

# Synthesis, characterisation and catalytic performance of HMCM-22 of different silica to alumina ratios

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## Abstract

MCM-22 with different Si/Al ratios were synthesised using hexamethylenimine as the structure directing agent. The synthesised materials were characterised by XRD, BET, TGA, FT-IR, DRIFT and SEM techniques. The catalytic activity of the materials was examined in the vapour phase *tert*-butylation of phenol using *tert*-butyl alcohol as the alkylating agent. The influence of reaction parameters such as reaction temperature, reactant feed ratio, WHSV and time on stream was studied and the results are correlated with physicochemical characteristics of the catalysts. 4-*tert*-Butyl phenol (4-TBP) was obtained with high selectivity. It is presumed that the 10 membered ring channel present in MCM-22 might be the cause for selective production of 4-TBP.

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**Keywords:** MCM-22; Zeolite; MWW; Phenol; *tert*-Butylation

## 1. Introduction

Zeolites are finding extensive applications as catalysts in petrochemical and fine chemical industries. In recent years, MCM-22 has been used as a promising catalyst for alkylation and isomerisation reactions. The structure of MCM-22 has been coded by the International Zeolite Association (IZA) structure commission as MWW. MCM-22 possesses two independent pore systems [1]. The first consists of two dimensional channels with 10 membered ring openings while the other consists of large super cages of 12 membered ring with dimensions of 7.1 Å × 7.1 Å × 18.2 Å. The super cages stack one above the other through double prismatic six membered rings and are accessed by slightly distorted elliptical 10 membered ring connecting channels. MCM-22 zeolites are very thin plates with large external surface area [2]. The protonic sites located in the channel and super cages played a significant role in

many catalytic reactions, in particular for the selective and steady production of ethyl benzene and cumene by benzene alkylation [3–5]. The catalytic reaction of phenol with *tert*-butyl alcohol, isobutene or methyl-*tert*-butyl ether is important because C-alkylated products such as 4-*tert*-butylphenol, 2,4-di-*tert*-butylphenol and 2,6-di-*tert*-butylphenol are commercially significant. 4-TBP has wide spread applications in manufacturing of varnish and lacquer resins, antioxidant for soaps, ingredient in de-emulsifiers and motor oil additives while DBPs are used in the production of substituted triaryl phosphates, antioxidants and other consumable items [6]. Thus, *tert*-butylation of phenol in the gas- or liquid-phase has been studied using different zeolites such as faujasite Y, dealuminated Y [7–10], beta [11,12] and mordenite [13]. The purity of the product is important for all such applications. Hence, selective conversion of phenol to a desired product has been continuous research interest in the alkylation of phenol. The present study reports the synthesis of MCM-22 with different Si/Al ratios and their catalytic activity in the *tert*-butylation of phenol using *tert*-butyl alcohol as the alkylating agent with specific objective of desired product.

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## 2. Experimental

### 2.1. Materials

Levasil (Aldrich) and aluminium sulphate (Merck) were used as the sources for silicon and aluminium, respectively. Hexamethylenimine (HMI, 99%, Aldrich) was used as the structure directing agent. Other chemicals such as sodium hydroxide, sulphuric acid, phenol and *tert*-butyl alcohol were purchased from Merck and used as such without further purification.

### 2.2. Preparation of catalysts

Sodium hydroxide (6 g) was dissolved in hexamethylenimine (12.4 g) and water (60.5 g). This solution was labeled as 'A'. This solution was slowly added to 50.7 g Levasil (30 wt% SiO<sub>2</sub> in H<sub>2</sub>O) under stirring for few minutes and continued until a homogeneous solution was obtained. The whole mixture was labeled as 'B'. Aluminium sulphate (3.5 g) was dissolved in 87.5 g of water and this solution was labeled as 'C'. The solution B was added drop by drop to solution C with continuous stirring for about 30 min. Finally sulphuric acid (4.5 g) was added dropwise to the solution mixture with simultaneous stirring and the stirring continued for about 10 min. The whole solution was transferred to 250 ml stainless autoclave and kept in an oven at 150 °C for 4 days under rotation. After 4 days, the autoclave was cooled to room temperature and then the solid material was filtered, washed several times with deionised water and dried at 80 °C overnight. The solid material was calcined at 540 °C for 6 h by stepwise heating under oxygen atmosphere.

MCM-22 zeolite is converted into H-form by the following procedure: MCM-22 zeolite and 1 M NH<sub>4</sub>NO<sub>3</sub> solution (15 ml/g of zeolite) were placed in a round bottom flask fitted with an air condenser. The mixture was stirred at 80 °C for 24 h. Then the material was filtered under suction and washed with distilled water. The filtered material was dried at 120 °C for 6 h. The dried material was once again treated with 1 M NH<sub>4</sub>NO<sub>3</sub> by adopting the same procedure. This cycle was repeated thrice in order to achieve maximum exchange of Na<sup>+</sup> ion. The ammonium form of MCM-22 was converted into H-form by calcination in air at 550 °C for 6 h.

### 2.3. Characterization

The powder X-ray diffraction patterns of calcined materials were recorded on a PANalytical X'pert PRO diffractometer using Cu K $\alpha$  ( $\lambda = 0.154$  nm) radiation. The diffractograms were recorded in the  $2\theta$  range 5–50° in steps of 0.02° with a scan rate of 1.2° per min and count time of 20 s at each point. The surface area and pore volume were measured by nitrogen adsorption at –196 °C using SMARTSORB 92/93 from Smart Instruments Company, India. The sample was degassed at 200 °C for 2 h under nitrogen atmosphere prior to analysis. Surface area and pore volume of the catalyst were estimated by the built-in software in the instrument. Al and Si contents in HMCM-22 samples were determined using an atomic absorption spectrometer (AAS) (Hitachi Z 7000 Zeeman polarised instrument). The

calcined samples (0.1 g) were dissolved in a mixture containing 4 ml HCl and 2 ml HNO<sub>3</sub>. This solution was diluted to 100 ml with deionised water in a standard flask. FT-IR spectra of the materials were recorded on a Nicloet (Avatar 360) FT-IR spectrophotometer using KBr pellet technique. About 15 mg of the sample was pressed (under a pressure of 2 tonnes/cm<sup>2</sup>) into a self-supported wafer of 13 mm diameter. This pellet was used to record the infrared spectra in the range 4000–400 cm<sup>-1</sup>. The *in situ* DRIFT spectra were recorded in a Nicolet (Avatar 360) FT-IR spectrophotometer equipped with a high temperature vacuum chamber. About 15 mg of powdered catalyst was heated under vacuum (10<sup>-5</sup> mbar) at 250 °C and then cooled to room temperature. Pyridine was adsorbed at the same temperature and allowed to equilibrate. The catalyst was then evacuated under vacuum (10<sup>-5</sup> mbar) at 150 °C for 30 min. The sample was then cooled to room temperature and the spectrum was recorded. Thermogravimetric analysis was carried out on a Perkin-Elmer TG/DTA system under nitrogen atmosphere in the temperature range 50–700 °C with a heating rate of 10 °C min<sup>-1</sup>. The size and morphology of HMCM-22(54) sample was recorded using a scanning electron microscope (SEM) (JEOL 640). The samples were sputtered with gold (ca. 10 nm) to reduce the effect of charging.

### 2.4. Catalytic studies

*tert*-Butylation of phenol was carried out in a fixed-bed, flow-type reactor made of Borosil glass tube of length 40 cm and internal diameter 2 cm. About 0.5 g of catalyst placed in the middle of the reactor tube was heated to the reaction temperature with the help of a tubular furnace controlled by a digital temperature controller cum indicator. Reactants were fed into the reactor using a syringe infusion pump that could be operated at different flow rates. The bottom of the reactor tube was connected to a coiled condenser and a receiver to collect the products. The liquid products were analysed with a gas chromatograph (Shimadzu GC-17A) using DB-5 capillary column equipped with flame ionization detector. Further, the products were also identified using a GC-MS (Perkin-Elmer) Auto System XL gas chromatograph equipped with a mass spectrometer (Turbo) with helium as the carrier gas.

## 3. Results and discussion

### 3.1. Characterisation

The XRD patterns of H form of calcined MCM-22 zeolite of Si/Al ratios 27, 54 and 76 are shown in Fig. 1. Distinct patterns are observed for MCM-22(27) and MCM-22(54) and the  $2\theta$  values of the patterns are comparable to those reported in the literature [14]. But the pattern of MCM-22(76) reveals slight decrease in the crystallinity. Hence, gel composition with Si/Al ratio 76 and above might not be convenient to synthesis MCM-22. Thus, this study suggested that the workable range of Si/Al ratio for good synthesis of MCM-22 lies between 27 and 76. MCM-22 with Si/Al ratio less than 27 does not yield MCM-22 as reported by Okumura et al. [14]. The Si/Al ratio adopted in

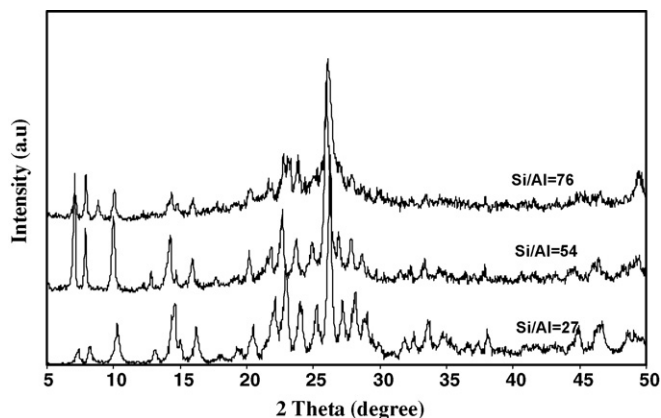


Fig. 1. XRD patterns of calcined HMCM-22 of different Si/Al ratios.

Table 1  
Textural properties of HMCM-22

Catalyst	$n\text{Si}/n\text{Al}$		$A_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )
	Gel	Product		
HMCM-22(27)	25	27	460	0.52
HMCM-22(54)	50	54	452	0.60
HMCM-22(76)	75	76	440	0.65

the present study lies in the range reported earlier. The elemental composition of HMCM-22 materials is presented in Table 1. In all cases, the Si/Al ratio of synthesised materials is higher than Si/Al ratio taken in the synthesis gel though the difference is not very significant. The surface area and pore volume of calcined HMCM-22 are shown in Table 1. The difference in the surface area of the materials is not significant though they differ in their aluminium contents.

The mid infrared FT-IR spectra of as-synthesised HMCM-22(27), (54) and (76) are shown in Fig. 2. All the three spectra show characteristic peaks for MCM-22 as reported earlier. The weak and broad envelope between  $2500$  and  $3700\text{ cm}^{-1}$  is

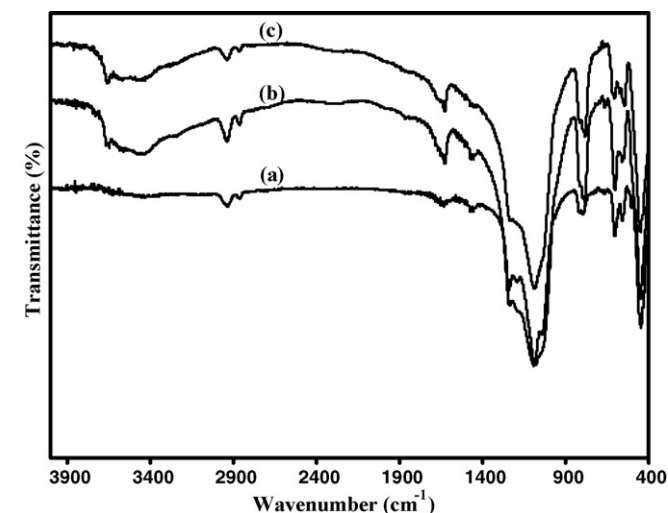


Fig. 2. FT-IR spectra of as-synthesised HMCM-22 with Si/Al ratio: (a) 27, (b) 54 and (c) 76.

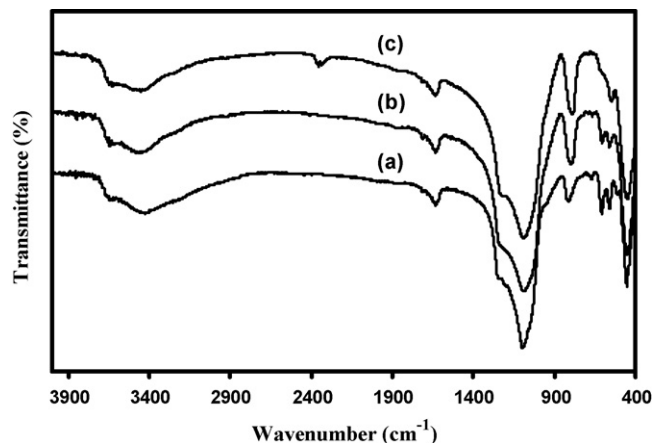


Fig. 3. FT-IR spectra of calcined HMCM-22 with Si/Al ratio: (a) 27, (b) 54 and (c) 76.

assigned to OH stretching of defective Si–OH groupings and water. This envelope appears with minimum intensity for MCM-22(27) which clearly indicates that MCM-22(27) may possess minimum defective Si–OH groupings. The presence of water is confirmed by its  $\text{OH}_2$  bending at about  $1630\text{ cm}^{-1}$ . The peaks appear just below  $3000\text{ cm}^{-1}$  are due to  $\text{CH}_2$  vibration of the locked-in template and their corresponding bending modes appear as a weak peak at about  $1410\text{ cm}^{-1}$ . The framework asymmetric vibrations produce their characteristic intense broad peak between  $900$  and  $1400\text{ cm}^{-1}$ . The corresponding symmetric modes appear close to  $900\text{ cm}^{-1}$ . The peaks appear below  $900\text{ cm}^{-1}$  are due to bending modes. The mid infrared spectra of calcined MCM-22(27), (54) and (76) are shown in Fig. 3. These spectra carry all the essential characteristics as that of Fig. 2 except the peaks due to  $\text{CH}_2$  vibrations of template and its bending mode. The complete loss of template as a result of calcination is clearly evident from the spectra. The hydrophilic nature of the catalysts is also evident from the broad envelope in the higher wavenumber region.

The results of thermogravimetric analysis of as-synthesised MCM-22(27), (54) and (76) are shown in Fig. 4. The tem-

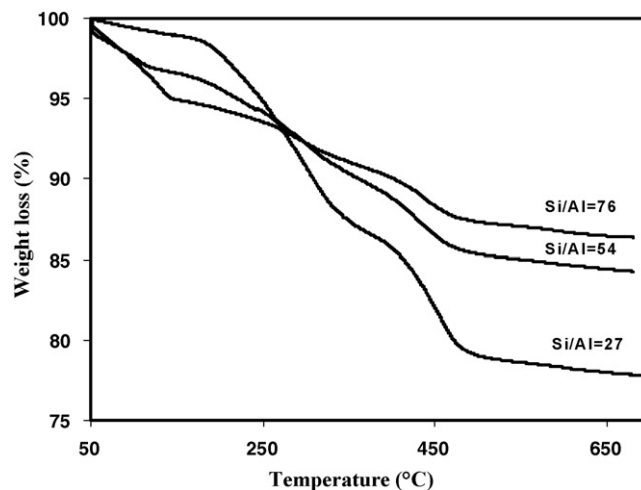


Fig. 4. TGA curves of as-synthesised HMCM-22 with different Si/Al ratios.

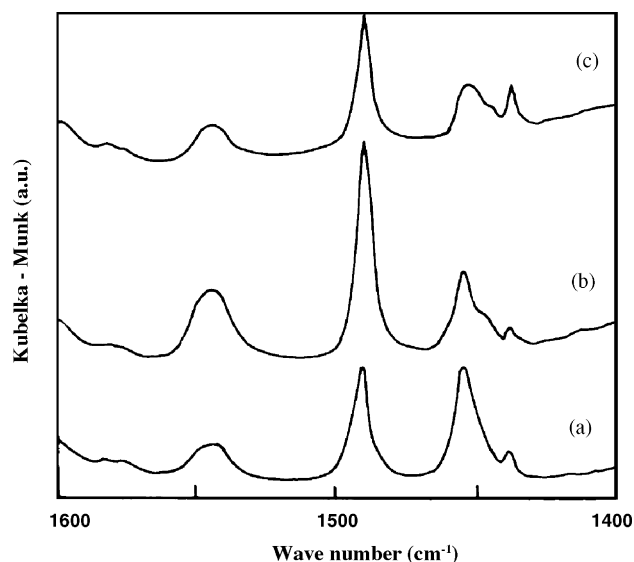


Fig. 5. DRIFT spectra of pyridine adsorption over (a) HMCM-22(27), (b) HMCM-22(54) and (c) HMCM-22(76).

plate degradation occurs in two stages between 150 and 475 °C. The degradation again appears to follow the same mechanism in all the materials. The percentage weight loss increases in the order MCM-22(27) > MCM-22(54) > MCM-22(76). As this order is the same as that of aluminium content, entrapment of hexamethylenimine template inside the channel depends on the aluminium content. The weight loss occurs below 150 °C is due to desorption of water. The *in situ* DRIFT spectra of pyridine adsorbed catalysts are shown in Fig. 5. The peak at 1450 cm<sup>-1</sup> is due to pyridine adsorbed on Lewis acid sites. Pyridine adsorbed on Bronsted acid sites give its peak at 1550 cm<sup>-1</sup>. The combination of both gives a peak at 1490 cm<sup>-1</sup>. The literature reports revealed that MCM-22 with low Si/Al ratio is difficult to synthesise [14]. It is also reflected by Lewis acid sites whose intensity decreases with increase in Si/Al ratio. MCM-22(27) gives higher intensity for pyridine adsorbed on Lewis acid sites than MCM-22(76) and the intensity due to MCM-22(54) lies in between them. The difficulty in synthesising MCM-22 with high Si/Al ratio is again observed in this study. It is because of this, the intensity of the peak at 1450 cm<sup>-1</sup> is less but its XRD pattern gives less intense peaks than MCM-22(54). The SEM pictures of MCM-22 are shown in Fig. 6. There are aggregates of platelets with irregular shape. The platelets are not seen to possess well-defined morphology. Such types of platelets for MCM-22 were also reported by Unverricht et al. [15] and Dahlhoff et al. [16]. Since most of the platelets appear to possess more than 1 μm size, there are well defined XRD pattern for this material than MCM-22(27) and (76). The intensity of the pattern is also higher than others.

The vapour phase *tert*-butylation of phenol was studied over HMCM-22(27), (54) and (76) catalysts at 150, 175, 200, 225, 250 and 275 °C with a feed ratio 1:3 (phenol: *tert*-butyl alcohol) and WHSV 5.13 h<sup>-1</sup>. The products were 2-*tert*-butylphenol (2-TBP), 4-*tert*-butylphenol (4-TBP) and 2,4 di-*tert*-butylphenol

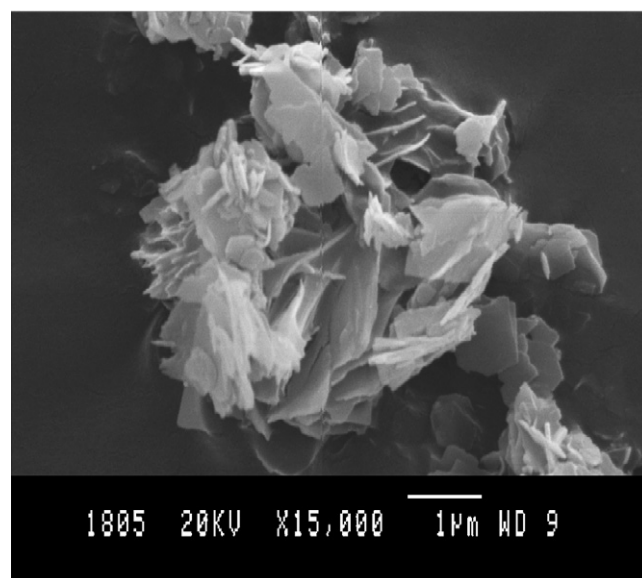
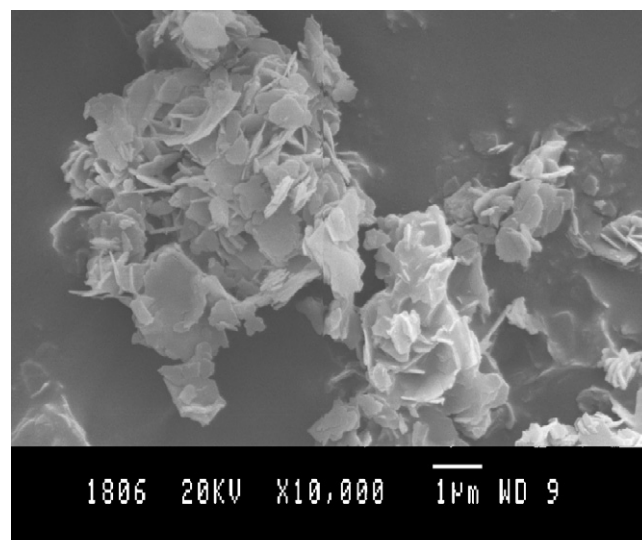


Fig. 6. SEM images of calcined HMCM-22(54).

(2,4-DTBP). The phenol conversion and products selectivity are presented in Table 2. The phenol conversion increases from 58 to 77% when the temperature increases from 150 to 175 °C and further increase of temperature decreases the conversion. The decrease in conversion above 175 °C is due to coke formation. The order of activity of catalyst is HMCM-22(54) > HMCM-22(76) > HMCM-22(27). The order of activity of catalysts implies that it is not only the density but also the strength of acid sites is important to account for the trend of activity of the catalysts. Actually HMCM-22(76) should exhibit more active than HMCM-22(54), as it has high silica to alumina ratio. But the reversal of activity illustrates requirement of enough density of acid sites in addition to acid strength. The selectivity of 2-TBP is less than other products over all the catalysts. This observation suggests the reaction of chemisorbed *tert*-butyl cation and phenol on the catalyst surface. Chemisorbed phenol precludes its *ortho* position for electrophilic reaction since alkyl cations cannot be closer to the *ortho* position of aromatic

Table 2  
Effect of temperature on *tert*-butylation of phenol over HMCM-22

Catalyst <sup>a</sup>	Temperature (°C)	Phenol conversion (wt%)	Products selectivity (wt%)		
			2-TBP	4-TBP	2,4-DTBP
HMCM-22(27)	150	58	3	59	38
	175	77	5	82	13
	200	51	5	92	3
	225	35	6	91	3
	250	14	–	100	–
	275	8	–	100	–
HMCM-22(54)	150	78	4	56	40
	175	85	4	76	20
	200	69	6	83	11
	225	46	7	88	5
	250	32	6	94	–
	275	17	–	100	–
HMCM-22(76)	150	70	8	40	52
	175	78	6	77	17
	200	61	7	80	13
	225	43	4	73	23
	250	24	10	90	–
	275	12	–	100	–

Phenol: *tert*-butyl alcohol feed ratio: 1:3, WHSV: 5.13 h<sup>-1</sup>.

<sup>a</sup> Catalyst weight: 0.5 g.

ring. But the *para* position can be close to any *tert*-butyl cation. The aromatic ring of chemisorbed phenol is actually planar with respect to channel surface and hence the selectivity of 4-TBP is higher than other products as the *para* position alone is the ultimate one for electrophilic attack.

In addition, the selectivity of 4-TBP is equal to or slightly less than 100% at higher temperature as the coke formation might reduce the pore size and confer selectivity to *para* products. But the conversion is less at 275 °C though the selectivity to 4-TBP is 100% over all the catalysts. HMCM-22(27) Exhibits 100% selectivity to 4-TBP at 250 °C but the conversion is only 14%. The selectivity to 2,4-DTBP decreases with the increase in temperature due to pore size contraction as a result of coke formation. Nearly similar behaviour is observed over all the catalysts. This study concludes that HMCM-22(54) is more active than others in the alkylation of phenol. The selectivity to 4-TBP is about 6% less over HMCM-22(54) than HMCM-22(27) at 175 °C, but based on the high conversion HMCM-22(54) is considered to be more active one. Based on the disproportionation of toluene over MCM-22 as reported by Wu et al. [17], it could be predicted that 10 MR ring channel might be more suitable to produce 4-TBP selectively. The super cage may permit polyalkylation of phenol but the product cannot just escape through the micropore as only 2,4 or 2,4-isomers alone can escape through the pore.

The effect of feed ratio on phenol conversion and product selectivity was studied over HMCM-22(54) at 175 °C and WHSV of 5.13 h<sup>-1</sup>. The phenol conversion and products selectivity are depicted in Fig. 7. As the reaction requires formation of *tert*-butyl cation, chemisorption of phenol should be reduced significantly. Hence, the increase of *tert*-butyl alcohol content in the feed increases the phenol conversion from 1:1 to 1:3 but

the conversion is less by about 10% at 1:4 compared to 1:3. This may be attributed to dilution of phenol by *tert*-butyl alcohol, which suppressed electrophilic reaction. In fact 1:4 feed ratio should provide more 2-TBP due to suppression of chemisorption of phenol but the selectivity is less due to its conversion to 2,4-DTBP. The examination of the selectivities of 2-TBP and 4-TBP illustrates that it is the latter which is subsequently alkylated to give 2,4-DTBP. Hence, there may be still more chemisorbed phenol even at 1:4 feed ratio. Thus, the optimum feed ratio for this reaction is 1:3 as it gave higher conversion.

The effect of WHSV on phenol conversion and products selectivity was studied over HMCM-22(54) at 175 °C with a feed ratio 1:3. The results are depicted in Fig. 8. The phenol conversion increased from 1.71 to 5.13 h<sup>-1</sup>. But there was a sudden drop in conversion at WHSV 6.85 h<sup>-1</sup>. Hence, it appears

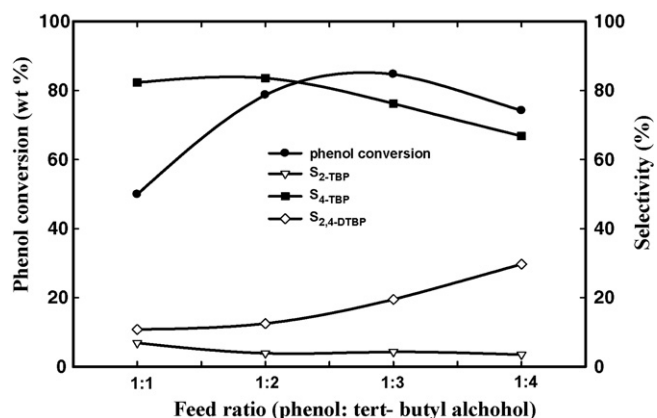


Fig. 7. Effect of feed ratio on phenol conversion and products selectivity over MCM-22 (54) at 175 °C.

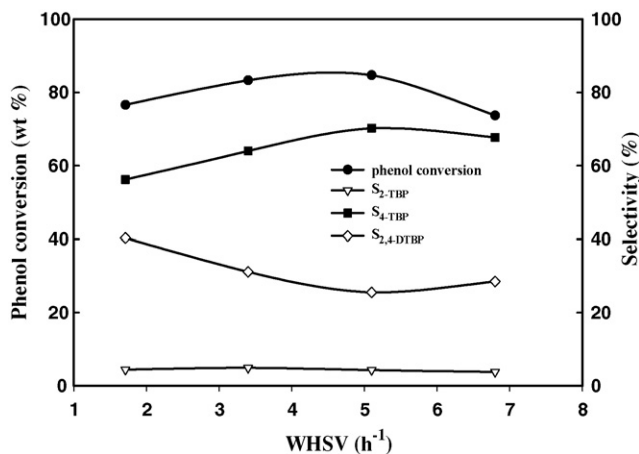


Fig. 8. Effect of WHSV on phenol conversion and products selectivity over HMCM-22(54) at 175 °C with the feed ratio 1:3 (phenol: *tert*-butyl alcohol).

that increase in the flow rate from 1.71 to 5.13 h<sup>-1</sup> is not adequate enough to suppress chemisorption of either *tert*-butylation or phenol on the catalyst surface whereas the effect is clearly distinct at 6.85 h<sup>-1</sup>. Similarly the selectivity of 4-TBP also increased for the change of feed ratio from 1.71 to 5.13 h<sup>-1</sup> but there was a sudden drop in the selectivity at 6.85 h<sup>-1</sup>. The less selectivity at 6.85 h<sup>-1</sup> might be due to conversion of 4-TBP to 2,4-DTBP. Hence, the optimum WHSV was found to be 5.13 h<sup>-1</sup> as the conversion and selectivity of 4-TBP were higher than at other WHSVs.

The effect of time on stream on phenol conversion and products selectivity was studied for 6 h at 175 °C over HMCM-22(54). The feed ratio was set at 1:3 and WHSV 5.13 h<sup>-1</sup>. The results are presented in Fig. 9. The conversion remained almost the same without any significant change over the entire period of stream. This is attributed to avoidance of coke formation. The selectivity of products also did not show any drastic change. Hence, absence of coke formation and avoidance of change in the mechanism of the reaction are clearly evident. The low reaction temperature might be the cause for such observation in this study. As the major part of the reaction occurred only in 10 MR

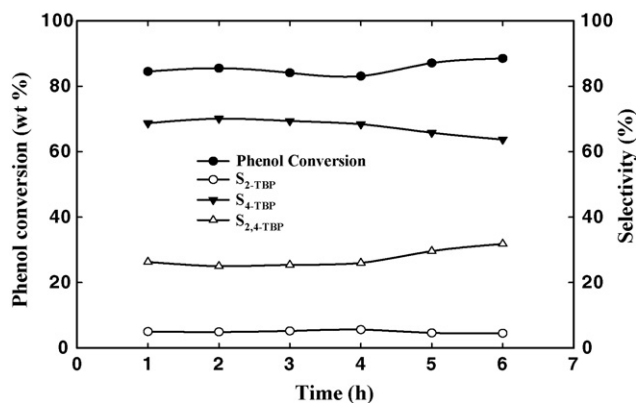


Fig. 9. Effect of time on stream study on phenol conversion and products selectivity over HMCM-22(54) at 175 °C with the feed ratio 1:3 (phenol: *tert*-butyl alcohol).

ring channels, coke formation might be largely restricted since the space is not sufficient for polyalkylation.

#### 4. Conclusion

The experimental results revealed that the workable range of Si/Al ratio for the synthesis of MCM-22 is 24–76. In the *tert*-butylation of phenol with *tert*-butyl alcohol, the chemisorbed state of phenol appears to be advantageous as it suppresses *ortho* butylation and enhances selectivity to *para* butylation. The 10-membered ring channel is found to be better for the selective production of 4-TBP. The study of time on stream at 175 °C illustrates delay in catalyst deactivation by coke formation. The selectivity of the product also remains unaltered, which is also an added advantage in this study. This observation concludes that the major part of the reaction occurs mainly in the 10-membered ring channel which restricts polyalkylation leading to coke formation. The present investigation reveals the convenience in employing MCM-22 for the selective production of 4-TBP in the *tert*-butylation of phenol.

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#### References

- [1] M.E. Leonowicz, J.A. Lawton, S.L. Lawton, M.K. Rubin, *Science* 264 (1994) 1910.
- [2] S.L. Lawton, M.E. Leonowicz, R.D. Partridge, P. Chu, M.K. Rubin, *Microporous Mesoporous Mater.* 23 (1998) 109.
- [3] C. Perego, S. Amarilli, R. Millini, G. Bellussi, G. Girotti, I. Terzoni, *Microporous Mater.* 6 (1996) 395.
- [4] A. Corma, V. Martínez-Soria, E. Schnoefeld, *J. Catal.* 192 (2000) 163.
- [5] J.S. Beck, A.B. Dandekar, T.F. Degnan, in: M. Guisnet, J.-P. Gilson (Eds.), *Zeolites for Cleaner Technologies*, Catalytic Science Series, vol. 3, Imperial College Press, London, 2002, p. 223.
- [6] J.S. Beck, W.O. Haag, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, vol. 5, Wiley-VCH, Weinheim, 1997, p. 2131.
- [7] A. Corma, H. Garcia, J. Primo, *J. Chem. Res.* 40 (1988) 1.
- [8] K. Zhang, H. Zhang, G. Xu, S. Xiang, D. Xu, S. Liu, H. Li, *Appl. Catal. A: Gen.* 207 (2001) 183.
- [9] R. Anand, R. Maheswari, K.U. Gore, B.B. Tope, *J. Mol. Catal. A: Chem.* 193 (2003) 251.
- [10] E. Dumitriu, V. Hulea, *J. Catal.* 218 (2003) 249.
- [11] R.F. Parton, J.M. Jacobs, D.R. Huybrechts, P.A. Jacobs, *Stud. Surf. Sci. Catal.* 46 (1989) 163.
- [12] K. Zhang, C. Huang, H. Zhang, S. Xiang, S. Liu, D. Xu, H. Li, *Appl. Catal. A: Gen.* 166 (1998) 89.

- [13] K. Zhang, S. Xiang, H. Zhang, S. Liu, H. Li, *React. Kinet. Catal. Lett.* 77 (2002) 13.
- [14] K. Okumura, M. Hashimoto, T. Mimura, M. Niwa, *J. Catal.* 206 (2002) 23.
- [15] S. Unverricht, M. Hunger, S. Ernst, H.G. Karge, J. Weitkamp, *Stud. Surf. Sci. Catal.* 84A (1994) 37.
- [16] G. Dahlhoff, U. Barsnick, W.F. Hölderich, *Appl. Catal. A. Gen.* 210 (2001) 83.
- [17] P. Wu, T. Komatsu, T. Yashima, *Microporous Mesoporous Mater.* 22 (1998) 343.