Synthesis of SiVPI-5 with Enhanced Activity in Acid Catalysed Reactions

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A novel method for the synthesis of silicon-substituted aluminophosphate VPI-5 with enhanced acid catalytic activity is described.

VPI-5 is a member of the AlPO family, the framework of which is permeated by one-dimensional channels circumscribed by 18-membered rings of alternating PO_4 and AlO_4 tetrahedra.[1] The free aperture of these channels is 12.1 Å, which gives VPI-5 the potential capability of processing large organic molecules. Therefore, there have been many different investigations aimed at the introduction of acid centres into the material, involving in most cases attempts to replace P by Si, *i.e.*, the substitution mechanism SM2 proposed by Flanigen *et al.*[2] for AlPO materials.

Silicon-containing VPI-5 samples have been produced by Davis *et al.*[3] by using dipropylamine. The resulting crystals contain very low amounts of amine, and the XPS and ^{29}Si MAS NMR results indicate the preferential substitution of Al + P pairs by 2 Si atoms (substitution mechanism 3). Similar results have been reported recently for the use of tetrabutylammonium hydroxide.[4]

Martens *et al.*[5] have found that a significant proportion of the Si atoms occupy P sites in a Si-containing VPI-5 material obtained from a gel containing tributylamine and dipentylamine. However, the Si content (not given) is reported to be low, whereas the carbon content is close to 5% (*m*/*m*).

Here we report the results obtained by using a new synthesis strategy in order to favour the replacement of P by Si in the VPI-5 framework. The method is based on the crystallization of SiVPI-5 from a two liquid phase system in the presence of a cationic surfactant. In the absence of the tensioactive agent MCM-9, a mixture of VPI-5 and AlPO-11 is found.[6–8] This method has already been found to modify the Si environment in SAPO-5.[9]

A typical synthesis was as follows: pseudoboehmite (9.38 g; Catapal B, Vista) was added to a solution of PO_4H_3 [15.91 g; Riedel; 85% (*m*/*m*) of acid] in deionized water (38.68 g) and the mixture stirred for 2 h at 20 °C. Then dipropylamine (6.98 g; Aldrich) was added and stirring was maintained for 2 h before the addition of a solution containing *n*-hexanol (41.26 g; Aldrich), tetraethylorthosilicate (TEOS; 6.71 g; Fluka) and hexadecyltrimethylammonium bromide [1.81 g; Panreac; 98% (*m*/*m*)]. After 15 min of stirring, the reaction mixture was introduced into 60 ml Teflon-lined stainless steel autoclaves which were heated at 5 °C min^{-1} up to 142 °C, and maintained at this temperature for 105 min. After this, the autoclaves were quenched in cool water, and their contents filtered, washed with water and ethanol, and dried at room temperature.

Following this procedure, gels of molar compositions 0.93 $Al_2O_3:P_2O_5:xSiO_2$:DPA:5.9 *n*-hexanol:7.2 × 10^{-2} CTABr:35 H_2O (x = 0.46 and 0.2 for samples 1 and 2, respectively) were prepared (Table 1). A reference sample R was prepared in the absence of surfactant following the procedure described by Davis *et al.*,[3] using Aerosil 200 (Degussa) instead of Ludox HS-40.

The three samples were identified as crystalline VPI-5 by X-ray powder diffraction, although a minor amount of $AlPO_4$-H_3 was detected in the sample with the lowest Si content. In contrast to this, a mixture of SAPO-11, VPI-5 and $AlPO_4$-H_3 was the major product obtained in the absence of surfactant. Therefore, the surfactant seems to stabilize the VFI topology under these synthesis conditions. Indeed, ^{13}C MAS NMR shows the presence of hexadecyltrimethylammonium cations in the solid besides dipropylamine (Fig. 1). The organic content of the samples prepared using surfactants is higher than that of the reference material R (Table 1), which suggests that preferential substitution of P for Si has taken place. Indeed, the high content of sample 2 indicates that the average charge per Si atom is higher than in sample 1. The ^{29}Si MAS NMR spectrum (Fig. 2) of sample 2 shows the presence of prominent shoulders in the δ −101 region, which can be assigned to SinAl ($0 < n < 4$) environments. This can be more clearly seen in the deconvoluted spectrum where a signal at δ −97.4 is the most intense of the spectrum. This signal can be attributed to Si(3Al1Si)

Table 1 SiO_2 and C content of the solids and catalytic activity in *m*-xylene isomerization (T = 350 °C; HC:N_2 = 4; X_0 = *ca.* 5%)

Sample	SiO_2 (% *m*/*m*)	C (% *m*/*m*)	V_0r^a/mol_{mx} g_{cat}^{-1} h^{-1}	TON^c/mol_{mx} mol_{Si}^{-1} h^{-1}
R	15.0	3.7	2.8 × 10^{-3}	1.4
1	12.3	4.9	1.4 × 10^{-2}	6.8
2	5.6	12.7	9.7 × 10^{-3}	10.4
SAPO-37[b]	—	—	5.6 × 10^{-2}	20.1

[a] V_0r = initial reaction rate calculated from the conversion at time on-stream = 0 (using the equation: $X_m = X_0 \times e^{-kt}$) divided by $w(g_{cat})/F(mol_{mx}\ h^{-1})$ adjusted to obtain an initial conversion (X_0) of *ca.* 5 mol%. [b] $(Al_{0.47}Si_{0.17}P_{0.36})O_2$. [c] TON = turnover number.

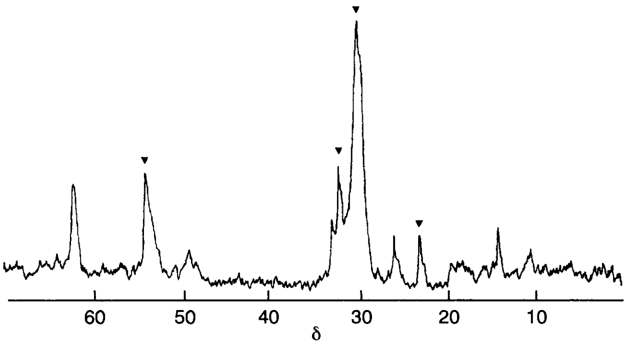

Fig. 1 ^{13}C CP/MAS NMR spectrum of sample 2 recorded with a Varian VXR S-400 WB. The ^1H–^{13}C contact time was 4 ms and the recycle delay 3 s. Peaks with ▼ correspond to the HDTMA.

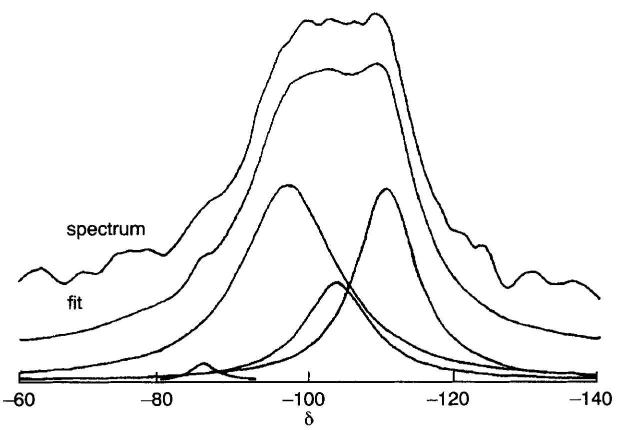

Fig. 2 ^{29}Si MAS NMR spectrum of sample 2. Pulses of 4 μs, a flip angle of 45° and a recycle delay of 40 s were used.

environments. The two other prominent signals at δ −103.9 and −110.7 can be assigned to Si(2Al2Si) and Si(4Si) environments, respectively. The presence of a large fraction of Si atoms with at least one Al atom in the first coordination shell can be attributed in the first instance to a large reduction of the silica domains present in the material, since these silicon environments should appear in the border region between the Si islands and the pure AlPO domains. However, the presence of silica–alumina, zeolite-type domains cannot be excluded.

The main consequence of this modification to the normal mechanism of silicon incorporation into the VFI framework should be a large increase in the catalytic activity of the material in acid catalysed reactions. For this reason, a portion of the solid was calcined first at 550 °C in a N_2 flow, and then in air for 3 h to remove the last traces of organic materials. Under these conditions, the VPI-5 structure transforms into $AlPO_4$-8. The calcined solids obtained from surfactant-containing gels show much higher activity than the reference sample in the isomerization–disproportionation of *m*-xylene (Table 1). Indeed, the activity per silicon atom of sample 2 is much higher than the reference sample R, and reaches a value half as high as that observed for a SAPO-37 sample with 33 Si atoms per unit cell.[10]

In conclusion, it has been shown that the presence of a cationic surfactant in a two liquid phase system facilitates the production of highly crystalline SiVPI-5 which shows enhanced catalytic activity in acid catalysed reactions.

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