Titanium Substitution in Silicon-free Molecular Sieves: Anatase-free $TAPO_4$-5 and $TAPO_4$-11 Synthesis and Characterisation for Hydroxylation of Phenol

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Titanium-substituted $ALPO_4$-5 and $ALPO_4$-11 are synthesised using a modified procedure; they catalyse the hydroxylation of phenol to the extent of *ca.* 32%, with good selectivity to catechol.

Titanium-containing molecular sieves are of current interest in zeolite science, with respect to redox catalytic behaviour.[1] After the patented report on the synthesis and properties of TS-1,[2] there has been increased interest in the titanium-containing materials.[3–7] Ti substitution is well established in the topologies of MFI, MEL,[3] BET,[4] ZSM-48[5] HMS and MCM-41.[6] Recently, Ti substitution in $SAPO_4$-5 ($TAPSO_4$-5) was reported by Tuel *et al.*[7] In all these molecular sieves the environment around titanium consists of silicon and it is believed that Ti–O–Si bonds are essential for redox catalytic activity.[7] Ti substitutions in the aluminophosphate ($ALPO_4$) are expected to result in Ti–O–P bonds.[8] Since aluminophosphates are more hydrophilic than silicalites, different chemistry and selectivity can be expected. Ti substitution in $ALPO_4$ molecular sieves has been claimed,[9] but the position of substitution and the extent of catalytic activity are not known.[10] Ti substitution in pure $ALPO_4$ is reported to be difficult and requires modification of the procedure for gel preparation, without modifying the gel composition; this also can lead to an anatase-free phase. We now report the direct synthesis of titanium-substituted $ALPO_4$-5 and $ALPO_4$-11 molecular sieves free from anatase, their properties and their catalytic activity in the hydroxylation of phenol.

$TAPO_4$-5 and $TAPO_4$-11 were prepared from the gel composition R : $x$$TiO_2$: Al_2O_3 : P_2O_5 : $40H_2O$, where R is triethylamine or tripropylamine for AFI topology and dibutylamine or dipropylamine for AEL topology, and x varied from 0.02 to 0.125. The preparation of gel A and solution B is typical. Gel A was prepared by soaking aluminium isopropoxide (28.6 g) in water (35 ml); the mixture was kept overnight and homogenised for 2–3 h. Solution B consisted of water (10 ml) and phosphoric acid (8.9 ml), to which titanium tetrabutoxide (2.4 ml; x = 0.1) was added, followed by 30% H_2O_2 (2.4 ml), which resulted a clear dark orange solution in 10 min. Solution B was added to gel A, followed by the addition of the appropriate template. The resulting gel was heated between 150 and 200 °C in a 300 ml stainless steel autoclave. The well crystallised $TAPO_4$s were obtained 2–4 h earlier than $ALPO_4$s.

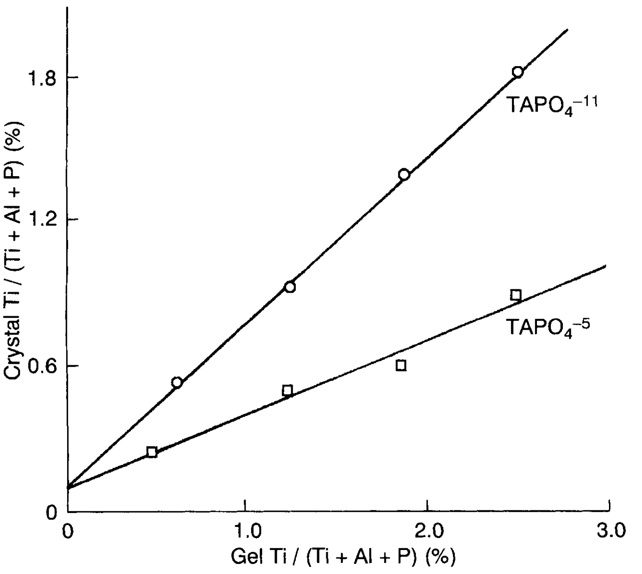

Fig. 1 Molar Ti content in gel *vs.* crystal $TAPO_4$-5 and $TAPO_4$-11 samples

The extent of Ti incorporation into the crystal lattice depends on the gel composition (Fig. 1). The ratio Ti/(Ti + Al + P) is lower in the crystal lattice than in the gel, especially for AFI, though higher values have been reported for $TAPSO_4$-5.[7]

Peaks at 230 nm in the diffuse reflectance spectra indicate that Ti^{4+} is in the tetrahedral positions and the absence of a peak or shoulder at 330 nm suggests the absence of anatase.[11] The absence of a strong peak at 140 cm^{-1} in the Laser–Raman spectra[12] of calcined $TAPO_4$s confirms the absence of anatase (Fig. 2). A shoulder at 1040 cm^{-1} in the FT–IR spectra of calcined $TAPO_4$ and its absence in that of $ALPO_4$ is assigned to the presence of Ti in the framework.

^{27}Al and ^{31}P MAS NMR spectra of $TAPO_4$-5 and $TAPO_4$-11 show a single symmetrical peak with spinning side bands confirming Al and P in tetrahedral positions. SEM showed that the particles formed agglomerated rectangular polycrystals with

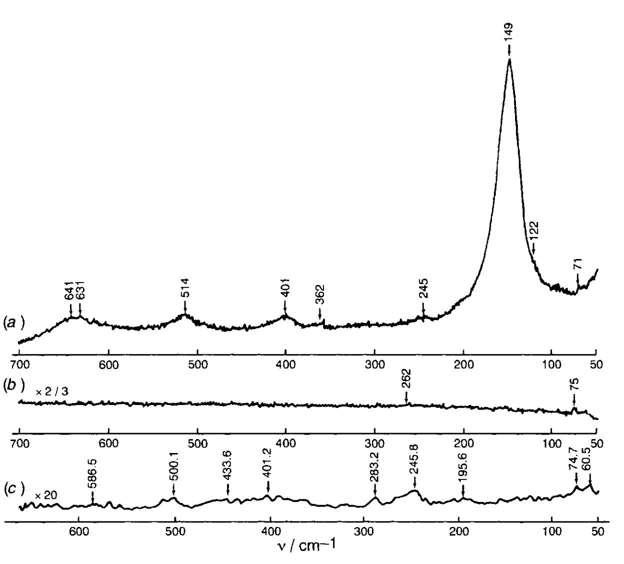

Fig. 2 Laser–Raman spectra of (*a*) 2% (*m*/*m*) anatase and $TAPO_4$-5, (*b*) calcined $TAPO_4$-11 (1.46) and (*c*) calcined $TAPO_4$-5 (1.68)

Table 1 Direct hydroxylation of phenol by $TAPO_4$-5 and $TAPO_4$-11 with dilute hydrogen peroxide[a]

Catalyst	Ti (mol%)	Phenol conversion (%)	Yield (mol%) Catechol	Yield (mol%) Hydroquinone
$ALPO_4$-5	0.00	4.5[b]	0.8	—
$TAPO_4$-5	0.90	13.2[b]	9.3	—
	1.68	17.1	11.5	5.0
$TAPO_4$-11	0.91	25.8	17.6	7.9
	1.46	32.2	21.3	10.5

[a] Reaction conditions: H_2O_2/phenol molar ratio = 3, catalyst 200 mg, phenol 1.9 ml, 30% H_2O_2 5 ml, water 5 ml, T = 80 °C, 5 h. Products were homogenised by acetone and analysed by HP-5890 GC (OV-17 column). [b] Other products were not identified.

spherical shape with sizes in the ranges 22–25 μm and 5–8 μm for $TAPO_4$-5 and $TAPO_4$-11, respectively.

Titanium substitution in the framework of $TAPO_4$ was evident from the direct hydroxylation of phenol (Table 1). Hydroxylation occurs to the extent of 32.2% and 17.1% for $TAPO_4$-5 (1.68 Ti mol%) and $TAPO_4$-11 (1.46 Ti mol%), respectively. The catalytic hydroxylation by $TAPO_4$ was comparable to that of TS-1.[13]

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