

ALKYLATION OF TOLUENE WITH METHANOL OVER MCM-22 AND MCM-36

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ABSTRACT. MCM-36 materials were prepared by swelling the layered MCM-22 precursors with large organic molecules and then pillaring the resulting material with polymeric silica. The BET surface area of MCM-36 was 2.5 to 3 times higher than that of MCM-22. The catalytic activity and selectivity of both MCM-36 and MCM-22 were investigated in the gas-phase alkylation of toluene with methanol at reaction temperatures ranging from 498 to 673K. The methylation of toluene produces a mixture of xylenes as main products. The influence of reaction temperature, pulse number, and toluene/methanol ratio upon the conversion of toluene and selectivities of the products were investigated. The superior catalytic performance of MCM-36 compared with MCM-22 for this reaction indicates that the open mesoporous structure can be successfully utilized to make acid sites of the layers accessible to large molecules.

1. Introduction

The gas phase alkylation of toluene with methanol over zeolite catalysts to xylenes was reported by Venuto in the early sixties [1]. This reaction could be of great interest to industry as a potential source of p- and o-xylene provided that the loss of methanol in side reactions, clearly seen from the literature data [2], is eliminated or, at least, greatly suppressed.

Various zeolites, such as ZSM-5, REY, SAPOs were tested as catalysts in the alkylation of toluene with methanol [3-5]. It is now accepted that the alkylation reaction proceeds through a Rideal-mechanism [6], where the Bronsted acid sites are the active centers and the reaction intermediates are carbenium ions [1].

The previous studies showed that the selectivity in this reaction is strongly influenced by the acidity strength and the pore size of the catalyst. Thus, medium pore zeolites such as M-ZSM-5 (M = B, Cr, Fe), which possess only weak and medium acid sites, are very selective towards p-xylene in the alkylation of toluene with methanol [7].

In our study two new zeolites, MCM-22 and MCM-36, have been tested as catalysts in gas phase alkylation of toluene with methanol. Zeolite MCM-22 combines the properties of 10 MR (membered rings) and 12 MR porosity [8]. The narrow access to the 12 MR channels through the 10 MR openings, seriously hampering the diffusion of bulky molecules. To avoid this limitation, the pillared

zeolite MCM-36 has been developed [9-10]. This material combines the benefits of microporous, crystalline zeolite layers with those of the pillared mesoporous structures. Due to this doubly porous structure, an increased accessibility of parts of the crystalline surface, a high thermal stability, and a large sorption capacity, these materials are promising catalysts for the conversion of hydrocarbons, especially in reactions involving larger, bulkier molecules [11].

2. Experimental

MCM-22 and MCM-36 were synthesised according the methode reported elsewhere [12]. The materials were characterized by various methods: XRD (Philips PW 1800 diffractometer and STOE STADI-P, $\text{CuK}\alpha$), nitrogen adsorption (Micromeritics ASAP 2100, sample activation at 523K for 18h), scanning electron microscopy (SEM, PHILIPS XL,30).

The catalytic reactions using toluene and methanol (high purity reagents) were run in a pulse type microreactor containing 30 mg of catalyst with particle size 0.25-0.43 mm. The microreactor consisted in a stainless steel tube (o.d. 6 mm, i.d. 3.5 mm and length 80 mm) with catalyst particles packed between quartz plugs. Prior to reaction, the catalyst was activated under airflow at 500°C for 3h, followed by cooling to the reaction temperature under nitrogen flow (26 ml/min, 140 kPa). Samples of 1.0 μl of the reagents were injected at constant temperature and the reaction products were analyzed using an on-line GC equipped with FI detector.

3. Results and discussion

3.1. Characterization of the catalysts. The first data concerning the synthesis of MCM-22 have been reported by the scientists from Mobil in 1990 [13]. The structure of MCM-22 has been shown to consist of layers linked together along the c-axis by oxygen bridges and contains two independent pore systems [14-15]. Within the layers are two-dimensional sinusoidal 10-M ring channels, and between two adjacent layers are 12-M ring supercages ($\sim 0.71 \times 0.71 \times 1.82$ nm) communicating with each other through 10-M ring apertures.

The unusual structure of zeolite MCM-22 is formed from a layered precursor designated as an MCM-22(P) [13], which is able to condensate the silanol groups present on the layer surfaces by calcination, and leading to the formation of the 3D structure shown in Figure 1.

The pillared zeolite MCM-36 can be prepared from the same MCM-22(P) starting materials, using large molecules, such as cethyltrimethylammonium chloride (CTMAC) and polymeric silica (Figure 1).

We have synthesized a MCM-22(P) samples with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 100. The diffraction pattern of this material agrees well with those previously reported [16](Figure 2a). The calcined sample gives sharper reflections than as-synthesized samples, as shown in Figure 2b, and the (001) reflection characteristic to the layered structure of MCM-22(P) disappears. The high crystallinity and phase purity of the MCM-22 zeolite could be considered as prove for the quality of its precursor.

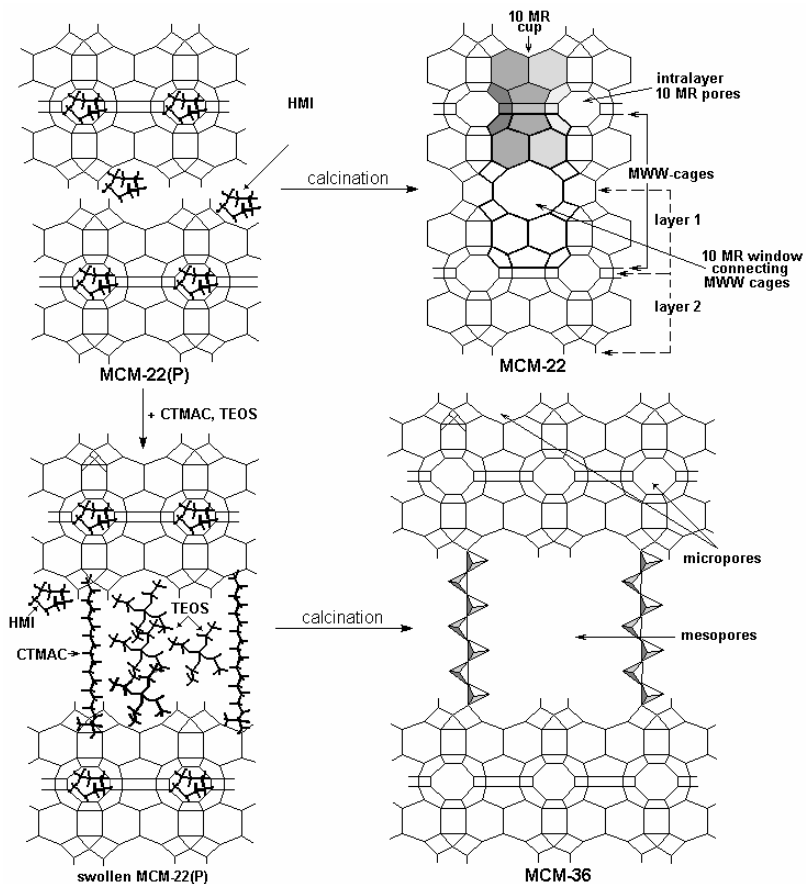


Figure 1. Schematic representation of MCM-22(P), MCM-22 and MCM-36 structures.

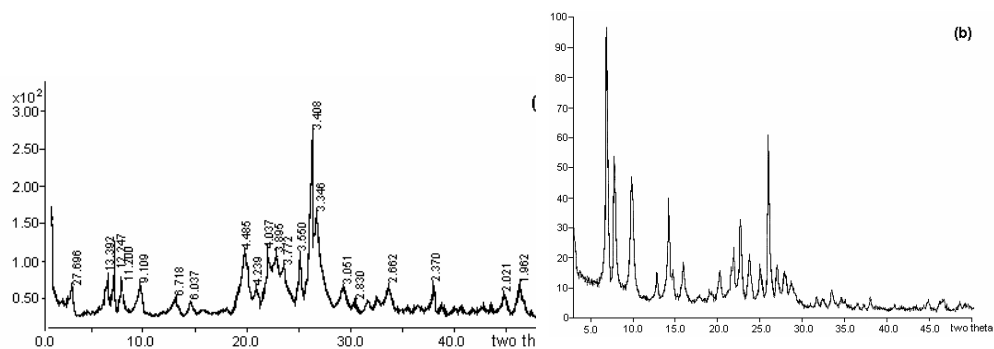


Figure 2. Powder XRD patterns of the (a) MCM-22(P) sample and (b) the calcined sample (MCM-22) synthesized from the mixture with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 100.

MCM-36 material was prepared by swelling the layered MCM-22 precursor with large molecules of CTMAC and then pillaring the resulting material with polymeric silica. As known, in the MCM-36 phase, the polymeric silica as pillars is formed during the hydrolysis and condensation of silicates from tetraethylorthosilicate. The hydrolysis reaction replaces the ethoxy groups with hydroxyl groups. In the next stage, the condensation reactions involving the silanol groups produce siloxane bonds, leading initially to oligomeric and polymeric structures.

Depending on the conditions, the final structures of the polymeric SiO_2 can be formed as nearly linear polymeric structures or three-dimensional branched structures.

The XRD pattern of the MCM-36 sample is shown in Figure 3. All peaks observed correspond perfectly to those of the MCM-36 material reported previously [12].

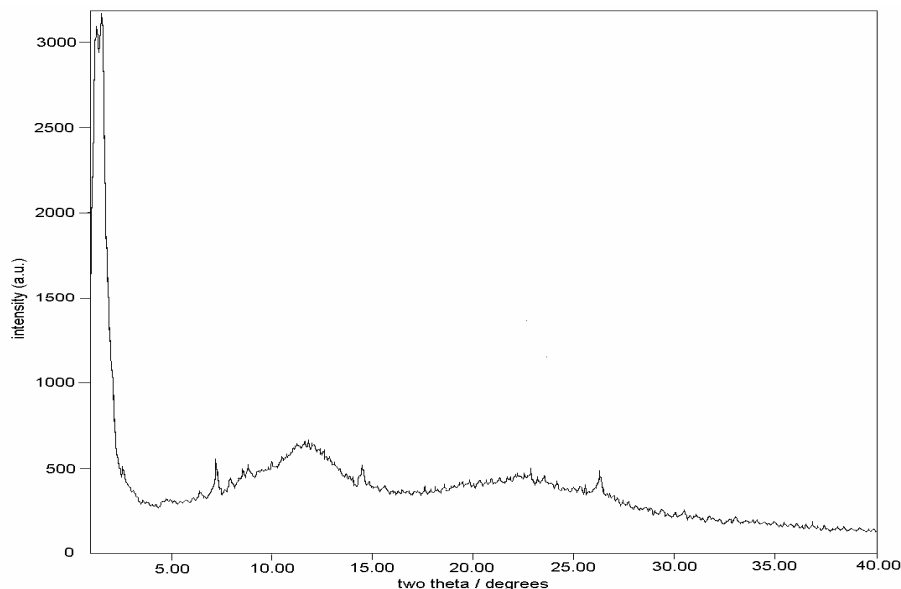


Figure 3. Powder X-ray diffraction pattern of MCM-36.

Compared with the pattern of MCM-22(P) in Figure 2, the characteristic 002 plane reflection at $2\theta \sim 6.6^\circ$ disappears upon pillaring. On the other hand, an intense low-angle reflection appears at 2θ between 1 and 2° , which corresponds to a d -spacing of 5.9 nm. This represents the new c -parameter of the unit cell. The d -value includes both the c -parameter of the unit cell of MCM-22 and the spacing distance between the layers of MCM-36. Therefore, the distance between two layers in MCM-36 can be calculated by subtracting the thickness of the layer (c -parameter of MCM-22 is equal to 2.51 nm [14]). The values for the sample obtained suggest an average interlayer distance of 3.4 nm.

The morphologies of crystals, determined by SEM, are mostly platelets of approximately 2 μm diameter and 0.1-0.2 thickness bunched into 4-5 μm particles.

The textural properties of the calcined MCM-22 and MCM-36 samples were measured by nitrogen adsorption. The pure MCM-22 sample gives a specific surface area (S_t) of 465 $\text{m}^2 \text{g}^{-1}$ and a total pore volume of 0.28 $\text{cm}^3 \text{g}^{-1}$ which are typical for this type of zeolite [17]. The higher specific area of MCM-36 (807 $\text{m}^2 \text{g}^{-1}$) sample than that of MCM-22 (465 $\text{m}^2 \text{g}^{-1}$), approximately twice, without doubt demonstrates that MCM-36 does not have pore system as MCM-22.

The external surface areas were estimated by using t -plots. Therefore, for MCM-22 zeolite resulted that the micropores are dominant ($V_{\text{micro}} = 0.12 \text{ cm}^3 \text{g}^{-1}$), while for the pillared structure of MCM-36 the mesopores are dominant ($V_{\text{meso}} = 0.497 \text{ cm}^3 \text{g}^{-1}$). The external surface area, S_{ext} , in the larger mesopores was estimated at about 76 $\text{m}^2 \text{g}^{-1}$. From a tubular model as $4V_{\text{meso}}/(S_t - S_{\text{ext}})$, the average mesopore size of approximately 3nm was estimated, and this value satisfactorily agrees with XRD data.

3.2. Alkylation of toluene with methanol. During the alkylation reaction of toluene with methanol on acid catalysts, para- and ortho-xylene are mainly formed, especially at low levels of conversion. Moreover, besides the primary alkylation, consecutive reactions, such as xylenes isomerization and toluene polyalkylation giving trimethylbenzenes (TMB) and tetramethylbenzenes (TeMB) can also occur. In the case of zeolites, the competition between these reactions and the selectivity of the alkylation process depends of both reaction conditions (temperature, contact time, pressure, etc) and textural properties of catalyst (shape and size of pores, external surface area, etc).

3.2.1. Effect of reaction temperature. Table 1 summarizes the main results of the alkylation reaction between toluene and methanol over MCM-22 and MCM-36, obtained in the range temperature of 498-673K, with a toluene/methanol molar ratio = 1.

Table 1.

The main results of the alkylation of toluene with methanol

	MCM-22			MCM-36		
Reaction temperature, K	498	548	673	498	548	673
Toluene conversion, %mol	22.4	32.5	46.5	7.9	19.1	35.7
Alkylated products, %mol						
Xylenes	18.13	22.49	30.3	7.35	13.42	24.06
Trimethylbenzenes	4.24	9.67	14.57	0.58	3.87	9.36
Tetramethylbenzenes	1.03	5.23	8.56	0.43	1.87	6.45
Xylenes selectivity, %						
p-xylene	72.14	52.69	30.39	28.29	29.95	29.42
m-xylene	16.76	26.76	50.51	17.55	22.20	43.51
o-xylene	11.08	20.54	19.09	54.14	47.83	27.01
TMBs selectivity, %						
1,3,5-TMB	0	6.10	20.59	0	0	19.01
1,2,4-TMB	97.40	86.24	66.98	55.17	59.68	69.01
1,2,3-TMB	2.60	7.65	12.42	44.83	40.32	11.96

These data lead to the following remarks:

- (i) As expected, the conversion of toluene increases with the reaction temperature. Compared to MCM-22, MCM-36 showed a lower toluene conversion for all temperatures.
- (ii) A high selectivity for the ring alkylation of toluene towards xylenes was obtained under our reaction conditions. However, over both zeolites, the amount of polyalkylated products, such as TMB and TeMB, increases when the reaction temperature increases.
- (iii) The reaction temperature affects the distribution of xylene isomers. But, this distribution also depends on the catalyst type. Thus, at low temperature, MCM-22 catalyst showed a high para-selectivity (more than 70% p-xylene in the mixture of xylenes), while MCM-36 leads to o-xylene as major isomer (about 55%). An important amount of p-xylene (amount 30%) was also obtained over MCM-36. It is known that the para- and ortho-isomers are the primary products of the electrophile substitution reactions.

The difference in behavior of MCM-22 and MCM-36 can be explained taking into account their porosity. The selectivity seems to be a consequence of product shape selectivity. Thus, in the case of MCM-22, the 10 MR windows of about 0.52 nm in diameter cause great hindrances in the diffusion of o-xylene isomer, while p-xylene, a "linear" molecule, can easily pass through these windows. On the contrary, the diffusion of products is not influenced by the mesopores of MCM-36, and the xylene isomer composition is similar to those of non-shape-selective catalysts. The ortho-rich product distribution is obtained as required by the principles of aromatic electrophilic substitution [18].

As can be seen from table 1 data, the increase in the reaction temperature leads to a decrease of both o- and p-xylene, while m-xylene increases and at 673K the xylene distribution becomes close to the thermodynamic equilibrium (50% m-xylene, 25% p-xylene and 25% o-xylene). At a high reaction temperature, the primary products p- and o-xylene are involved into the rearrangement reaction towards m-xylene, the highest thermodynamic stable dimethylbenzene isomer.

3.2.2. Effect of the toluene/methanol ratio. Some catalytic tests were performed over MCM-22 and MCM-36 at 498K, using three toluene/methanol initial ratio. It can be seen from Table 2 that with increase in toluene/methanol ratio, the selectivity to xylene increases too. An equimolar reagent ratio leads to the highest conversion of toluene.

Table 2.

The effect of toluene/methanol ratio on the catalysts behavior

Toluene/methanol, molar ratio	MCM-22			MCM-36		
	0.5	1	2	0.5	1	2
Toluene conversion, %mol	22.6	30.2	13.7	10.7	12.1	7.3
Xylene selectivity, %	67.4	77.5	81.1	86.7	90.0	90.3
TMB selectivity, %	32.6	22.5	18.9	13.3	10.0	90.7

3.2.3. Effect of time on stream. Generally, the activity and selectivity of zeolites change during the reactions of organic compounds, because of progressive blocking of acid sites and pores by coke. The rate of the coke formation strongly depends on the strength of acid sites and the pore size of catalyst. As can be seen from Figure 4, the catalytic activity of medium pore MCM-22, expressed in term of toluene conversion progressively decreases when the number of pulses increases. The selectivity to xylene decreases too. On the contrary, large pore MCM-36 shows a very high stability to coking. Thus, toluene conversion, xylenes and TMBs selectivities remain almost unchanged after 40 pulses (Figure 4).

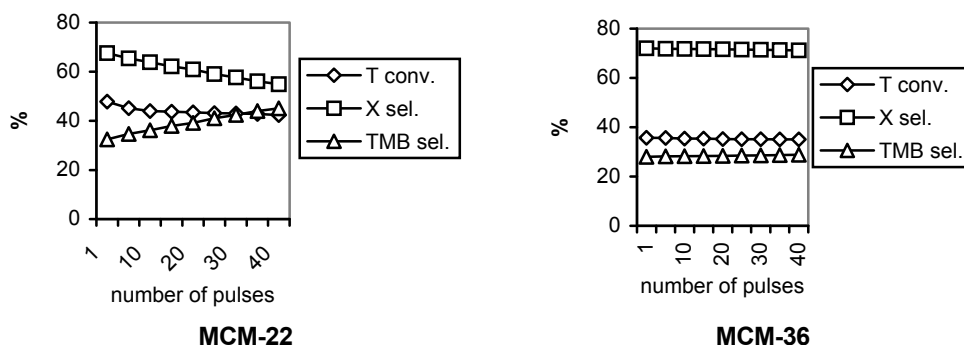


Figure 4. Variation of toluene conversion (T conv.), xylene selectivity (X sel.) and TMB selectivity (TMB sel.) as function of the number of pulses for MCM-22 and MCM-36, at 673K.

4. Conclusion

As stated before, both MCM-22 and MCM-36 zeolites are active catalysts in the gas phase alkylation of toluene with methanol. At a low reaction temperature, the selectivity to p- and o-xylene, the primary alkylation products, was very high over tested catalysts. Large pore MCM-36 is more stable to coking than medium pore MCM-22.

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