Silicoaluminophosphate number eighteen (SAPO-18): a new microporous solid acid catalyst

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SAPO-18, which has a microporous framework structure related to, but crystallographically distinct from, that of the solid acid catalyst SAPO-34, was synthesized hydrothermally from a silicoaluminophosphate gel containing N,N-diisopropylethylamine as a structure-directing template. Although both materials have similar Si/(Si + Al + P) ratios, the content of Brønsted acid sites in SAPO-18 is considerably less than that in SAPO-34. As catalysts for methanol conversion to light olefins, SAPO-18 and SAPO-34 have closely similar initial activity and selectivity, but the lifetime of SAPO-18 is distinctly superior to that of SAPO-34.

Keywords: coke; zeolites; catalyst regeneration; oxidation

1. Introduction

Substitution of heteroatoms into otherwise neutral microporous aluminophosphates [1–4] produces solid acids of variable acid strength. Nevertheless, not every type of aluminophosphate molecular sieve can be effectively converted into a Brønsted acid by heteroatom substitution. Among the silicon-substituted aluminophosphates, SAPO-34 and its analogues, which have a framework structure [5] identical to that of chabazite, a small-pore (4.3 Å free diameter) zeolite, have attracted considerable attention for they bear strong Brønsted acid sites [6,7] and are excellent shape-selective catalysts for the conversion of methanol to light hydrocarbons [8–11].

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AlPO$_4$-18 is a novel but chabazite-related aluminophosphate, the structure of which was solved recently [12]. The shape of the cavities and the size of the micropores in AlPO$_4$-18 are closely similar to those in SAPO-34. The main structural difference between the two lies in the orientation of the double six ring units of which both are built up. In AlPO$_4$-18 alternate layers of double six rings parallel to the *ab* plane are related by a *c*-glide and thereby possess different orientations. In SAPO-14, they are related by a simple translation and therefore have the same orientation (fig. 1). By analogy with the closely similar SAPO-34, a silicon-substituted AlPO$_4$-18 would be expected to possess strong Brønsted acidity and to act as a good solid catalyst. However, previous work has revealed [1] that SAPO-18 could not be obtained by using the same template (tetraethylammonium hydroxide) as that for AlPO$_4$-18 since in the presence of silicon this template led to the formation of SAPO-34 rather than SAPO-18.

In this paper, we report the first synthesis of SAPO-18 using N,N-diisopropylethylamine ($C_8H_{19}N$) as a structure-directing template. This template, to our knowledge, has not been used hitherto for the preparation of zeolitic materials.

2. Experimental

SAPO-34 was prepared by following the procedures described previously. Both AlPO$_4$-18 and SAPO-18 were synthesized by treating an aluminophosphate-based gel hydrothermally. Thus, for AlPO$_4$-18, aluminum hydroxide hydrate (Aldrich, 55 wt% Al_2O_3 and 45 wt% H_2O) was added to a solution of 85% phosphoric acid (Aldrich) in water, and the mixture was stirred until homogeneous. To this mixture, N,N-diisopropylethylamine ($C_8H_{19}N$) was added and a gel, which had the empirical composition $1.80C_8H_{19}N : Al_2O_3 : P_2O_5 : 50H_2O$, was formed by stirring the final reaction mixture vigorously. This gel was sealed in a Teflon-lined stainless autoclave and heated at 160–180°C under autogeneous pressure for 7 days. The solid product was recovered by filtration, washed with distilled water and dried in air at about 50°C. SAPO-18 was prepared similarly except that a cer-

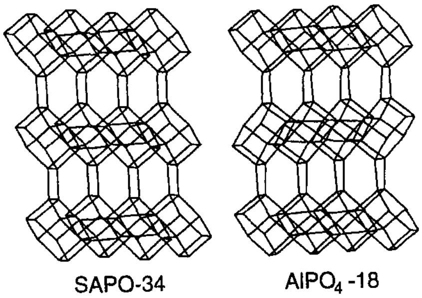

Fig. 1. Framework structures of SAPO-34 (CHA) and AlPO$_4$-18 (AEI). Only the connectivity of the tetrahedral atoms is shown.

tain amount of silica (Aerosil, Degussa) was added to the reaction mixture as the silicon source. Typically, a reaction gel with an empirical composition of $1.60C_8H_{19}N : 0.60SiO_2 : Al_2O_3 : 0.90P_2O_5 : 50H_2O$ was used for SAPO-18 preparation. A portion of each as-synthesized sample was calcined in a stream of dry oxygen at 550°C for 5–10 h to remove the occluded template without disruption of the framework.

X-ray powder diffraction (XRD) was performed on a Siemens diffractometer fitted with a Stoë rotating copper anode using a nickel filter. The diffractometer was fitted with a heatable stage to permit patterns to be taken at different sample temperatures. Infrared spectra of pelletized self-supported wafers were recorded on a Perkin-Elmer 1725X FTIR spectrometer fitted with a quartz cell with KBr windows. The pellets were mounted on a gold foil sample holder within the cell and heated in vacuum at 550°C for 30 min to remove adsorbed water. Catalytic testing was carried out in a tubular quartz reactor with 0.2 g of catalysts, and the reaction products were analyzed using a Perkin-Elmer gas chromatograph. The weight hourly space velocity (WHSV, in g reactant (g catalyst)$^{-1}$ h^{-1}) was 2.5 h^{-1}.

3. Results and discussion

Previously, $AlPO_4$-18 was reported to be synthesized in the presence of both tetraethylammonium hydroxide and hydrochloric acid, and the solid product contained $AlPO_4$-18 as the major crystalline phase as well as a minor amount of impurity [12,13]. However, by using N,N-diisopropylethylamine as the template, even without the presence of HCl, we have succeeded in the preparation of pure $AlPO_4$-18 [14]. Furthermore, divalent metals [14,15] and silicon can be incorporated into the structure readily by direct crystallization in the presence of silica in the reaction mixture, and the amount of the incorporated silicon varies within a certain range. The SAPO-18 reported in this paper is the one with the highest silicon content among the SAPO-18 samples we obtained, and has a $Si/(Si + Al + P)$ ratio (0.095) close to that for the SAPO-34 sample. (The content of silicon in SAPO-34 can vary only in a very narrow range, and typically, a SAPO-34 sample has a $Si/(Si + Al + P)$ ratio of 0.100; the aluminophosphate $AlPO_4$-34 or SAPO-34 with a low content of silicon being not obtainable under normal conditions for reasons as yet unknown.)

The relative amount of the template in the reaction mixture has been found to be crucial to the formation of pure $AlPO_4$-18 and SAPO-18 phases. If the ratio $C_8H_{19}N/(Si + Al + P) < 0.4$ in the reaction mixture, $AlPO_4$-5 or SAPO-5 is very likely to appear in the reaction product, and if the ratio is larger than 0.6, no crystalline product or product with very low crystallinity forms even after a long crystallization time (15 days). The crystallization temperature also plays an important role in the formation of $AlPO_4$-18 and SAPO-18. At 200°C or above, only dense phases crystallize.

The X-ray powder diffraction pattern (fig. 2) for the as-synthesized $AlPO_4$-18 is in good agreement with those reported earlier [12,13], but that for the as-synthesized SAPO-18 has some extra peaks (fig. 2, as asterisked). Close inspection [16] reveals that the as-synthesized SAPO-18 pattern may be considered as two superimposed patterns, which correspond closely to those for two different unit cells exemplified by as-synthesized $AlPO_4$-18 and calcined-dehydrated $AlPO_4$-18. It is known [12,17] that the unit cell dimensions and interaxial angles of $AlPO_4$-18 show considerable changes upon going from the as-synthesized form to the calcined-dehydrated and to the calcined-rehydrated forms. The XRD pattern of calcined-dehydrated SAPO-18 is compared with that of a similarly-treated sample of $AlPO_4$-18 in fig. 3. Only minor variations are observed between the calcined-dehydrated samples (figs. 3b and 3c) and all closely represent the pattern (fig. 3a) simulated from the structure parameters reported in the literature [12].

The infrared spectra of template-free $AlPO_4$-18 and SAPO-18 samples within the hydroxyl stretching absorption region are shown in fig. 4. $AlPO_4$-18 has one main absorption band at 3676 cm^{-1}, attributable to P–OH groups and observed for almost all aluminophosphate-based molecular sieves. These groups probably originate from defects present in the structure. Besides the P–OH absorption, SAPO-18 has a weak absorption at 3743 cm^{-1} (silanol groups) and two distinct bands at 3600 and 3626 cm^{-1}. These distinct bands have also been observed for SAPO-34: the higher frequency absorption is thought to belong to hydroxyls located in the large cages and the lower frequency one to hydroxyls associated with the double six rings [6,7,18]. These hydroxyls must stem from the attachment of

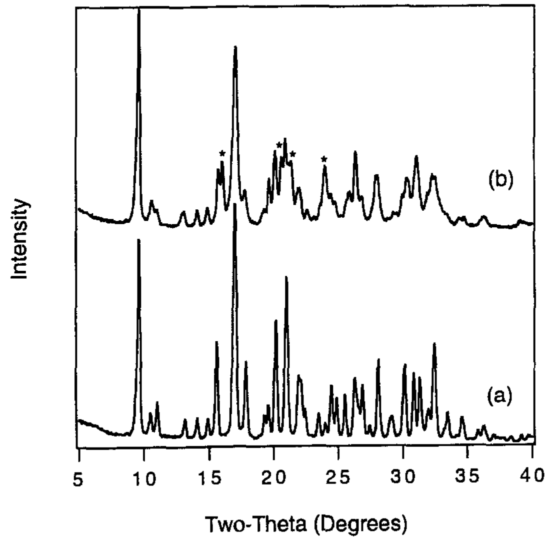

Fig. 2. X-ray powder diffraction patterns of as-synthesized (a) $AlPO_4$-18 and (b) SAPO-18. Extra peaks in the SAPO pattern (asterisked) are due to silicon-rich regions of the structure that have a different unit cell from the as-synthesized $AlPO_4$-18.

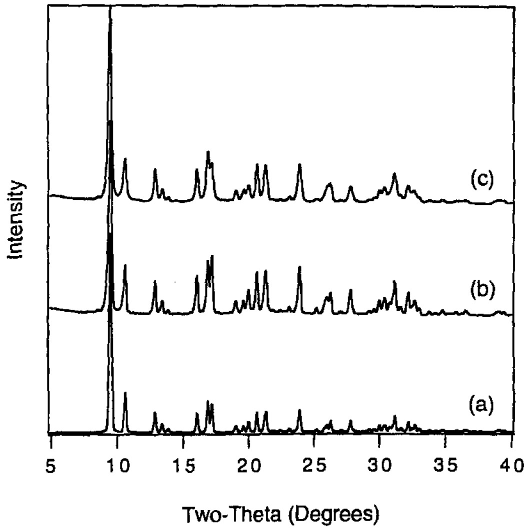

Fig. 3. X-ray powder diffraction patterns (a) simulated on the basis of the $AlPO_4$-18 framework structure reported in the literature (ref. [12]), and of calcined (b) $AlPO_4$-18 and (c) SAPO-18.

charge-balancing protons to framework O atoms bridging a Si and an Al atom, and infer Brønsted acidity. SAPO-34, in which the Si/(Si + Al + P) ratio (0.10) is similar to that (0.095) in SAPO-18, has a much higher concentration (fig. 4) of bridging OH groups than the SAPO-18 sample on the basis of the normalized band areas of the 3626 and 3600 cm^{-1} absorptions.

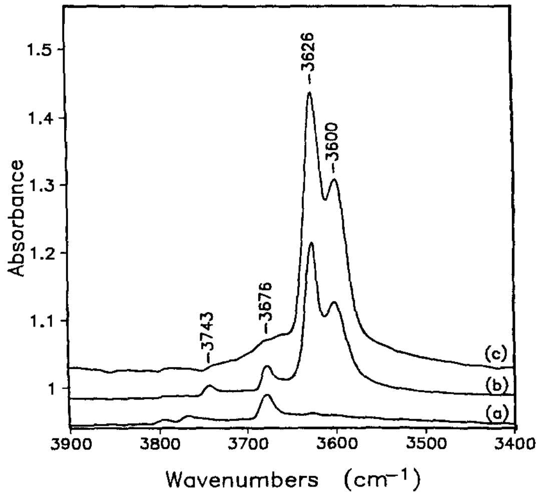

Fig. 4. Infrared spectra (normalized against mass) of calcined-dehydrated (a) $AlPO_4$-18, (b) SAPO-18 and (c) SAPO-34. Peaks at 3626 and 3600 cm^{-1} are those attributed to bridging hydroxyls (Brønsted acid sites). (See text for assignment of the remaining peaks).

Considering the stoichiometry of the parent aluminophosphate framework, $AlPO_4$, each silicon substituting for phosphorus alone (Si → P, which we designate mechanism I) results in the production of one net negative charge and hence one Brønsted acid site. The coupled substitution 2Si → Al + P (so-called mechanism II) retains framework neutrality and therefore introduces no Brønsted acidity. For SAPO-34, the substitution mechanism has been shown to be exclusively of the former type [16,18] so that one Brønsted acid site is produced for every silicon incorporated in the framework. For the SAPO-18 samples, however, this is not so as we will show elsewhere [16]: only a fraction of Si substitutes via mechanism I, the remaining Si substituting via mechanism II. This explains why SAPO-18 contains fewer bridging Si–OH–Al groups (Brønsted acid sites) than SAPO-34, although these two SAPO samples have a similar $Si/(Si+Al+P)$ ratio. The fact that in SAPO-18 silicon substitutes via two mechanisms is further confirmed by MAS NMR studies [16]. As expected, $AlPO_4$-18 shows no bridging hydroxyl absorption, and therefore contains no Brønsted acid sites as confirmed by its poor catalytic performance discussed below.

Preliminary catalytic testing for methanol conversion to hydrocarbons has been conducted on the $AlPO_4$-18 and SAPO-18 samples alongside the SAPO-34 sample. Whereas $AlPO_4$-18 catalyzes methanol conversion only to dimethyl ether due to its minimum Brønsted acidity, both SAPO-18 and SAPO-34 are very active and selective for methanol conversion to ethene and propene. At 350°C or above, the initial conversion of methanol to hydrocarbons (within 10 min of time on stream) on both SAPO samples reaches 100% and the maximum distribution of ethene and propene in the hydrocarbon products is 80%.

With increasing time on stream, the catalytic activity for both SAPO-18 and SAPO-34 decreases (fig. 5). However, the activity decrease for SAPO-18 is much slower than for SAPO-34. The activity of SAPO-34 is lost by 90% in 4 h of time on

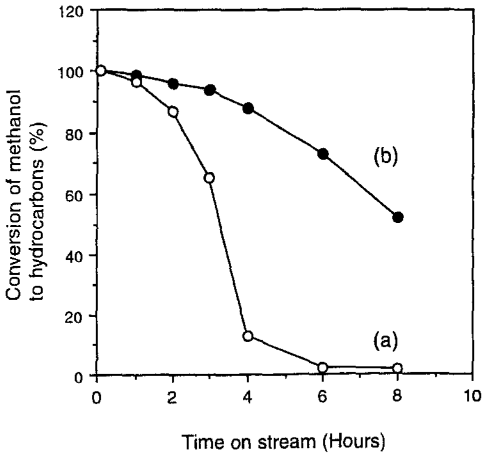

Fig. 5. Deactivation of (a) SAPO-18 and (b) SAPO-34 for methanol conversion to hydrocarbons at 400°C.

stream, whereas after 8 h, SAPO-18 still retains half of its initial activity. We believe that the difference in lifetime between SAPO-18 and SAPO-34 is caused mainly by the concentration difference in Brønsted acid sites between these two materials. As revealed by the IR study (fig. 4), SAPO-34 contains many more bridging Si–OH–Al groups (Brønsted acid sites) than SAPO-18. The more the Brønsted acid sites, the faster the coke formation during methanol conversion reaction, and therefore, the faster the deactivation for the corresponding catalyst [19–21].

4. Conclusion

Silicon can be incorporated into the $AlPO_4$-18 structure to form SAPO-18 by direct hydrothermal preparation in the presence of silica and N,N-diisopropylethylamine as a template. In thus formed SAPO-18, the incorporated silicon substitutes for aluminum as well as phosphorus, but the amount of substituted phosphorus is larger than that of the substituted aluminum, yielding Brønsted acidity. In contrast, the incorporated silicon in SAPO-34 substitutes only for phosphorus, and as a result, with a similar $Si/(Si + Al + P)$ ratio, SAPO-34 contains many more Brønsted acid sites than SAPO-18. This factor renders SAPO-18 a solid acid superior to SAPO-34 in terms of lifetime for methanol conversion to light olefins.

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