J. Indian Inst. Sci., May–Aug. 2004, **84**, 99–105
© Indian Institute of Science.

Short Communication

Silicoaluminophosphate molecular sieve SAPO-41: Synthesis, characterization and alkylation of toluene with alcohol

N. VENKATATHRI* AND R. SRIVATSAVA
Catalysis Division, National Chemical Laboratory, Pune 411 008, India.
email: venkat@cata.ncl.res.in; Phone/Fax: +91-20-25893761.

Received on July 7, 2003; Revised on May 31, 2004.

Abstract

A silicoaluminophosphate molecular sieve SAPO-41 has been synthesized and characterized by XRD, ^{27}Al, ^{31}P, ^{29}Si MASNMR, FT-IR spectroscopy, TG/DTA, scanning electron microscopy and chemical analysis. Catalytic activity of these materials in the alkylation of toluene with alcohol has been studied. SEM reveals the morphology (spherical) and particle size (10 *m*m) of the sample. Hydroxyl region infrared spectroscopy reveals the presence of peaks at 3625, 3650, 3670 and 3730 cm^{-1}, which are due to the presence of silanol, P-OH and Si-OH groups. ^{27}Al and ^{31}P MASNMR results show the presence of tetrahedrally coordinated aluminium and phosphorous atoms. However, ^{29}Si MASNMR shows peaks at –92, –95, –100 and –107 ppm due to silicon surrounded by four AlO_4 tetrahedra and to silicon surrounded by $3AlO_4$, $2AlO_4$ and $1AlO_4$ respectively. In the case of toluene, alkylation with alcohol *para* isomer is predominant over the *ortho* and *meta* isomers.

Keywords: Molecular sieves, catalytic activity, Bronsted acidity, zeolites and alkylation of toluene.

1. Introduction

In recent years, considerable attention has been devoted to novel molecular sieves, namely, aluminophosphates ($AlPO_4$s) with defined microporous structure and adsorption properties [1]. Their crystal framework consists of alternating AlO_4 and PO_4 tetrahedra [2], a composition which preserves the electroneutrality of the framework. The $AlPO_4$ molecular sieves do not possess any Bronsted-acid sites, which are important in various catalytic reactions. It has been suggested that for the formation of Bronsted-acid sites in $AlPO_4$ samples it is necessary to replace *n*-valent tetrahedral framework cations by (*n*–1) valent cations [3] which would lead to a net negative charge of the framework. This can be done, for instance, either by replacing the pentavalent phosphorous by tetravalent silicon (forming SAPO molecular sieves) or by replacing the trivalent aluminium by a divalent ion (Ca, Mg, Mn; forming MeAPOs) [3]. In both the cases, Bronsted acid sites are generated.

The framework topology of SAPO-41 consists of $4.6^2.5.10$ layers connected by U.D.U.D chains. SAPO-41 molecular sieve belongs to the medium-pore silicoaluminophosphates

---

*Author for correspondence.

with a pore size of ca. 5.70 × 4.3 Å, having orthorhombic symmetry and chemical composition $Al_{20}P_{20}O_{80}$ with unit cell constants $a = 9.73$ and $b = 25.83$ Å [4]. Whereas the synthesis of SAPO-41 using di-*n*-propylamine and characterization is well documented [5–7], no information is available on the synthesis of the same aluminophosphate using diethyl amine. The aim of the present work is to synthesize SAPO-41 using diethylamine as a template and to contribute some new experimental data concerning physicochemical as well as its catalytic properties.

2. Experimental

The following synthetic procedure was carried out using the optimized composition of the gel: 3.58 g of pseudoboehmite (74.2%, Al_2O_3, Vista Chemicals, USA), 5.75 g of orthophosphoric acid (85%, SD Fine Chemicals, India) and 10 ml of distilled water. The suspension was vigorously stirred until homogeneous. Then the thick white paste was aged for overnight at room temperature. 0.453 g of fumed silica (99.5%, Fluka, USA) along with 2.159 g (98%, Aldrich, USA) of diethylamine and 10 ml of distilled water were added to the aged paste. The mixture was again stirred and the resulting gel (having the composition 1.16 DEA:$1.0Al_2O_3$:$1.0P_2O_5$:$0.3SiO_2$:$45H_2O$) was sealed in a stainless-steel pressure vessel lined with an inert plastic material and heated in an oven at 473 ± 2 K under autogeneous pressure for 5 days. The solid reaction product was filtered and washed with distilled water until its pH became neutral and dried in air at 383 K. A portion of the product was calcined in air at 823 K for 8 h for decomposing the template material. It was checked by X-ray diffraction (XRD) that the product was stable to at least 1273 K.

Alkylation of toluene with alcohol was carried out in glass reactor. 1 g of calcined SAPO was used for each reaction. Alcohol and toluene was taken in 1 : 2 ratio. The flow rate for feed was 6 ml/h. Nitrogen was used as diluent. The liquid products were condensed and analyzed with gas chromatography and the structure of the product was identified by GC-MS.

X-ray diffraction patterns were recorded on a Rigaku (D/MAX III VC) instrument in the $2q$ region of 5–45°. Scanning electron microscope pictures were taken using a JEOL JSM 5200 microscope. Chemical analysis was carried out by XRF using a Rigaku 3070 X-ray spectrometer. Carbon and nitrogen were estimated by microanalysis. The framework IR spectra were recorded in the diffuse reflectance mode using 300 : 1 ratio sample in KBr (Nicolet 60SXB). To study the nature of the surface hydroxyl groups in the transmittance mode, self-supported wafers (~ 10 mg/cm^{-2}) and an IR cell with controlled environment chamber were used. The sample was activated *in situ* at 673 K under vacuum (10^{-6} torr) for 4 h and then cooled to 323 K before recording the spectrum (4 cm^{-1} resolution, averaged over 500 scans). MASNMR spectra were recorded in the solid state with a Bruker DRX-500 spectrometer operating at a field of 11.7 Tesla. ^{27}Al spectra were recorded at a frequency of 130.3 MHz, with a pulse length of 2 *m*s and a spinning speed of 3–5 kHz. ^{31}P spectra were recorded at a frequency of 202.45 MHz with a pulse length of 1.5 *m*s and the recycle delay was 4 s. ^{29}Si NMR spectra were recorded at 99.3 MHz, 2 *m*s (45°) pulse width and repetition time of 2 s. Tetramethylsilane (for silicon), 1 M $Al(NO_3)_3$ and 1 M H_3PO_4 solutions (for aluminium and phosphorous) were used as standards.

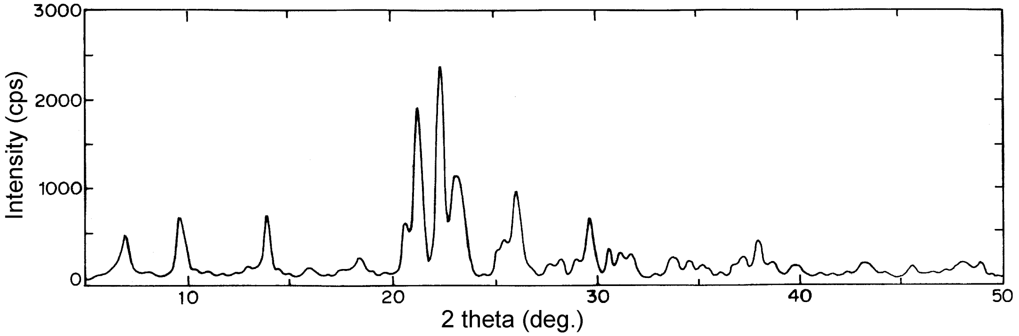

FIG. 1. X-ray diffraction pattern of SAPO-41.

3. Results and discussion

Two different procedures were reported for the synthesis of SAPO-41 using di-*n*-propylamine (DPA) template. They are: (i) Gel composition Al_2O_3:1.2P_2O_5:0.1SiO_2:4DPA:55H_2O, motor stirring, static, temperature = 453 K, time = 252 h [8] and (ii) Gel composition 0.85Al_2O_3:1.0P_2O_5:0.1SiO_2:3.0DPA:50H_2O, motor stirring, static, temperature = 473 K, time = 24 h [5]. The present investigation, however, uses di-ethylamine (DEA) template and the gel composition is Al_2O_3:P_2O_5:0.3SiO_2:1.16DEA:45H_2O, aging = overnight (12 h), hand stirring, static, temperature = 473 K, time = 120 h. The procedure is novel and the template and synthesis are carried out with more silicon content.

Both the synthesis procedure and the material used are novel. Its physicochemical characteristics differ from the earlier reported samples. Although XRD pattern is similar, the peak intensities vary. In earlier samples, the peak was the largest at 21°, whereas here the largest is at 22.5°. The XRD pattern of the as-synthesized SAPO-41 sample (Fig. 1) is nearly identical to that of Flanigen and co-workers [9]. The unit cell parameters are $a = 9.85$ and $b = 25.95$ Å (orthorhombic). The enhanacement in unit cell values shows the increase in unit cell volume on insertion of silicon into the aluminophosphate framework. The typical shape of the synthesized SAPO-41 crystals (Fig. 2) shows that earlier samples [5, 8] are cuboids with particle size of 1.5 *m*m. The samples here are spherical with 10 *m*m particle size. These particles are formed by the aggregation of smaller crystals of 1 *m*m or less and are clearly visible in the figure. On the surface of some of the spherical particles, many very small microcrystals were found, grown on surface crystallization centres.

Elemental analysis shows that the SAPO-41 consists of $0.04Et_2NH(Si_{0.05}Al_{0.51}P_{0.45})O_2 \times H_2O$ and two template molecules per unit cell. The elemental composition of the organics did not vary much on change in template from di-*n*-propylamine to diethylamine. However, it is found that there is increase in silicon uptake ($0.039Pr_2NH\ (Si_{0.04}Al_{0.50}P_{0.47})O_2 \times H_2O$). This may be due to the excess space on small template molecule available in the framework. The influence of thermal treatment on the properties of SAPO-41 samples was investigated by thermal desorption. Figure 3 shows the TG and DTA results of the product measured after synthesis (as-synthesized form). The weight loss in TG of the reported sample shows lesser value (6%) and reveals the presence of amorphous materials. In the DTA

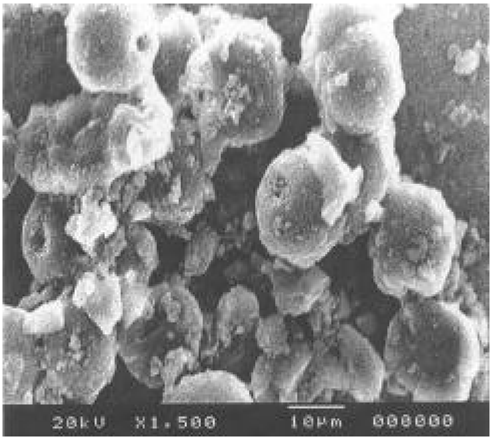

FIG. 2. SEM photograph of SAPO-41.

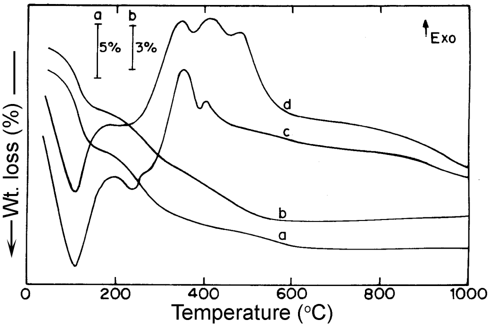

FIG. 3. TG(a, b)/DTA(c, d) pattern of (a, c) $AlPO_4$-41 and (b, d) SAPO-41.

of the as-synthesized form, four peaks can be distinguished. The first (endothermic at 373) is obviously due to the desorption of water and diethylamine. The three remaining exothermic peaks are due to the decomposition and combustion of template chemically adsorbed on Bronsted-acid sites (599, 643 and 714 K).

Both AlO_6 and PO_4 groups have their asymmetric and symmetric stretching vibrational frequencies in the range of 900–1200 cm^{-1} and 600–400 cm^{-1} and bending frequencies in the 400–550 cm^{-1} range, respectively. The range 1200–900 cm^{-1} may also contain bands due to Al-OH bending modes of vibration. The IR spectra of SAPO-41 show bands at 3730, 3670, 3650 and 3625 cm^{-1} (Fig. 4), the first two of which correspond to Si-OH, and P-OH groups [10], respectively, and that at 3620 and 3650 cm^{-1} to acidic bridging OH groups [11]. The FT-IR spectrum in the hydroxyl region of the reported sample shows the presence of single silanol group at 3627 cm^{-1} [5, 8] indicating probably a multiple silicon environment.

^{27}Al and ^{31}P MASNMR spectra of the SAPO-41 sample with the above composition are shown in Fig. 5. The ^{27}Al NMR spectrum of the calcined sample shows two signals. The dominant line at 38.04 ppm can possibly be ascribed to tetrahedrally coordinated aluminium atoms bonded via oxygen to four phosphorous atoms [12]. The value of the chemical shift fits well in the range observed for other silicoaluminophosphates [13–16]. The small line at ca. 8.32 ppm is most probably caused by octahedrally coordinated aluminium atoms of unreacted starting material.

The observed value of the chemical shift of –29.43 ppm for the calcined sample in ^{31}P MASNMR spectrum is typical of phosphorous-linked with four AlO_4 tetrahedra [17]. Neither the ^{27}Al nor the ^{31}P MASNMR spectra give evidence for the incorporation of silicon into the framework (Fig. 5). We assign the four lines –92, –95, –100 and –107 ppm as done by other researchers to silicon surrounded by four AlO_4 tetrahedra and to silicon surrounded by $3AlO_4$, $2AlO_4$ and $1AlO_4$, respectively. Even though the ^{27}Al and ^{31}P MAS NMR are similar to the reported one, the silicon NMR gives four different peak species; however, the reported one contains only one peak for Si : 4 Al species [5, 8]. From the spectral intensities it follows that only ca. 25 wt% of the silicon, found by chemical analysis of the calcined

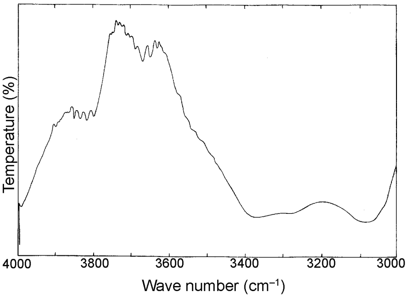

FIG. 4. FT-IR spectrum of SAPO-41 in the –OH region.

Table I
Alkylation of toluene with alcohol

Alcohol	Temp. (K)	Conversion	Selectivity *o*-isomer	*p*-isomer	*m*-isomer	Others
MeOH	600	54.3	10.7	40.7	27.9	20.8
EtOH	600	51.7	8.3	42.5	30.7	18.5
i-PrOH	600	51.0	3.7	50.6	32.4	13.3
MeOH	650	56.7	11.4	38.7	27.7	22.2
EtOH	650	54.5	9.3	39.8	30.3	20.6
i-PrOH	650	53.2	3.1	48.2	26.7	22.0
MeOH	700	63.4	7.7	37.3	23.4	31.6

samples, was incorporated as monomeric silicon into the SAPO-41 framework. Only the isolated silicon atoms in the framework can produce Bronsted acidity.

The activity of SAPO-41 catalyst for toluene alkylation (Table I) is higher than in the earlier reports [8]. It is assumed that alcohol reacts with zeolitic proton forming and oxonium ion and is followed by the transfer of methyl group to the aromatic ring and of the proton back to the catalyst site. It can be seen that in all the cases *p*-isomer is predominant. The reason is very obvious, i.e. due to steric effect. It is also seen from the table that as we move from MeOH to *i*-PrOH, the selectivity for *p*-isomer increases. This is due to the fact that the secondary carbonium ion is more stable and produces more steric hindrance. Apart from *ortho*, *para* and *meta* isomers, some other products are also formed. They are 1,3,5 trialkyl, 1,2,4 trialkyl and 1,2,3 trialkyl-substituted products. Among them, 1,2,4-substituted product occurs predominantly (Fig. 6). The transition state in the reaction of *para* isomer would occupy the minimum space as compared to those formed by *meta* and *ortho* isomers. Hence, the former can be formed in the restricted space inside the SAPO channel. Once formed, these two isomers diffuse out easily because of their lower kinetic diameter as compared to other isomers. This could be the reason for the preferential formation of both *p*-isomer as well as the 1,2,4-trialkylated product.

4. Conclusions

A typical shape of SAPO-41 particles is the sphere formed by aggregation of smaller particles. IR measurements have shown the bands of three different hydroxyl groups, namely,

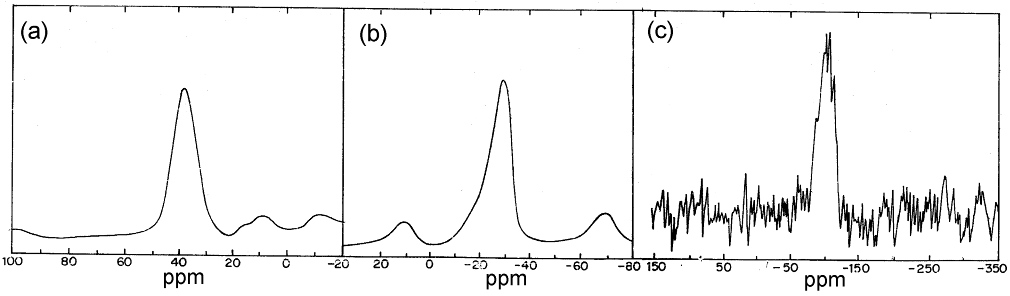

FIG. 5. ^{27}Al (a), ^{31}P (b) and ^{29}Si (c) MASNMR of SAPO-41.

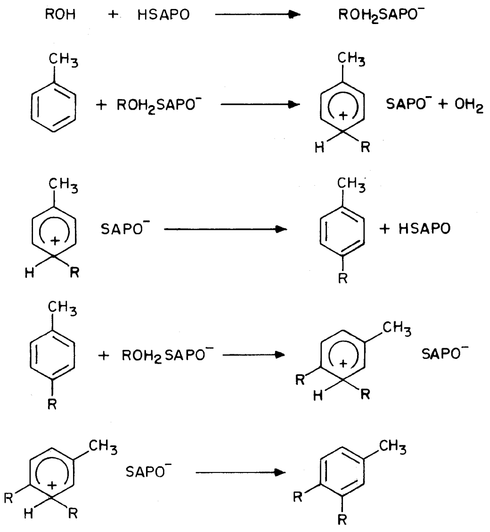

FIG. 6. Reaction scheme of the alkylation of toluene using alcohols by SAPO catalysts.

Si-OH, P-OH and bridging OH groups. ^{27}Al and ^{31}P MASNMR aluminium and phosphorous are tetrahedrally coordinated in the framework of SAPO-41. From ^{29}Si MASNMR it follows that most of the silicon is incorporated in monomeric form as Si: [4Al], Si: [3Al : Si], Si: [2Al : 2Si], Si: [Al : 3Si]. The SAPO-41 molecular sieve shows good catalytic activity in the alkylation of toluene.

Acknowledgements

The authors thank the CSIR, New Delhi, for Research Associate fellowship.

References

1. S. T. Wilson, B. M. Lok and E. M. Flanigen, *Crystalline metallophosphate compositions,* US Patent, 4,310,440 (1982).
2. J. M. Bennett, W. J. Dytrych, J. J. Pluth, J. W. Richardson and J. V. Smith, Structural features of aluminophosphate materials with Al/P = 1, *Zeolites*, **6**, 349–359 (1986).
3. N. J. Tapp, N. B. Milestone and D. M. Bibby, Generation of acid sites in substituted aluminophosphate molecular sieves, in *Innovations in zeolite material science* (P. J. Grobet, W. J. Mortier, E. F. Vansant and G. Schulz-Ekloff (eds)), Elsevier, pp. 393–402 (1988).
4. W. M. Meier and D. H. Olson (eds), Atlas of zeolite structures, *Zeolites*, **12**, 28–29 (1992).
5. P. Meriaudeau, V. A. Tuan, F. Lefebvre, V. T. Nghiem and C. Naccache, Synthesis and characterization of SAPO-41: Effect of the silicon content and the crystal size on the hydroisomerization of *n*-octane over Pt-Pd/SAPO-41, *Microporous Mesoporous Mater.*, **26**, 161–173 (1998).
6. M. Hartmann, A. M. Prakash and L. Kevan, Multinuclear MASNMR study on the microporous aluminophosphates $AlPO_4$-41 and SAPO-41, *J. Chem. Soc. Faraday Trans.*, **94**, 723–727 (1998).
7. H. Robson and K. P. Lillerud (eds), *Verified synthesis of zeolite materials,* Elsevier, pp. 102–103 (2001).
8. A. M. Prakash, V. V. Satyanarayana Chilukuri, R. P. Bagwe, S. Ashtekar and D. K. Chakrabarty, Silicoaluminophosphate molecular sieves SAPO-11, SAPO-31 and SAPO-41: Synthesis, characterization and alkylation of toluene with methanol, *Micoporous Mater.*, **6**, 89–97 (1996).

9. B. M. Lok, C. A. Messina, R. L. Patton, R. T. Gajek, T. R. Cannan and E. M. Flanigen, Silicoaluminophosphate molecular sieves: Another new class of microporous crystalline inorganic solids, *J. Am. Chem. Soc.*, **106**, 6092–6093 (1984).

10. S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, Aluminophosphate molecular sieves: A new class of microporous crystalline inorganic solids, in intrazeolite Chemistry, *ACS Symp. Ser.*, **218**, 79–106 (1983).

11. S. G. Hegde, P. Ratnasamy, L. M. Kustov and V. B. Kazanasky, Acidity and catalytic activity of SAPO-5 and $AlPO_4$-5 molecular sieves, *Zeolites*, **8**, 137–141 (1988).

12. D. Muller, W. Gessner, A. Samoson, E. Lippmaa and G. Scheler, Solid-state aluminium-27 nuclear magnetic resonance chemical shift and quadrupole coupling data for condensed AlO_4 tetrahedra, *J. Chem. Soc., Dalton Trans.*, 1277–1281 (1986).

13. L. Sierra de Saldarriaga, C. Saldarriaga and M. E. Davis, Investigations into the nature of a silicoaluminophosphate with the Faujasite structure, *J. Am. Chem. Soc.*, **109**, 2686–2691 (1987).

14. C. S. Blackwell and R. L. Patton, Solid-state NMR of silicoaluminophosphate molecular sieves and aluminophosphate materials, *J. Phys. Chem.*, **92**, 3965–3970 (1988).

15. D. Hasha, L. Sierra de Saldarriaga, C. Saldarriaga, P. E. Hathaway, D. F. Cox and M. E. Davis, Studies of silicoaluminophosphates with the sodalite structure, *J. Am. Chem. Soc.*, **110**, 2127–2135 (1988).

16. M. Goepper, F. Guth, L. Delmotte, J. L. Guth and H. Kessler, Effect of template removal and rehydration on the structure of $AlPO_4$ and $AlPO_4$-based microporous crystalline solids, in *Zeolites: Facts, figures, future* (P. A. Jacobs and R. A. van Santen (eds)), Elsevier, pp. 857–866 (1989).

17. D. Muller, E. Jahn, G. Ladwig and U. Haubenreisser, High resolution solid state ^{27}Al and ^{31}P NMR: correlation between chemical shift and mean Al-O-P angle in $AlPO_4$ polymorphs, *Chem. Phys. Lett.*, **109**, 332–336 (1984).

18. J. A. Mertens, M. Martens, P. J. Grobet and P. A. Jacobs, Synthesis and characterization of silicon-rich SAPO-5, in *Innovation in zeolite materials science* (P. J. Grobet, W. J. Mortier, E. F. Vansant and G. Schulz-Ekloff (eds)), Elsevier, pp. 97–105 (1988).

19. E. Brunner, H. Ernst, D. Freude, M. Hunger and H. Pfeifer, Characterization of zeolites by magic angle spinning NMR, in *Innovations in zeolite materials science* (P. J. Grobet, W. J. Mortier, E. F. Vansant and G. Schulz-Ekloff (eds)), Elsevier, pp. 155–165 (1988).