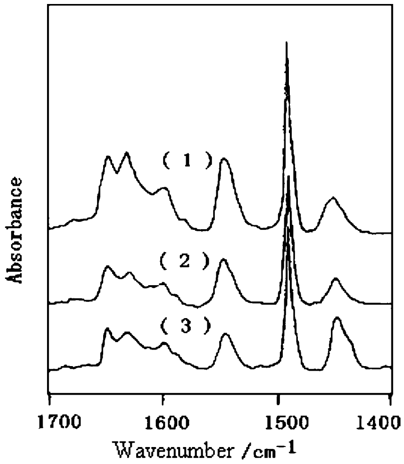

Fig. 4. IR spectra of the modified MCM-22: (1) MCM-22, (2) Si-MCM-22i, (3) La-MCM-22.

3.2. Comparison between toluene alkylation over different zeolites

The experimental results in Table 2 show that alkylation of toluene with methanol is of the highest selectivity with high catalytic activity over MCM-22, and SAPO-11 also has a good selectivity but low catalytic activity. The by-reaction of toluene disproportionation, corresponding to the formation of benzene of products, decreases in the order being in accordance with the acidic strength of zeolites. There is the most by-reaction of toluene disproportionation over mordenite, although being the highest toluene conversion. MCM-22 catalysts, especially La-MCM-22, show low catalytic activity for toluene disproportination with a little of produced benzene. Therefore, it may be considered that the acidic sites, needed for catalyzing alkylation of toluene with methanol, are relatively weaker than that for catalyzing toluene disproportionation.

MCM-22, ZSM-5 and SAPO-11 belong to zeolites of 10-membered ring openings, but MCM-22 is zeolite of 10-membered ring pores with two different intracrystalline pore systems including large supercages of 12-membered ring [16]. The experimental results clearly indicate the characteristics of MCM-22 structure consisting of large intracrystalline cages, with forming a lot of trimethyl-benzene. Moreover, during modification with Si under the same condition, the effect of MCM-22 modification (i.e., *para*-xylene selectivity) is not as good as that of ZSM-5. Therefore, it is considered that a part of supercages may locate on the surface of MCM-22, which greatly influences removing of the acidic sites on surface during modification.

3.3. Catalytic performance of MCM-22 catalysts with time-on-stream

The results depicted in Fig. 5 show that the total toluene conversion decreases with the following order: MCM-22

Table 2
Results of methylation of toluene over zeolites

Sample	Catalytic performance (%)			
	Dis[a]	Alk[b]	Tri[c]	C_T[d]
Mordenite	64.3	21.2	14.6	50.1
SAPO-11	9.2	83.4	7.3	31.2
ZSM-5	40.6	50.2	9.3	43.9
MCM-22	11.0	76.5	12.4	41.5
Si-MCM-22	5.5	84.3	10.3	13.3
La-MCM-22	2.8	88.5	8.7	23.2

[a] Selectivity of toluene disproportionation calculated from benzene.

[b] Selectivity of toluene alkylation calculated from xylene (the partial xylene produced from toluene disproportionation has been cut-off).

[c] Selectivity of trimethylbenzene and aromatic molecules with larger sizes.

[d] Toluene conversion.

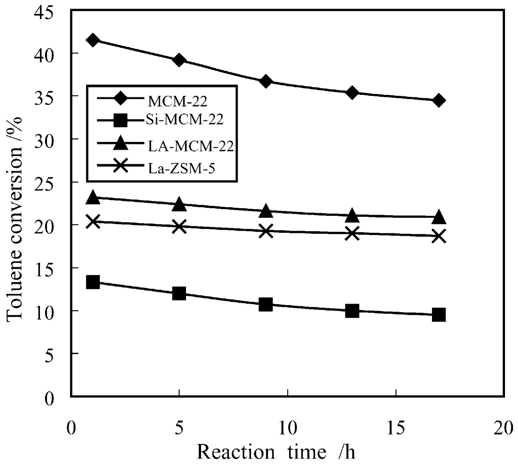

Fig. 5. Catalytic activity of MCM-22 and modified MCM-22/ZSM-5 with time-on-stream.

> La-MCM-22 > Si-MCM-22. The above order for catalytic activity is approximately in accordance with their acid amount determined by NH_3-TPD. However, the deactivation of MCM-22 catalyst is quicker than that of two modified MCM-22 catalysts, due to the relative stronger acidity of unmodified MCM-22 which is easy to result in the formation of coke [17]. Whereas, La-MCM-22 shows relatively better stability, thank to effective modification of stronger Bronsted acid sites. On the other hand, Si-MCM-22 is lower than La-MCM-22 in catalytic activity due to less total acid amount. Comparatively, the larger amount of Lewis acid sites over La-MCM-22 is a main factor to result in higher catalytic activity. Therefore, it may be considered that alkylation of toluene with methanol is catalyzed by both Bronsted and Lewis acids.

The by-reaction of toluene disproportionation decreases in the order being in agreement with the Bronsted acid sites of MCM-22 catalysts, with little benzene formation over modified La-MCM-22. It was also reported that toluene disproportionation was catalyzed mainly by Bronsted acid [18]. The selectivity of *para*-xylene, shown in Fig. 6, especially for La-MCM-22, is obviously improved thanks to its smaller opening of channels resulting from surface modification of $La(NO_3)_3$ or silicone. In addition, less trimethylbenzene or larger size molecules are produced over two modified MCM-22 catalysts due to the partial coverage of supercages on surface (Fig. 6).

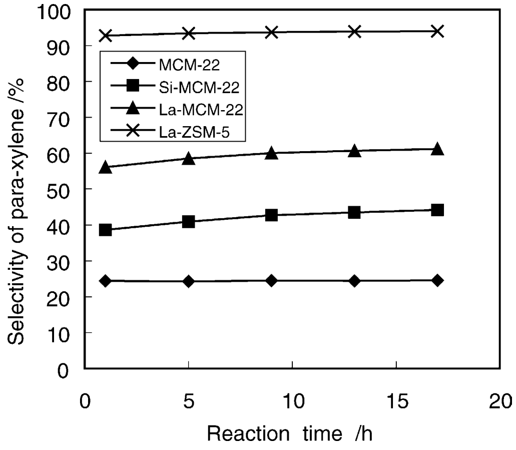

Fig. 6. Catalytic selectivity of MCM-22 and modified MCM-22/ZSM-5 with time-on-stream.

4. Conclusion

MCM-22 zeolite with mid-strong acidity and openings of 10-membered ring channels is suitable for alkylation of toluene with methanol. The acidic sites, needed for catalyzing alkylation of toluene with methanol, are weaker than that for catalyzing toluene disproportionation. Compared with silicon as a modifier, modification of MCM-22 with rare earth is a promising way to improve the selectivity of *para*-xylene of products. On the other hand, the experimental results also clearly indicate the characteristics of MCM-22 structure consisting of large intracrystalline cages, some of which may locate on surface of MCM-22 and influence removing of the acidic sites on surface during modification.

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