

Influence of aluminium sources on the synthesis and catalytic activity of mesoporous AlMCM-41 molecular sieves

S.K. Badamali, A. Sakthivel, P. Selvam*

Department of Chemistry, Indian Institute of Technology-Bombay, Powai, Mumbai 400 076, India

Abstract

Mesoporous AlMCM-41 molecular sieves were synthesized using various aluminium sources, viz., sodium aluminate, aluminium sulphate, aluminium isopropoxide and pseudoboehmite. The influence of different aluminium sources on the framework substitution of aluminium as well as on the catalytic properties of *t*-butylation of phenol was studied. Among the aluminium sources, the use of sodium aluminate for the AlMCM-41 synthesis showed maximum incorporation of aluminium in the framework. Further, the catalyst also showed good catalytic activity for the chosen reaction. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: AlMCM-41; *p-t*-Butylphenol; Alkylation; Mesoporous molecular sieves

1. Introduction

Acid catalyzed reactions, e.g., Friedel–Crafts alkylation or acylation, rearrangement, isomerization, cracking, etc., are important processes in organic synthesis, fine chemicals production as well as in petrochemical industry [1,2]. In recent years, solid acid catalysts such as zeolites or zeolite-like molecular sieves [3–5] have been replacing the conventional homogenous mineral acid catalysts [2]. However, the micropore size of zeolitic materials limits their application as catalysts for bulkier molecules. The *p*-isomer product of the *t*-butylation of phenol reaction, viz., *p-t*-butylphenol (*p-t*-Bp), is widely used in the manufacture of phenolic resins, antioxidants and polymerization inhibitor [6]. Numerous reports on the production of these alkyl-substituted phenols are available in literature [7–19]. However, it is worth

mentioning here that the selectivity of the products depends mainly on the acidic characteristics of the catalyst [7,8,14–19]. That is, weak acidic catalyst, e.g., Na⁺- or K⁺-exchanged zeolite-Y, leads to oxygen alkylated product (phenyl alkyl ether, *t*-BPE) as a major product [1,14]. The reaction on strong acidic catalyst like zeolite-β [19] produces carbon alkylated product, viz., *m-t*-butylphenol (*m-t*-Bp), which is formed by the secondary isomerization of initially formed *o*- and *p*-isomers [17–19]. On the other hand, moderate acidic catalysts such as ZSM-12 [10], SAPO-11 [8] and zeolite-Y [14] are suitable for the formation of *p*-isomer.

However, the aluminium analogue of the recently discovered [20,21] mesoporous MCM-41 silicates, i.e., AlMCM-41, are attractive owing to their tunable pore size (15–100 Å), much larger surface area (~1200 m² g⁻¹) and moderate acidity [28,29,31]. But the extent of aluminium substitution in the tetrahedral framework is greatly dependent on the aluminium sources used for the preparation of the materials [22–27]. For example, Janicke et al. [22], and Reddy

* Corresponding author. Fax: +91-22-572-3480/
+91-22-576-7152.
E-mail address: selvam@ether.chem.iitb.ernet.in (P. Selvam).

and Song [25,27] have reported that aluminium isopropoxide is a better source for the incorporation of Al(III) in MCM-41 while Luan et al. [24] have reported aluminium sulphate as the best choice among the several aluminium sources. On the contrary, Borade and Clearfield [23] have claimed sodium aluminate as the source for a maximum incorporation. In view of the above controversies and, in addition, realising the importance of acid catalyzed reaction for the conversion of bulkier molecules, we synthesized a series of AIMCM-41 employing various aluminium sources, viz., sodium aluminate, aluminium sulphate, aluminium isopropoxide and pseudoboehmite. The catalytic activity of these samples was tested for the vapour phase alkylation of phenol with *t*-butyl alcohol.

2. Experimental

2.1. Starting materials

Sodium aluminate (EM Science, 32.9% Al), aluminium sulphate (SDS, 98%), aluminium isopropoxide (Aldrich, 99%) and pseudoboehmite (VISTA, 70% Al₂O₃) were used as the aluminium sources. Fumed silica (Aldrich, 99.8%) and cetyltrimethylammonium bromide (CTAB, Aldrich, 99%) were used as sources for silicon and template, respectively. Tetramethylammonium hydroxide (TMAOH, Aldrich, 25 wt.%) and sodium hydroxide (Loba, 98%) were used as organic base and alkali source, respectively.

2.2. Synthesis of AIMCM-41

The sodium form of the samples (Na-AIMCM-41) were prepared according to a similar procedure described elsewhere [23,24] with a synthesis gel having a chemical (molar) composition of 2SiO₂:0.27(CTA)₂O:0.26Na₂O:0.26(TMA)₂O:0.033-Al₂O₃:120H₂O. The typical synthesis procedure is as follows: first TMAOH was dissolved in water and stirred for 5 min. To this, fumed silica was added slowly and the resulting solution was designated as A. Another solution B was prepared by mixing CTAB and NaOH in distilled water and stirred for about 30 min. Both these solutions, viz., A and B were mixed together and a gel was formed. To this, aqueous solutions of aluminium sources were added and

then it was stirred for an hour for homogenization. The final gel pH was adjusted to 11.5 and was transferred into teflon-lined stainless steel autoclaves. The reaction vessel was kept in an air oven for crystallization at 373 K for 24 h. The solid product obtained was washed, filtered and dried overnight at 373 K. The resulting samples were designated as as-synthesized AIMCM-41.

2.3. Calcination and protonation of AIMCM-41

The as-synthesized Na-AIMCM-41 samples were calcined at 823 K in nitrogen atmosphere for 3 h followed by air for 9 h at a heating rate of 2 K min⁻¹. The calcined samples were protonated (H-AIMCM-41) by repeated ion-exchanging using 1 M ammonium acetate solution at 353 K for 6 h followed by recalcining the ammonium exchanged samples (NH₄-AIMCM-41) at 823 K for 6 h in air.

2.4. Characterization

All the samples were systematically characterized by various analytical and spectroscopic techniques, viz., powder X-ray diffraction (XRD, Rigaku), simultaneous thermogravimetry–differential thermal analysis (TG–DTA, Shimadzu), Fourier transform-infrared (FT-IR, Nicolet), BET surface area (Smartsorb 90), inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Labtam Plasma 8440) and ²⁷Al magic angle spinning-nuclear magnetic resonance (MAS-NMR, Varian) spectroscopy.

2.5. Reaction procedure

The *t*-butylation of phenol was carried out using 750 mg of H-AIMCM-41 catalyst in a fixed-bed flow reactor. Prior to the reaction, the catalyst was activated at 773 K in a flow of air for 8 h followed by cooling to reaction temperature (448 K) in nitrogen atmosphere. After an hour, the reactant mixture, i.e., phenol and *t*-butyl alcohol, with a desired ratio and weight hour space velocity (WHSV) was fed into the reactor using a liquid injection pump (Sigmamotor) and nitrogen as the carrier gas. The gaseous products were cooled and the condensed liquid products were collected at every 30 min interval. The products, viz., *p*-*t*-Bp,

o-*t*-butylphenol (*o*-*t*-Bp) and 2,4-di-*t*-butylphenol (2,4-Di-*t*-Bp), were identified by gas chromatography (NUCON 5700) with SE-30 column. The *m*-*t*-Bp was identified by employing AT1000 column. Further, the products were confirmed using a combined gas chromatography–mass spectrometry (GC–MS, Hewlett G1800A) with HP-5 capillary column.

3. Results and discussion

XRD patterns of the as-synthesized AIMCM-41 samples obtained from different aluminium sources are depicted in Fig. 1. It can be seen from the figure that the diffraction patterns are typical of mesoporous (hexagonal) MCM-41 structure [20,21]. However, in the case of the sample prepared using aluminium sulphate source, the reflections are broadened due to a possible decrease in crystallinity [25]. This could be attributed to the lowering of pH of the synthesis gel prepared using aluminium sulphate source. TG–DTA of as-synthesized AIMCM-41 using various aluminium sources showed ~50% weight loss suggesting the mesoporous nature of the samples. Further, BET surface area of the samples (see Table 1) supported the mesoporous nature of AIMCM-41. However, it is interesting to note that the surface area of the sample prepared using aluminium sulphate source is considerably decreased. This suggests a poorly crystallized nature of samples in agreement with XRD results.

The FT-IR spectra of the samples showed (not reproduced here) typical characteristics of AIMCM-41 structure. Further, the occurrence of broad bands between 3200 and 3800 cm^{-1} indicated the presence of internal surface hydroxyl groups typical of mesoporous MCM-41. Table 1 presents ICP-AES results of the calcined samples. It can be seen from this table that the observed higher aluminium content in the calcined sample may be due to an incomplete condensation of silica, which remains as soluble silica during the synthesis. The ^{27}Al MAS-NMR spectra of (Fig. 2) sample prepared from sodium aluminate source showed nearly all Al(III) in tetrahedral coordination. However, the samples prepared using aluminium sulphate and aluminium isopropoxide showed considerable amount of octahedral Al(III). On the other hand, the samples prepared using pseudoboehmite showed nearly equal amount both octahedral and tetrahedral Al(III). The

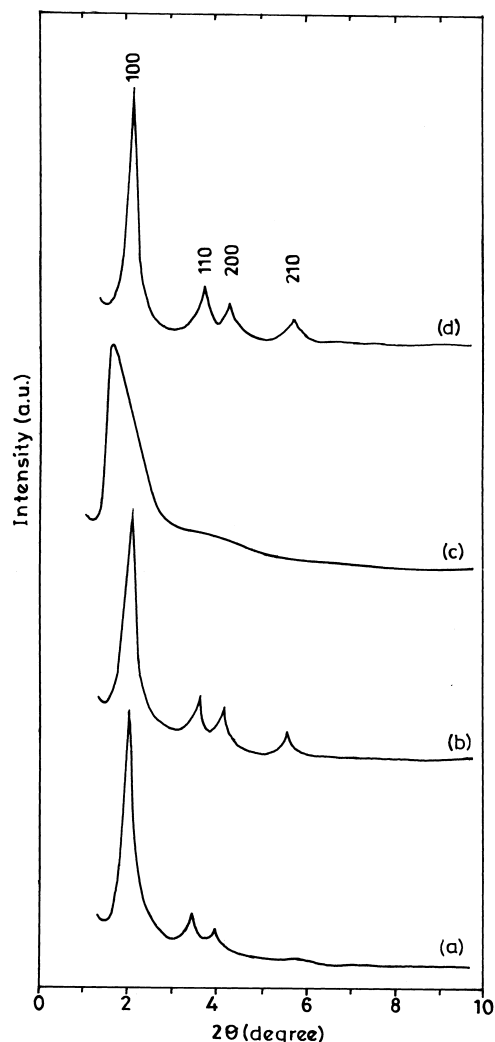


Fig. 1. XRD pattern of as-synthesized: (a) catalyst-1; (b) catalyst-2; (c) catalyst-3; (d) catalyst-4.

observed differences in the isomorphous substitution of Al(III) in the silicate matrix may, however, be due to the fact that the incorporation mainly depends upon the generation of reactive monomeric (tetraordinated) $\text{Al}(\text{OH})_4^-$ species [24]. That is, sodium aluminate readily yields monomeric Al(III) and hence may effectively be incorporated in the framework structure of MCM-41. A similar observation was noticed for the samples prepared using aluminium isopropoxide source as it also produces monomeric Al(III) on hydrolysis. On the other hand, aluminium sulphate pro-

Table 1
BET surface area and ICP-AES results of various AIMCM-41 samples obtained using different aluminium sources

Label	Aluminium source	Surface area (m ² g ⁻¹)	Si/Al molar ratio	
			Gel ^a	Calcined
Catalyst-1	Sodium aluminate	854	30	28
Catalyst-2	Aluminium isopropoxide	806	30	22
Catalyst-3	Aluminium sulphate	574	30	25
Catalyst-4	Pseudoboehmite	1075	30	22

^a Synthesis gel composition.

duces dimeric form on hydrolysis, while the colloidal nature of pseudoboehmite are less favoured for the incorporation of Al(III) in tetrahedral network.

The results of *t*-butylation of phenol over AIMCM-41 prepared using different aluminium sources are presented in Table 2. It can be seen from this table that

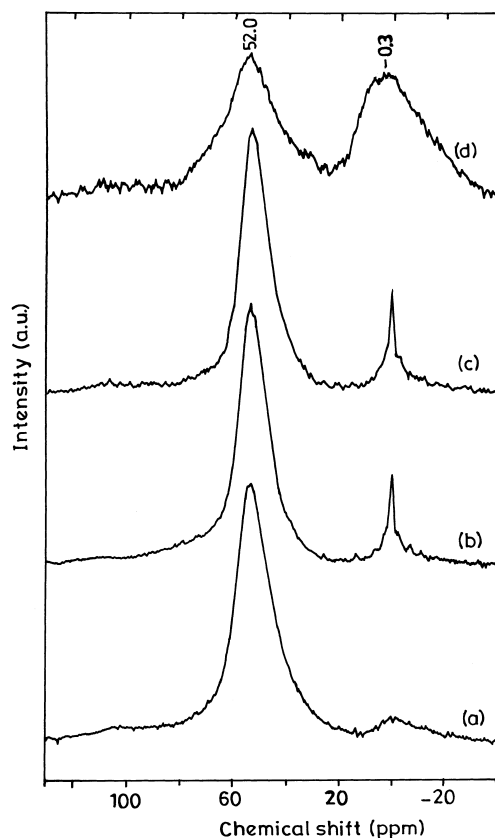


Fig. 2. ²⁷Al MAS-NMR spectra of calcined: (a) catalyst-1; (b) catalyst-2; (c) catalyst-3; (d) catalyst-4.

Table 2
Tertiary butylation of phenol over H-AIMCM-41 catalysts^a

	Catalyst-1	Catalyst-2	Catalyst-3	Catalyst-4
Phenol conversion (wt.%)	13.4	12.1	8.6	12.4
<i>Selectivity</i>				
<i>o-t</i> -Bp	5.2	7.0	5.8	8.9
<i>p-t</i> -Bp	68.7	74.4	70.9	81.5
<i>m-t</i> -Bp	25.4	18.6	23.3	9.6
2,4-Di- <i>t</i> -Bp	0.7	–	–	–

^a Reaction conditions: catalyst = 0.75 g, phenol:*t*-butyl alcohol ratio = 2:1, temperature = 448 K, WHSV = 4.8 h⁻¹, TOS = 60–90 min.

the catalyst-3 showed a lower conversion than the other catalysts. This could be attributed to the lower surface area of this catalyst. The other three catalysts showed nearly the same conversion. However, the selectivity of *p-t*-Bp over these three catalysts follows the order: catalyst-1 < catalyst-2 < catalyst-4. While the opposite trends appears for the *m-t*-Bp, it is likely that presence of more aluminium in the framework sites may lead to increase the acid sites [30]. This may initiate the secondary reaction, viz., formation of *m*-isomer through isomerization of *o*- and *p*-isomers. On the other hand, catalyst-2 and catalyst-4 may contain less number of aluminium in the tetrahedral framework sites which may expected to have lower acid sites and therefore lead to low *m-t*-Bp.

4. Conclusion

From the above study, it is clear that different aluminium sources used for the synthesis of AIMCM-41 significantly influence the extent of aluminium substitution in the framework as well as the crystallinity,

which further affects the catalytic activity of the samples. Among the various aluminium sources employed, sodium aluminate was found to be a promising source for the incorporation of Al(III) in the tetrahedral network. Further work is in progress in order to rationalize the observation with different Si/Al content.

Acknowledgements

We thank Dr. P. Veluchamy for XRD and RSIC for MAS-NMR, TG-DTA and GC-MS measurements.

References

- [1] G.A. Olah, Friedel-Crafts and Related Reactions, Vols. 2–3, Interscience, New York, 1964.
- [2] P.B. Venuto, P.S. Landis, *Adv. Catal.* 18 (1968) 259.
- [3] W. Holderich, M. Hesse, F. Naumann, *Angew. Chem. Int. Ed. Engl.* 27 (1988) 226.
- [4] C.B. Dartt, M.E. Davis, *Catal. Today* 19 (1994) 51.
- [5] J.H. Clark, D.J. Macquarrie, *Org. Process. Res. Dev.* 1 (1997) 149–162.
- [6] A. Knop, L.A. Pilato, *Phenolic Resins Chemistry*, Springer, Berlin, 1985.
- [7] A.J. Kolka, J.P. Napolitano, G.G. Elike, *J. Org. Chem.* 21 (1956) 712.
- [8] S. Subramanian, A. Mitra, C.V.V. Satyanarayana, D.K. Chakrabarty, *Appl. Catal. A* 159 (1997) 229.
- [9] K. Kanekichi, T. Yasuo, Japanese Patent 75 112 325 (1975).
- [10] C.D. Chang, S.D. Hellring, US Patent 5 288 927 (1994).
- [11] M. Yamamoto, A. Akyama, Japanese Patent 6 122 639 (1994).
- [12] A.U.B. Queiroz, L.T. Aikawa, French Patent 2 694 000 (1994).
- [13] E.M. Viorica, E.S.A. Merou, H. Justin, O. Maria, C. Eleonora, Rom Patent 73 994 (1981).
- [14] A. Corma, H. Garcia, J. Primo, *J. Chem. Res.* (1988) 40.
- [15] K. Zhang, C. Hunag, H. Zhang, S. Xiang, S. Liu, D. Xu, H. Li, *Appl. Catal. A* 166 (1998) 89.
- [16] S.K. Badamali, A. Sakthivel, P. Selvam, *Catal. Lett.* 65 (2000) 153.
- [17] S. Namba, T. Yahima, Y. Itaba, N. Hara, *Stud. Surf. Sci. Catal.* 5 (1980) 105.
- [18] R.F. Parton, J.M. Jacobs, D.R. Huybrechts, P.A. Jacobs, *Stud. Surf. Sci. Catal.* 46 (1988) 163.
- [19] A. Mitra, Ph.D. Thesis, IIT Bombay, Powai, Mumbai, 1997, p. 55.
- [20] C.T. Kresge, M.E. Leonowicz, W.T. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710.
- [21] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schelinker, *J. Am. Chem. Soc.* 114 (1992) 10834.
- [22] M. Janicke, D. Kumar, G.D. Stucky, B.F. Chemlka, *Stud. Surf. Sci. Catal.* 84 (1994) 243.
- [23] R.B. Borade, A. Clearfield, *Catal. Lett.* 31 (1995) 267.
- [24] Z. Luan, C.F. Cheng, W. Zhou, J. Kilnowski, *J. Phys. Chem.* 99 (1995) 1018.
- [25] K.M. Reddy, C. Song, *Catal. Lett.* 36 (1996) 103.
- [26] S. Biz, M.L. Occelli, *Catal. Rev. Sci. Eng.* 40 (1998) 329.
- [27] K.M. Reddy, C. Song, *Catal. Today* 31 (1996) 137.
- [28] H. Kosslick, H. Landmesser, R. Fricke, *J. Chem. Soc., Faraday Trans.* 93 (1997) 1849.
- [29] S.B. Pu, J.B. Kim, M. Seno, T. Inui, *Microporous Mater.* 10 (1997) 25.
- [30] S.K. Badamali, A. Sakthivel, P. Selvam, in: Do (Ed.), *Proc. Second Pacific Basian Conf. Ads. Sci. Technol.*, World Scientific, Singapore, 2000, p. 553.
- [31] H. Kosslick, G. Lischke, B. Parlitz, W. Storek, R. Fricke, *Appl. Catal. A* 184 (1999) 49.