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H-MCM-22 zeolitic catalysts modified by chemical liquid deposition for shape-selective disproportionation of toluene

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Abstract Catalysts were prepared by dealumination of H-MCM-22 zeolite with oxalic acid leaching, followed by shaping and liquid phase modification with siloxane. The catalytic performance was measured with selective disproportionation of toluene in a fixed-bed reactor. The unmodified H-MCM-22 zeolite exhibited much higher initial activity than H-ZSM-5 with a thermodynamic equilibrium distribution of xylene products. The oxalic acid treatment of H-MCM-22 improved the selectivity for para-xylene by 10–18%. The modification by siloxane of the oxalic acid treated H-MCM-22 turned out to be highly selective for para-xylene, however, with the expense of the conversion. It is proposed that the high para-selectivity was closely associated with the contraction of micropore windows and the elimination of acid sites at the external surface by the deposited silica. Therefore, the modified H-MCM-22 is a potential catalyst for the selective disproportionation of toluene with a high para-selectivity.

Keywords MCM-22 · Disproportionation of toluene · Para-xylene · Dealumination · Chemical liquid deposition

Introduction

Disproportionation of toluene is a commercially important process for the manufacture of para-xylene. Over H-ZSM-5 zeolite, the concentration of xylene isomers is typically close to the thermodynamic equilibrium with 24% ortho-xylene, 53% meta-xylene and 23% para-xylene [1]. Therefore, modification of the zeolite is necessary to enhance the para-selectivity. Numerous patents and public reports appeared on the modification of ZSM-5 zeolite [1, 2], such as metal oxide impregnation [3], coke-induced selectivation [2, 4], and silylation [5–9], through which the para-selectivity has been improved remarkably. Among these modifications, the deposition of an inert silica layer onto the external surface of ZSM-5 crystals by chemical vapor deposition (CVD) [5–8] or chemical liquid deposition (CLD) [8, 9] eliminates the external acid sites [5, 8] and regulates the pore mouth of ZSM-5 zeolite [9–11], thus leading to a high para-selectivity. CLD has been applied to commercial catalysts. However, a high reaction temperature is usually needed to obtain a high conversion over modified or unmodified H-ZSM-5 catalysts [1, 2]. The search for alternative zeolite catalyst other than ZSM-5 is desirable.

MCM-22 is a high silica zeolite first synthesized by Mobil in 1990 [12]. The framework topology is composed of two independent pore systems [13]. One of them is defined by two-dimensional sinusoidal channels, which maintain an effective 10-MR diameter (0.41 × 0.51 nm) throughout the structure, and the other consists of supercages with 12-MR inner free diameter of 0.71 nm and inner height of 1.82 nm, and with 10-MR windows (0.40 × 0.55 nm). The application of MCM-22 in catalytic reactions has been investigated [14–21]. It is notable that the size of 10-MR windows of MCM-22 is very close to that of ZSM-5 [20] and their acidities are very similar to each other [22]. This makes MCM-22 an attractive candidate as shape-selective catalysts for para-xylene production from the disproportionation of tolune [20, 23–26] and the methylation of toluene with methanol [27]. Wu et al. [20] investigated the disproportionation of toluene over MCM-22 dealuminated by calcination or steaming, followed

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by leaching with HNO_3. A high para-selectivity of 85.3% was achieved with a toluene conversion of 7.8% at reaction time on stream (TOS) of 15 min. Park et al. [23] observed that the acid sites on the external surface of MCM-22 can be selectively poisoned by 1,1,1,3,3,3-hexamethyldisilazane with CVD, and the para-selectivity increased by 30%. Although CLD with silicone is a very effective approach for ZSM-5 to enhance para-selectivity, it is noteworthy that CLD has not been employed to modify MCM-22 as catalyst for toluene disproportionation so far.

In this work, organic acid treatment combined with CLD by 3-glycidoxypropyltrimethoxysilane (KH560) were utilized to modify the external surface of MCM-22, and over this catalyst, a very high para-selectivity up to 97% was obtained.

Experimental

Catalyst preparation and characterization

Na-MCM-22 (Si/Al = 30) was synthesized using hexamethyleneimine as the structure-directing reagent according to the previous description [12]. The protonic form of MCM-22 (H-MCM-22) was obtained by four successive exchanges with a 1 M NH_4NO_3 solution for 1 h at 80°C, followed by calcination at 550°C for 3 h. H-ZSM-5, as a control catalyst, was obtained by the same ion exchange procedure as above with Na-ZSM-5 (Si/Al = 28) purchased from Nankai Catalyst Plant. The dealuminated H-MCM-22 sample, denoted as DMCM, was prepared by leaching of H-MCM-22 with refluxing in 0.2 M aqueous solution of oxalic acid at 90°C for 2 h, followed by washing, drying and calcination in air at 550°C for 3 h.

The final form of catalyst was achieved by shaping DMCM followed with CLD silylation. In detail, DMCM was admixed with montmorillonite clay, as well as cellulose and deionized water. The resulting mixture was extruded with a 2 mm diameter, followed with drying and calcination. 10 g of shaped sample was suspended in 100 mL of hexane and heated under reflux with stirring. 4 mL of KH560 was added into the mixture and the CLD silylation was carried out for 8 h under reflux. Hexane was removed by evaporation and the sample was calcined at 550°C in dry air for 4 h. The catalyst was referred to as DMCMS1. The DMCMS2 and DMCMS3 were obtained by repeating the above-described procedure two and three times, respectively. All the chemicals were purchased form Shanghai Chemical Reagent Corporation, and they were analytical grade reagents and were used without further purification.

X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE powder diffractometer using Ni-filtered Cu Kα radiation source at 40 kV and 20 mA with a scan rate of 1.2°/min. Energy Dispersive X-ray Analysis (EDS) was obtained by EDAX Genesis 2000. BET surface area was measured on a Quantachrome CHEMBET-3000 apparatus using nitrogen as adsorbate at –196°C. The acidic properties of catalysts were tested by NH_3-TPD technique using a fixed-bed flow apparatus with TCD as a detector. 0.1 g of catalyst was charged in the quartz tube and heated in situ at 600°C for 1 h in He flow. After this, the catalyst was cooled to 120°C and saturated with NH_3. The NH_3-TPD profiles were obtained in the temperature range of 120–600°C with a heating rate of 10°C/min.

Disproportionation of toluene

The disproportionation of toluene was performed in a fixed-bed reactor loaded with 1.0 g catalyst diluted by 5.0 g quartz sand under atmospheric pressure. After the catalyst was activated in N_2 stream at 500°C for 1 h, the catalyst bed was cooled to the preset reaction temperature. The reaction conditions are as follows: reaction temperature 300°C, weight hourly space velocity (WHSV) 6.7 h^{-1} and molar ratio of hydrogen to toluene 2. The product was sampled periodically from a cold trap. Quantitative analysis was done by a gas chromatograph equipped with a 25 m B-34 capillary column with FID as a detector. The conversion and selectivity were calculated according to equations. Conv. $= (M_{n0} - M_n)/M_{n0} \times 100\%$, where Conv. is the conversion of toluene, Mn_0 is the molar percentage of toluene in the feed, and Mn is the molar percentage of toluene in the product. Sel. $= M_{PX}/M_X \times 100\%$, where Sel. is the selectivity of para-xylene, M_{PX} is the molar percentage of para-xylene in product, and M_X is the sum of molar percentage of xylene isomers including para-, ortho- and meta-xylene.

Results and discussion

Disproportionation of toluene over H-MCM-22

Disproportionation of toluene forms benzene and xylene. Reactions other than disproportionation were not observed under reaction conditions of this work. Results obtained over H-MCM-22 and H-ZSM-5 at different TOS are presented in Table 1. It can be seen that the fresh H-MCM-22 zeolite exhibited much higher conversions than those of H-ZSM-5 over the time period specified. Toluene disproportionation was supposed to proceed through a bulky intermediate containing two toluene molecules [28, 29]. Because of the limited space of 10-MR channels in H-ZSM-5 zeolite, it does not allow the formation of the intermediate at the reaction temperature employed in this work [28]. By contrast, toluene disproportionation tended to take place in the supercages of H-MCM-22 [20], with a space large enough for the formation of the intermediate.

Table 1 Comparison of activity over H-MCM-22 and H-ZSM-5 in disproportionation of toluene

Catalyst	H-MCM-22				H-ZSM-5			
TOS/min	30	60	90	120	30	60	90	120
Conversion of toluene/%	18.3	7.0	4.1	3.2	0.9	1.0	0.9	0.9
Selectivity for para-xylene/%	24.8	33.1	35.0	35.4	24.3	24.5	24.4	24.5

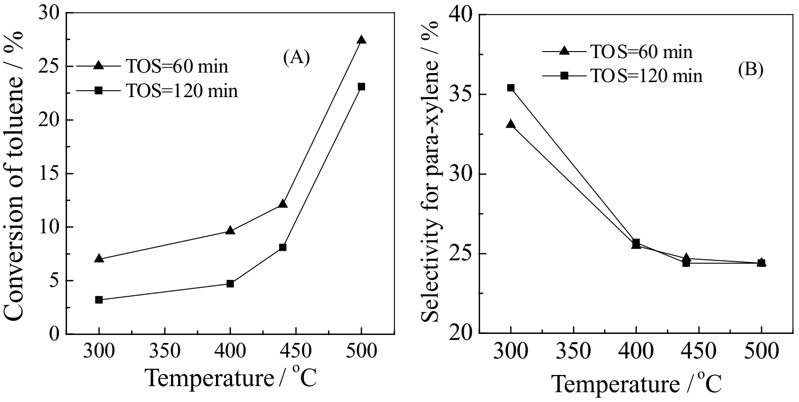

Fig. 1 Effect of reaction temperature on catalytic conversion (A) and para-selectivity (B) over H-MCM-22 in disproportionation of toluene at 60 and 120 min on stream

On the other hand, as shown in Table 1, H-ZSM-5 showed a stable but very low activity and a para-selectivity close to the equilibrium value. For H-MCM-22, remarkable deactivation occurred with the increase of TOS, while the selectivity for para-xylene increased with the decrease of conversion. At 120 min of TOS, the conversion dropped to 3.5%, and the para-selectivity was 35.4%, which exceeded the equilibrium value by about 10%. It was found in another experiment that the used H-MCM-22 can be totally regenerated with calcination in flowing air. It is thus suggested that the rapid deactivation of H-MCM-22 is ascribed to the formation of coke in the supercages [30–32]. Meanwhile, the coke might also cover the unselective acid sites in the half supercages on the external surface of H-MCM-22 crystal [20, 30, 32] and reduce the number of the 10-MR openings of the internal pore system, which suppresses the secondary isomerization of para-xylene occurring on external acid sites [20, 31] and therefore enhances the para-selectivity.

Figure 1 shows toluene conversion and para-selectivity over H-MCM-22 at various temperatures at TOS of 60 and 120 min. It can be seen that the increase of reaction temperature improved the toluene conversion but lowed the para-selectivity. Comparing the toluene conversion at TOS of 30 min with that at 120 min, one can find that the deactivation at higher reaction temperatures was less severe than that at lower temperatures. The high para-selectivity at low reaction temperature may be attributed to the coke formed in the supercages and at the external surface [20], as mentioned above. A higher temperature may lead to the fast formation of coke in the supercages and result in the deactivation of sites in the supercages. However, the high reaction temperature also activates effectively the acid sites located in sinusoidal channels for toluene disproportionation and for secondary isomerization [30]. This results in the equilibrium selectivity and a high conversion, which is similar to the case of HZSM-5 [1].

Effect of dealumination of H-MCM-22 by oxalic acid

The XRD patterns of H-MCM-22 and DMCM are shown in Fig. 2. The XRD curve of H-MCM-22 matched well with that reported previously [12, 14], indicating a well crystallization. Moreover, the intensity and location of peaks for DMCM are very similar to those of H-MCM-22, showing a high comparative crystallinity. The BET surface of DMCM, 384 m^2/g, is only slightly lower than that of H-MCM-22, 401 m^2/g.

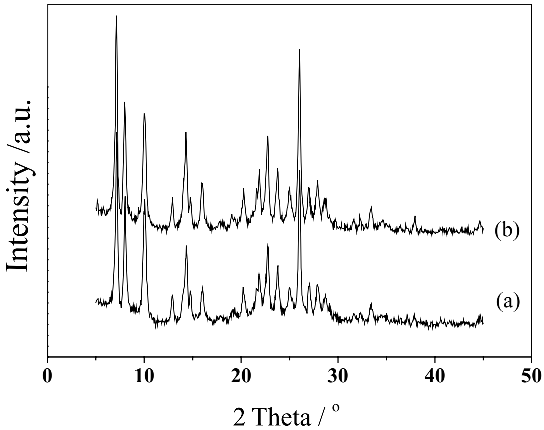

Fig. 2 XRD patterns of H-MCM-22 (a) and DMCM (b)

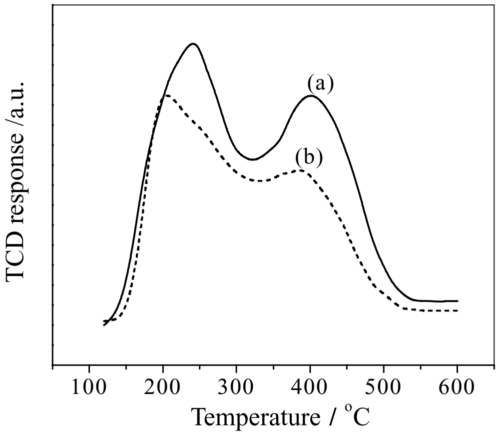

Fig. 3 NH_3-TPD profiles of H-MCM-22 (a) and DMCM (b)

Figure 3 shows NH_3-TPD profiles H-MCM-22 and DMCM. It was evident that the total acid amount of DMCM was lower than that of H-MCM-22. In principle, oxalic acid can only remove the skeletal Al at the external surface and/or in large half-cavities widely opened on the external surface of the crystals because the size of oxalate ion is larger than the pore opening of the zeolite [33, 34]. It is known that MCM-22 zeolite possesses relatively large external surface and more external acid sites locating in the half-supercages than other zeolite materials like ZSM-5 [35]. Consequently, dealumination at external surface by oxalic acid can reduce obviously the total amount of acid sites of H-MCM-22. In fact, the EDS analysis showed a higher atom ratio of Si to Al on the external surface of DMCM (13.5) than that of H-MCM-22 (11.5).

The conversion and selectivity as a function of reaction time in the disproportionation of toluene over H-MCM-22 and DMCM are compared in Fig. 4. It can be seen that DMCM shows a more or less similar result to H-MCM-22 (Fig. 4(A)), and nevertheless, give a significant increase in the selectivity for para-xylene, which exceeded that of H-MCM-22 by 10–18% at various conversions (Fig. 4(B)). This may be explained by the mechanism proposed by Wu et al. [20] that on H-MCM-22, para-xylene formed within the supercage as a primary product was isomerized into ortho- and meta-xylene on acid sites at external surfaces. For DMCM, the selective dealumination by oxalic acid could partly remove the unselective acid sites at external surface and result in the enhancement of para-selectivity without decreasing the conversion. Other dealumination methods, such as HNO_3 treatment [20] and steaming [20, 23] improve the para-xylene selectivity by decreasing the catalytic activity, because the elimination of acid sites is not selective.

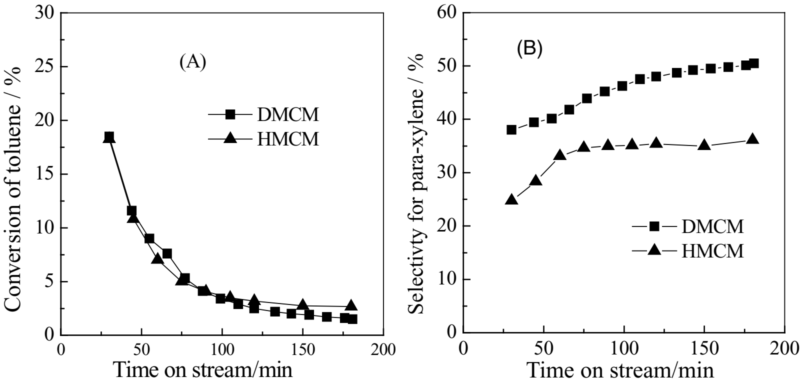

Fig. 4 Conversion (A) and para-selectivity over DMCM and H-MCM-22 catalysts in the disproportionation of toluene

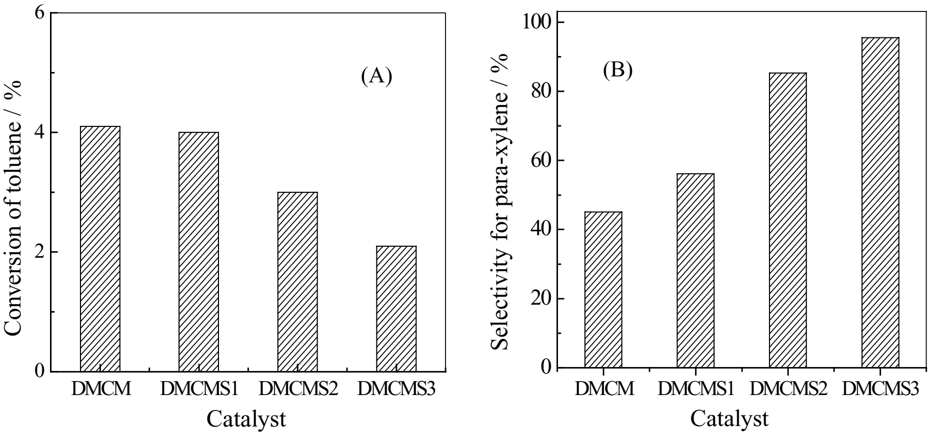

Fig. 5 The activity and selectivity of various H-MCM-22 catalysts modified by CLD in toluene disproportionation

Effect of chemical liquid disposition

Silylation by CLD is one of the effective and simple methods to enhance the para-selectivity [8, 11, 33, 36]. In our previous work [37], high para-selectivity in the same reaction was achieved over the pelletized H-ZSM-5 catalyst modified by CLD with siloxane at a reaction temperature of 440°C. In this work, CLD was applied to modify dealuminated H-MCM-22 zeolite in order to enhance the para-selectivity. Effect of CLD treatment times on the toluene conversion and para-selectivity are illustrated in Fig. 5. It is shown that the conversion decreased gradually with the increase of treatment times by CLD, and meanwhile, the para-selectivity was greatly enhanced. It is noteworthy that the para-selectivity reached a very high level of 97% after three times of modification by CLD.

As the molecular size of KH560 is too large to enter the interior channels through the 10-MR windows during CLD, it can only react with hydroxyl groups on the external surface and the pore mouth region of MCM-22 crystal. Thus, the resulting inert SiO_2 layer passivates the unselective acid sites, which restrains the secondary isomerization of para-xylene, and on the other hand, the 10-MR ring pore mouth was narrowed, which leads to the increase of the difference in diffusion of xylene isomers [38, 39]. This explains the great enhancement of para-selectivity over dealuminated H-MCM-22 zeolite modified by CLD.

Conclusions

H-MCM-22 exhibited a much higher catalytic activity and para-selectivity in the disproportionation toluene than H-ZSM-5 at low reaction temperatures around 300°C. However, it deactivated quickly due to coking. The increase of reaction temperature leads to a slow deactivation. Oxalic acid treatment could partially eliminate the unselective acid sites at the external surface of zeolite and thus improve the para-selectivity. The para-selectivity reached 97% at the expense of conversion over a three-time CLD modified catalyst by silicone. The CLD treatment for MCM-22 zeolite by silicone combined with dealumination by oxalic acid proved to be an effective way to enhance the para-selectivity in the disproportionation of toluene.

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