# = CHEMICAL KINETICS = AND CATALYSIS

# Preparation of H-Mordenite/MCM-48 Composite and Its Catalytic Performance in the Alkylation of Toluene with *tert*-Butanol<sup>1</sup>

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Abstract—A series of HM/MCM-48 samples with different  $SiO_2/Al_2O_3$  molar ratio were prepared by sol-gel method. The prepared catalysts were characterized by XRD,  $N_2$  adsorption-desorption, NH<sub>3</sub>-TPD, FT-IR, SEM, and TEM techniques, and their catalytic performance was investigated in alkylation of toluene with *tert*-butanol.The adsorption capacity and the acid sites amount of HM/MCM-48-4 sample prepared by growing MCM-48 on the surface of HM zeolite are much higher than that of their mechanical mixture (HM/MCM-48(4) sample) due to its biporous structure; it shows higher catalytic performance of HM/MCM-48-4 samples. The influence of reaction conditions on the catalytic performance of HM/MCM-48-4 zeolite was discussed. Toluene conversion of 41.4% and *p-tert*-butyltoluene selectivity of 73.5% were obtained at the weight ratio of toluene to HM/MCM-48-4 of 5, reaction temperature of 453 K, reaction time of 5 h and the molar ratio of toluene to *tert*-butanol of 0.5.

*Keywords:* toluene, HM/Al-MCM-48, sol-gel method, *tert*-butylation, *p-tert*-butyltoluene **DOI:** 10.1134/S0036024417090345

## INTRODUCTION

As an important chemical raw material, *p-tert*-butyltoluene (PTBT) is widely used in the synthesis of pharmaceuticals, pesticides and food additives. In the industry, it is always prepared by alkylation of toluene with different reagents in the presence of liquid catalysts, such as AlCl<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and polyphosphoric acid, etc. [1], which are corrosive and generally not reusable. Some solid acid catalysts including zeolites have been developed to avoid these problems due to their environmental viability, lack of corrosivity, and good reusability [2–7].

The selectivity of alkylation process toward PTBT over mordenite is higher than over other zeolites, because its pore size is very close to the molecular diameter of PTBT [8]. However, its catalytic activity is rather limited due to its minor pore size, which causes diffusion hindrance, critical carbon deposition and fast deactivation [9, 10]. To solve these problems, ordered mesoporous materials, such as M41S and SBA, have been explored [11]. As an important member of M41S family, the mesoporous molecular sieve MCM-48 is more predominant than MCM-41 in catalysis, adsorption and separation processes, In this work, a series of HM/MCM-48 samples with different Si : Al molar ratio were successfully prepared by growing MCM-48 on the surface of NaM zeolite. Catalytic performance of the prepared composites was investigated in *tert*-butylation of toluene.

# 1. EXPERIMENTAL SECTION

## 1.1. Catalyst Preparation

NaM zeolite (Si : AI = 25) was purchased from the Catalyst Plant of Nankai University. NaM/MCM-48 samples with different Si : Al molar ratio were synthesized according to the literature using cetyltrimeth-ylammonium bromide (CTAB) as a structure-directing

because of its special cubic three-dimensional structure [12], which can increase the diffusion speed of reactants and reduce the frequent blocking. However, the lack of hydrothermal stability becomes a more and more significant obstacle for their practical applications [13]. To overcome the above disadvantages, one of the efforts is to introduce zeolites into the framework of mesoporous materials and prepare the samples with optimal properties [14–17]. However, the synthesis of HM/MCM-48 materials was not yet published because of the narrow synthesis cross-region and harsh synthesis conditions of MCM-48 [18–20].

<sup>&</sup>lt;sup>1</sup> The article is published in the original.

agent [20, 21]. In a typical procedure, 0.083 g NaAlO<sub>2</sub>, 7 g CTAB, and 0.6 g NaOH were added to 40 g of distilled water at room temperature. After stirring for 0.5 h, tetraethoxysilane (9 mL) was added dropwise, and the mixture was kept for another 0.5 h. NaM zeolite (4 g) powder was added to the gel formed. The mixture was transferred to a Teflon-lined autoclave and heated at 373 K under autogenous pressure without agitation for 72 h. The product was collected by filtration, washed with distilled water and dried at 353 K for 12 h. The prepared sample was calcined in static air at 823 K for 6 h to remove the organic template and marked as NaM/MCM-48-2. The prepared samples are referred as NaM/MCM-48-*n* (where *n* is the mass ratio of NaM to MCM-48). For comparison, the MCM-48 sample was prepared in the absence of NaM. All prepared samples were subjected to ion exchange with  $NH_4NO_3$  to obtain HM/MCM-48-*n* catalysts, which were then evaluated in the alkylation of toluene with tert-butanol. For comparison, the sample marked as HM/MCM-48(4) was prepared by mechanical mixing HM with MCM-48 taken in a weight ratio of 4.

#### 1.2. Catalyst Characterization

X-ray powder diffraction patterns of the samples were obtained on a Bruker D8 instrument with Ni-filtered Cu $K_{\alpha}$  radiation ( $\lambda = 0.154$  nm) at 40 kV and 30 mA. The scanning rate was 0.05 deg/s; the patterns were recorded in  $2\overline{\theta}$  ranges of  $1^{\circ}-\overline{5}^{\circ}$  and  $\overline{5}^{\circ}-70^{\circ}$ . Nitrogen adsorption-desorption isotherms of the samples were measured at 77 K using Micromeritics Tristar 3000 system. The surface area was calculated by the BET method in the partial pressure  $(P/P_0)$  range from 0.01 to 0.99. The volume of mesopores was calculated from the adsorption branch of the isotherms using the BJH model [22]; the volume of micropores was determined by *t*-plot method [23]. Temperatureprogrammed desorption of ammonia was carried out in a quartz U-tube reactor; 300 mg sample was used for each measurement. The sample was pretreated in the He stream at 823 K for 60 min and then cooled down to 373 K. After that, 5% (vol/vol) NH<sub>3</sub>/He mixture was passed for 30 min and then the reactor was purged with the He stream for 40 min. The temperature was raised from 373 to 1073 K at a rate of 10 K min<sup>-1</sup>. The consumption of NH<sub>3</sub> from the reactant stream was recorded by TCD. Fourier transforminfrared spectra were measured on the Thermo Nicolet NEXUS spectrometer in KBr pellets. The sample was pretreated in vacuum ( $10^{-2}$  Pa) at 573 K for 3 h and then cooled down to room temperature. The Si/Al ratio was measured by inductively coupled plasma OES (Optima 2000 DV, PerkinElmer, USA) after the sample had been dissolved in HF solution. The morphology of the prepared catalysts was studied by SEM using a Hitachi S-4800 field-emission scanning electron microscope (FESEM), and by TEM using a JEOL JEM-200CX transmission electron microscope.

#### 1.3. Catalytic Reaction

The catalytic alkylation of toluene with tert-butanol was carried out in a 100 mL stainless steel autoclave equipped with a magnetically driven impeller. The catalyst sample (0.2 g) was added to a mixture of *tert*-butanol and toluene (with various molar ratios); n-hexane was used as the solvent. The reactor was flushed for multiple times with nitrogen to replace air. The experiments were carried out at the initial pressure of 0.6 MPa by filling with N2. The final reaction pressure wolud depend on the reaction temperature, at a stirring speed of 800 rpm, at different temperatures. Then the reactor was cooled down to room temperature and the reaction mixture was analyzed on a SP-6890 gas chromatograph equipped with a SE-30 column (0.25  $\mu$ m  $\times$  50 m) and a flame ionization detector (FID).

#### 2. RESULTS AND DISCUSSION

#### 2.1. Catalyst Characterization

**2.1.1. XRD patterns.** The XRD patterns of the prepared samples are shown in Fig. 1. It can be seen from Fig. 1a that the neat MCM-48 sample shows well-defined XRD peaks at  $2.7^{\circ}$  and  $3.1^{\circ}$ , which can be assigned to (211) and (220) reflections. The characteristic diffraction peak for HM/MCM-48-*n* samples corresponding to (220) reflection disappeared, and the peak intensity of (211) reflection decreased with increase in HM amount in the sample. This can be attributed to the partial destruction of ordered pores. From Fig. 1b, all the samples exhibit the same characteristic peaks as the parent HM sample. Rather than HM/MCM-48(4) sample, the intensities of peaks decreased gradually with the increase in the weight amount of MCM-48.

**2.1.2.** Nitrogen adsorption-desorption isotherms. Nitrogen adsorption-desorption isotherms for different samples are shown in Fig. 2. The HM zeolite sample is characterized by a typical type I isotherms, which indicate its microporous structure. Similar to MCM-48, all the HM/MCM-48-*n* samples have a type IV adsorption-desorption isotherms, suggesting their mesoporous character. The adsorption capacity of the HM/MCM-48-*n* samples decreased with the increase of amount of HM. In spite of the same weight ratio of HM to MCM-48, the adsorption capacity of HM/MCM-48-4 is much higher than observed for the HM/MCM-48(4) sample, which may be attributed to its biporous structure.

Table 1 summarizes the physical properties of different samples. It can be seen that Si : Al molar ratio, total pore volume and the specific surface area of the



Fig. 1. (a) Low-angle and (b) wide-angle XRD patterns of (a) MCM-48, (b) HM/MCM-48-2, (c) HM/MCM-48-3, (d) HM/MCM-48-4, (e) HM/MCM-48-5, (f) HM/MCM-48(4), (g) HM.



Fig. 2. Liquid N<sub>2</sub> adsorption-desorption isotherms for (a) MCM-48, (b) HM/MCM-48-2, (c) HM/MCM-48-3, (d) HM/MCM-48-4, (e) HM/MCM-48-5, (f) HM/MCM-48(4), (g) HM.

HM/MCM-48-*n* samples decreased with increase in the weight amount of HM in the sample. Compared to the HM/MCM-48-4 sample, the specific surface area, Si: Al molar ratio, and total pore volume of HM/MCM-48(4) sample prepared by mechanical mixing was higher because of their independence between HM and MCM-48 zeolites.

**2.1.3.** NH<sub>3</sub>-TPD curves. Figure 3 shows NH<sub>3</sub>-TPD curves for different samples. Two ammonia desorption peaks, one at low temperature (503 K) and another at high temperature (773 K), were observed for all samples. The HM sample is mainly in weak acidity, whereas the MCM-48 is mainly in strong acidity. Compared to the MCM-48 sample, the weak acidity of HM/MCM-48-*n* samples has been promoted, and the acid strength of HM/MCM-48-*n* samples

increases with the increase in weight amount of HM zeolite. Compared to the HM/MCM-48(4) sample, the acid sites amount of HM/MCM-48-4 sample are much higher, especially the weak acidity, which is owing to the decrease of Al-OH in the structure of MCM-48 [25].

**2.1.4. FT-IR spectra.** FT-IR spectra of 2,4dimethylquinoline adsorbed on different samples are shown in Fig. 4. The band at 1645 cm<sup>-1</sup> can be assigned to the interaction between 2,4-dimethylquinoline and Brønsted acid sites [15]. From Fig. 4, the maximum band for HM zeolite and minimum band for MCM-48 sample at 1645 cm<sup>-1</sup> are observed, which indicates that Brønsted acid sites on HM zeolite are much higher than MCM-48 sample. The Brønsted acid sites would be promoted for different

Samples	$V_{\rm micro}  ({\rm cm}^3  {\rm g}^{-1})^{\rm a}$	$V_{\rm meso}  ({\rm cm}^3  {\rm g}^{-1})^{\rm b}$	$V_{\text{total}} (\mathrm{cm}^3\mathrm{g}^{-1})$	Average pore size, nm	$n(Si:Al)^{c}$	$S_{\rm BET}$ (m <sup>2</sup> /g)
MCM-48	0.06	0.71	0.92	3.59	43	973.07
HM/MCM-48-2	0.15	0.38	0.58	3.35	31	693.20
HM/MCM-48-3	0.16	0.33	0.52	2.93	28	618.67
HM/MCM-48-4	0.22	0.26	0.49	2.67	26	522.72
HM/MCM-48-5	0.25	0.19	0.46	2.65	25	488.09
HM/MCM-48(4)	0.24	0.23	0.51	2.83	28	550.17
HM	0.28	0.03	0.29	1.87	23	425.75

Table 1. Physical properties of different samples

<sup>a</sup> *t*-Plot method.

<sup>b</sup> BJH method.

<sup>c</sup> Measured by ICP-AES

HM/MCM-48-*n* samples with the weight amount of HM zeolite increasing. However, the band at 1645 cm<sup>-1</sup> of HM/MCM-48-*n* samples is lower than HM/MCM-48 (4) sample, which may be owing to the cap of MCM-48 on the surface of HM zeolite [15].

**2.1.5. SEM analysis.** SEM micrographs of different samples are shown in Fig. 5. It can be seen that MCM-48 sample consists from amorphous floccules and HM is composed of elliptic particles. The HM/MCM-48-n samples basically have the same morphology as the HM zeolite, but some flocculating substances on the surface can be observed due to the growth of MCM-48 on their surface. Meanwhile, the flocculating substances become less with the weight ratio of HM zeolite increasing.

**2.1.6. TEM analysis.** The TEM analysis for HM/MCM-48-4 sample is shown in Fig. 6. The translucent structure can be observed (Fig. 6a) at the edge of shadow and the lattice stripe of MCM-48 was

**Fig. 3.** NH<sub>3</sub>-TPD curves for (*a*) MCM-48, (*b*) HM/MCM-48-2, (*c*) HM/MCM-48-3, (*d*) HM/MCM-48-4, (*e*) HM/MCM-48-5, (*f*) HM/MCM-48(4), (*g*) HM.

clearly present when the scale was magnified to 20 nm, which is shown in Fig. 6b. Therefore, according to SEM, TEM, and FTIR results, we can conclude that MCM-48 was grown on the surface of HM zeolite.

# 2.2. Catalytic Tests

The catalytic performance of different samples in the alkylation of toluene with tert-butanol is summarized in Table 2. In all cases, the main products are identified as PTBT and *m-tert*-butyltoluene (MTBT). However, o-tert-butyltoluene (OTBT) cannot be found in the products; this is attributed to the sterical hindrance. 3,5-Di-tert-butyltoluene (DTBT) having two tert-butyl groups in the meta positions, is the minor byproduct of the reaction. It can be seen from Table 2 that toluene conversion is only 9.5% on the MCM-48 catalyst. Because it has higher concentration of acid sites, especially weak ones, toluene conversion of 18.4% can be obtained on the HM catalyst. Catalytic performance of HM/MCM-48-n catalyst is much higher than that of MCM-48, and toluene conversion can reach up to 21.2% on the HM/MCM-48-4, which may be owing to its appropriate BET surface, acidity and biporous structure. Compared to HM/MCM-48(4) catalyst, catalytic activity of HM/MCM-48-4 sample is higher because of its specific physicochemical properties, rather than simple mixture of HM and MCM-48. The selectivity of TBT on the HM zeolite is highest because of its smallest pore size. The selectivity towards PTBT increases with the weight ratio of HM zeolite increasing, whose pore size is close to the molecular diameter of PTBT. Because HM/MCM-48-4 catalyst shows the highest catalytic activity, the following studies on the effect of reaction conditions were performed using this catalyst.

# 2.3. Effect of Reaction Conditions

Figure 7a shows the effect of reaction temperature on the catalytic performance over HM/MCM-48-4 catalyst. Both toluene conversion and PTBT selectiv-



**Fig. 4.** FT-IR spectra of 2,4-dimethylquinoline adsorbed on (*a*) MCM-48, (*b*) HM/MCM-48-2, (*c*) HM/MCM-48-3, (*d*) HM/MCM-48-4, (*e*) HM/MCM-48-5, (*f*) HM/MCM-48(4), and (*g*) HM.



Fig. 5. SEM micrographs of (a) HM, (b) HM/MCM-48-2, (c) HM/MCM-48-3, (d) HM/MCM-48-4, (e) HM/MCM-48-5, and (f) MCM-48.



Fig. 6. TEM photos for HM/MCM-48-4 with different scales.

ity are affected severely by reaction temperature. A significant increase in toluene conversion from 15.6 to 21.2% can be obtained when reaction temperature was increased to 453 K. Upon further increase in reaction temperature, toluene conversion decreases, probably due to dealkylation of TBT at higher temperatures. It was probably on this account that a rise of TBT selectivity was obtained with the increase of reaction tem-

RUSSIAN JOURNAL OF PHYSICAL CHEMISTRY A Vol. 91 No. 9 2017

#### ZHIWEI ZHOU et al.

Catalysts	Toluene conversion, %	Distribution of products/%				S %	S %
		OTBT	MTBT	PTBT	DTBT	$S_{\text{TBT}}, \mathcal{M}$	SpTBT, 70
MCM-48	9.5	0	25.4	71.7	2.9	97.1	73.8
HM/MCM-48-2	13.7	0	23.2	74.8	2.0	98.0	76.3
HM/MCM-48-3	17.4	0	20.6	77.8	1.6	98.4	79.1
HM/MCM-48-4	21.2	0	20.0	78.7	1.3	98.7	79.7
HM/MCM-48-5	19.4	0	18.3	80.1	0.6	99.4	80.6
HM/MCM-48(4)	16.5	0	21.4	77.1	1.5	98.5	78.3
HM	18.4	0	18.2	81.5	0.3	99.7	81.7

Table 2. Catalytic performances of different samples for the alkylation of toluene with tert-butanol

Reaction conditions: W(toluene)/W(catalyst) = 10; calcination temperature of catalyst 523 K; n(toluene) : n(*tert*-butanol) : n(*n*-hexane) = 1 : 2 : 10; reaction temperature 453 K; initial pressure 1.0 MPa; reaction time 3 h.

 $S_{\text{TBT}}$  is the molar ratio of mono-tert-butyltoluene to TBT.  $S_{\text{PTBT}}$  is the molar ratio of PTBT to TBT.

perature. However, PTBT selectivity was declined as a result of the isomerization of PTBT into MTBT, which is more stable at higher temperatures [7]. PTBT selectivity of only 62.1% can be obtained at 493 K.

Figure 7b shows the influence of molar ratio of *tert*butanol to toluene on the catalytic performance of HM/MCM-48-4 catalyst. It can be seen from Fig. 7b that toluene conversion can reach up to 24.1% when the molar ratio of *tert*-butanol to toluene was 2. Because of oligomerization of the isobutene formed by dehydration of *tert*-butanol, carbonization and then covered the acid sites, a negative effect on toluene conversion was found when the molar ratio is more than 2. On the contrary, the PTBT selectivity increased slightly because of depressing of the isomerization of PTBT to MTBT.

The liquid phase alkylation of toluene with *tert*butanol with different catalyst loadings was investigated, and the results are shown in Fig. 7c. It can be seen that the catalyst loading affects both toluene con-



Fig. 7. Effect of reaction conditions on toluene conversion and PTBT selectivity (a) reaction temperature; (b) n(tert-buta-nol)/n(toluene); (c) W(catalyst)/W(toluene); (d) reaction time.

version and PTBT selectivity greatly. Toluene conversion can reach from 24.1 to 35.2% when W(toluene)/W(catalyst) is from 10 to 5. Toluene conversion kept constant with the catalyst loading further increasing because the alkylation of toluene with *tert*-butanol is a continuous and reversible reaction. PTBT selectivity was declined with the catalyst loading increasing as a result of the dealkylation of DTBT and the isomerization of PTBT [25].

The influence of reaction time on the catalytic performance of HM/MCM-48-4 was carried out, and the results are shown in Fig. 7d. Toluene conversion increased as the reaction time was prolonged, and it reaches up to 41.4% when the reaction time is 5 h. Toluene conversion kept constant when the reaction time is more than 5 h because the alkylation of toluene with *tert*-butanol was a continuous and reversible reaction, which suggests that the reaction reaches its steady state. PTBT selectivity was dropped when the reaction time was prolonged owing to the dealkylation of DTBT and the isomerization of PTBT to MTBT.

# CONCLUSIONS

The HM/MCM-48-*n* samples were successfully prepared under the hydrothermal conditions, and the catalytic performance was investigated in the *tert*-butylation of toluene with *tert*-butanol. TEM and FT-IR spectra of 2,4-dimethylquinoline-adsorbed results showed that the HM/MCM-48-*n* samples are formed by growth of MCM-48 on the surface of HM zeolites. HM/MCM-48-4 sample shows a higher catalytic activity than HM/MCM-48(4) prepared by the mechanical mixing owing to its biporous structure and larger acid amount, especially weak acidity. The reaction conditions on the catalytic performance of HM/MCM-48-4 sample are discussed, and toluene conversion 41.4% and PTBT selectivity 73.5% can be obtained.

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