

Synthesis and characterization of titanium-aluminophosphate molecular sieves of AFI and AEL topologies

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Titanium-aluminophosphate molecular sieves (TAPO₄) of AFI and AEL topologies, free of anatase have been synthesised by modified procedure and characterised by XRD, TGA, DTA, Laser-Raman, DRS, FT-IR, ²⁷Al, ³¹P and ¹³C MAS-NMR, SEM and chemical analysis. The synthesised TAPO₄s are crystalline and pure. The unit-cell constants are found to decrease on substitution of titanium, which occupies tetrahedral position. The chemical analysis and ³¹P MAS-NMR show the presence of traces of P₂O₅ in the channels.

Metal substituted molecular sieves (metal = Ti, V, Cr etc) are well known for their redox catalytic activities¹⁻³. Substitution of titanium in the framework of MFI, MEL, BEA, ZSM-48, HMS and MCM-41 has been well established⁴⁻⁸. Study on the substitution of titanium in silicate and aluminosilicate framework has become one of thrust areas of research.

Aluminophosphates are novel type of molecular sieves reported in early eighties⁹. Many of them offer useful potential applications like shape-selective sorption. Aluminophosphate and silicalite frameworks are electrically neutral, the former composed of alternate AlO₄ and PO₄ tetrahedral units, and the latter with SiO₄ tetrahedral units. The charge separation in the former makes it more hydrophilic than the latter. Though substitution of titanium in AlPO₄s have been claimed¹⁰, their characterisation and the position of titanium have not been done. Moreover, anatase-free TAPO₄-5 has not been authentically claimed so far. Titanium-substitution in SAPO₄-5 has been reported, in which titanium is in silica environment¹¹. Recently, we have reported some aspects on synthesis and characterisation¹² of titanium substituted AlPO₄-5 (TAPO₄-5) and AlPO₄-11 (TAPO₄-11). Their activity to conversion of phenol and their selectivity to dihydroxybenzene were tested in the liquid phase at 80°C using H₂O₂ as oxidant. It is observed that the extent of conversion of phenol and selectivity to dihydroxybenzene are influenced both on Ti content of the catalysts and their topology. The present work discusses the synthesis and characterisation of TAPO₄s in detail.

Materials and Methods

TAPO₄-5 and TAPO₄-11 were prepared by

heating a gel with composition R : x TiO₂ : Al₂O₃ : P₂O₅ : 40 H₂O at 175 and 195°C respectively at autogeneous pressure for 16-18 h in a 300 ml autoclave; R is triethylamine for TAPO₄-5 and di-*n*-propylamine for TAPO₄-11. The value of x varied from 0.0 to 0.125. The preparation of final gel involves preparation of gel 'A' and solution 'B'. Gel 'A' was prepared by dissolving 28.6 g of aluminiumtriisopropylate in 35 ml of water and kept overnight. It was homogenised by stirring for 2-3 h. Solution 'B' was prepared by mixing 8-9 ml of H₃PO₄, 15 ml of water, 2.4 ml of titaniumtetrabutoxide and 2.4 ml of 30% H₂O₂ (x = 0.10). The resulting clear solution 'B' was added to gel 'A' mixed thoroughly by adding 9.7 ml of triethylamine/9.4 ml di-*n*-propylamine to get final gel. A flow chart of TAPO₄-5 preparation is illustrated in Fig. 1. After crystallisation, the solid products were washed several times, centrifuged and dried at 110°C overnight. The materials were calcined at 600°C for more than 24 h in air.

The calcined samples were analysed by powder

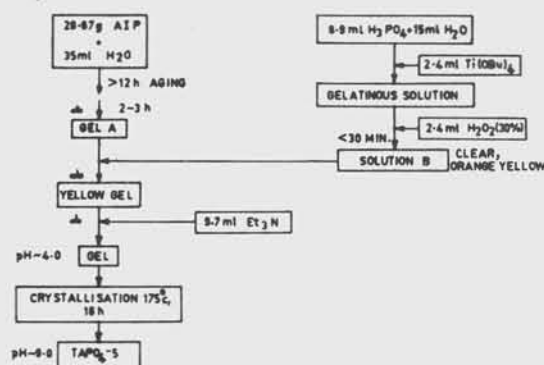


Fig. 1—Flow chart of typical TAPO₄-5 synthesis

XRD (Philips PW 1710) in the scan range of 2θ between $5-50^\circ$ with scan speed of $2^\circ/\text{min}$ using CuK_α as X-ray source and the unit-cells were indexed on comparison with compiled data¹³. The indexed data were refined by least square minimisation and the unit-cell constants were calculated.

Thermogravimetric analysis (TGA) was done in Mettler TA 3000 instrument with heating rate of $20^\circ/\text{min}$ upto 800°C in ambient air. Laser-Raman spectra were recorded by DILOR Z24 Raman spectrometer using argon laser excitation at 514.5 nm with laser power of 300 mW, slit width of 400 μm and spectral slit width of 4.29 cm^{-1} . The data were collected by single channel analyser between $50-700\text{ cm}^{-1}$ in sequential manner with integration time of 1 sec. Diffuse reflectance spectra (DRS) of pelletised powder samples were recorded using Carry-2390 UV-VIS-NIR spectrometer in the range 220–600 nm.

SEM pictures were taken using Hitachi S2400 instrument. Prior to analysis, samples were dispersed in alcohol, dried and gold coated. FT-IR spectra were recorded using Bruker IFS-66V spectrometer by KBr pellet technique. Prior to recording, the spectra chamber was evacuated to 10^{-3} torr and the data recorded between $400-4000\text{ cm}^{-1}$ and averaged over 65 scan. The MAS-NMR of ^{27}Al , ^{31}P and ^{13}C were recorded in Bruker MSL-300 spectrometer, with frequency 78.3, 121.5 and 75.5 MHz respectively and the sample spinning rate varied between 2.9–3.5 KHz. Dilute aluminium nitrate solution, 85% phosphoric acid and tetramethyl silane respectively were used as reference to calculate the chemical shift.

The calcined samples were dissolved in con. H_2SO_4 containing few drops of H_2O_2 , and the resulting solution was analysed by ICP minitorch-3410 instrument using the characteristic wavelength 308, 215 and 336 nm for Al, P and Ti respectively.

Results and Discussion

The preparation of TAPO₄s involve aqueous medium, in which titanium alkoxide rapidly hydrolyse to form anatase, which reduces the availa-

bility of titanium in the framework. To prevent this, we have modified the procedure for TAPO₄ preparation. Titanium was introduced as peroxytitanate by combining titanium isobutoxide with requisite amount of 30% H_2O_2 , followed by the addition of phosphoric acid, which resulted in a clear red-orange solution.

Figure 2 shows XRD patterns of as-synthesised TAPO₄-5 (Ti mol%=0.94) and TAPO₄-11 (Ti mol%=1.46). The patterns exactly matches with reported and compiled data¹³, confirming that they belong to AFI and AEL topologies. TAPO₄-5 occurs as single phase and TAPO₄-11 with traces of impurities and both are crystalline. The refined cell constants for as-synthesised samples are given in Table 1. The estimated standard deviations are within 0.001 for the co-ordinates. We have observed a decrease in cell volume for

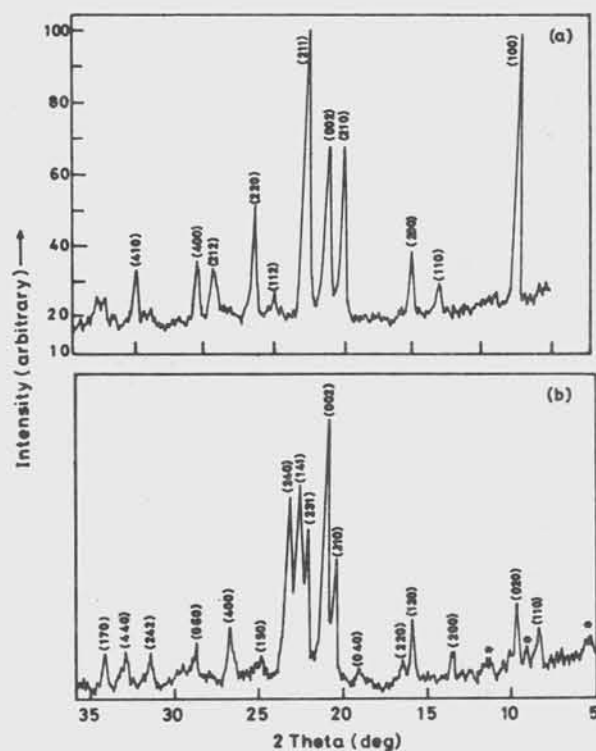


Fig. 2—XRD patterns of as-synthesised (a) TAPO₄-5 and (b) TAPO₄-11

Table 1—Unit-cell parameters of as-synthesised TAPO₄s

TAPO ₄ -5				TAPO ₄ -11				
Ti mol%	a(Å)	c(Å)	V(Å ³)	Ti mol%	a(Å)	b(Å)	c(Å)	V(Å ³)
0.00	13.629	8.517	1371	0.00	14.086	18.250	9.071	2094
0.48	13.638	8.058	1370	0.66	13.330	18.645	8.419	2092
0.95	13.631	8.491	1366	1.48	13.374	18.676	8.372	2090
1.68	13.599	8.460	1355	2.08	13.262	18.515	8.446	2074

all samples including the calcined. The decrease is proportional to the amount of titanium incorporated in the material for both $\text{TAPO}_4\text{-5}$ and $\text{TAPO}_4\text{-11}$. If titanium is replacing aluminium and phosphorous together, unit-cell reduction is expected, since the bond distances of Ti-O is 1.78 Å, Al-O is 1.75 Å and P-O is 1.53 Å (ref. 14). If titanium is replacing aluminium, not much difference is expected. Vanadium substitution in $\text{AlPO}_4\text{-5}$ was expected to increase its unit-cell volume, but no change was observed¹⁵. In silica analog of $\text{AlPO}_4\text{-5}$ (SSZ-24), no change in unit-cell volume is expected (bond distance of Si-O is 1.62 Å), but a decrease was observed. Structural analysis of SSZ-24 revealed a reduction in bond angle from 176.5° (Al-O2-P) to 142.2° (Si-O2-Si)¹⁶. A similar variation of bond angle in TAPO_4s is also expected, which may account for the reduction in cell constants.

TGA analysis of $\text{Et}_3\text{N-TAPO}_4\text{-5}$ (Ti mol % = 1.21) and $\text{Pr}_2\text{NH-TAPO}_4\text{-11}$ (Ti mol % = 0.39) are shown in Fig.3 along with differential thermogravimetric curves. The loss of triethylamine occurs at several steps, major loss occurring at 180, 264 and 458°C . The major loss of di-*n*-

propylamine occurs at 216°C . It was found that approximately two molecules of triethylamine and one molecule of di-*n*-propylamine exist in channels per unit cell.

Raman spectra of calcined $\text{TAPO}_4\text{-5}$ (Ti mol % = 1.68), $\text{TAPO}_4\text{-11}$ (Ti mol % = 1.46) and $\text{TAPO}_4\text{-5}$ mixed with 2.0 wt% anatase are given in Fig.4. The mixture shows a strong peak at 149 cm^{-1} , while pure TAPO_4s do not show any peak at this region confirming the absence of anatase¹⁷. Hence, it is presumed that titanium in TAPO_4 molecular sieves should be present in the framework.

The diffuse reflectance spectra (DRS) for calcined samples of $\text{TAPO}_4\text{-5}$ (Ti mol % = 0.95, 0.94) and $\text{TAPO}_4\text{-11}$ (Ti mol % = 2.08, 0.97, 0.66) were recorded. The peaks at 220-230 nm were assigned to tetrahedral Ti^{4+} . The peak intensity also increases with amount of titanium in the framework. As the DRS recordings were done in an open atmosphere, the absorption of moisture is unavoidable and it is reflected as band up to 320 nm, as a result of the coordination of water. The absence of peak or shoulder at 330 nm suggests the absence of anatase¹⁸.

The chemical composition of synthesised samples were as follows:

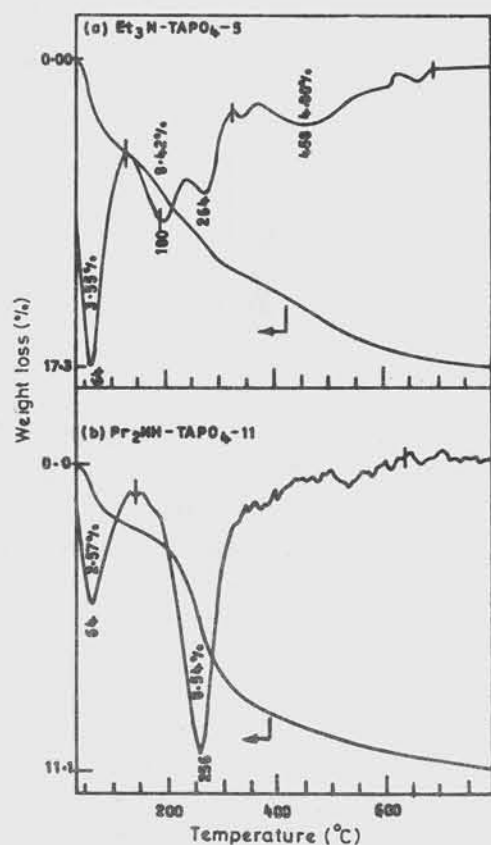


Fig. 3—TGA and DTG curves of (a) $\text{Et}_3\text{N-TAPO}_4\text{-5}$ and (b) $\text{Pr}_2\text{NH-TAPO}_4\text{-11}$

$\text{TAPO}_4\text{-5}$	$\text{TAPO}_4\text{-11}$
$\text{Ti}_{0.07}\text{Al}_{10.34}\text{P}_{13.58}\text{O}_{48}$	$\text{Ti}_{0.08}\text{Al}_{9.04}\text{P}_{10.88}\text{O}_{40}$
$\text{Ti}_{0.10}\text{Al}_{10.51}\text{P}_{13.39}\text{O}_{48}$	$\text{Ti}_{0.10}\text{Al}_{8.74}\text{P}_{11.16}\text{O}_{40}$
$\text{Ti}_{0.12}\text{Al}_{10.75}\text{P}_{13.12}\text{O}_{48}$	$\text{Ti}_{0.16}\text{Al}_{8.84}\text{P}_{11.00}\text{O}_{40}$
$\text{Ti}_{0.14}\text{Al}_{10.61}\text{P}_{13.25}\text{O}_{48}$	$\text{Ti}_{0.18}\text{Al}_{8.88}\text{P}_{10.94}\text{O}_{40}$

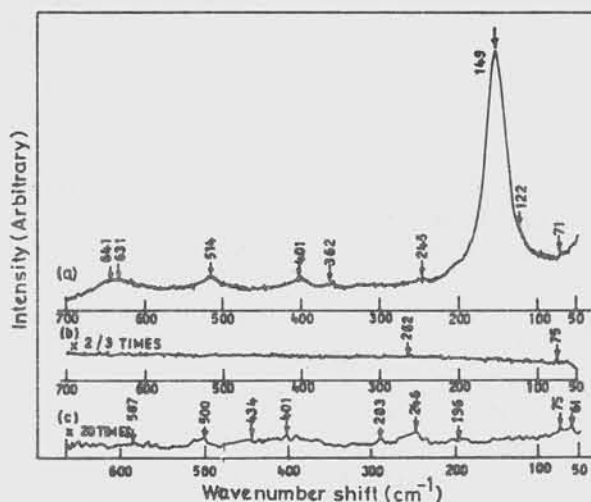


Fig. 4—Laser-Raman spectra of (a) $\text{TAPO}_4\text{-5}$ with 2 wt% anatase, (b) $\text{TAPO}_4\text{-11}$ and (c) $\text{TAPO}_4\text{-5}$

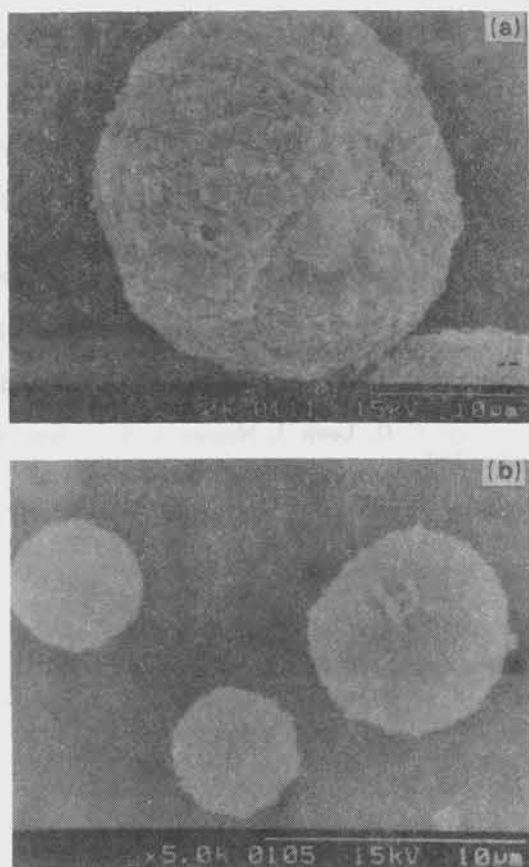


Fig.5—SEM picture of (a) TAPO₄-5 and (b) TAPO₄-11

The ratio of P/(Ti + Al) varies from 1.2-1.3, indicating the excess phosphorous present at P₂O₅ in the channels.

SEM pictures of TAPO₄-5 (Ti mol% = 0.94) and TAPO₄-11 (Ti 01 mol% = 1.46) are given in Fig.5. They crystallize in spherical agglomerate of size varying between 22-25 μm and 5-8 μm respectively. The pictures also confirm the phase purity.

The FT-IR of calcined TAPO₄-5 (Ti mol% = 0.95) and TAPO₄-11 (Ti mol% = 0.91) was recorded. The calcined TAPO₄-11 shows a shoulder at 1040 cm^{-1} , which is absent in as-synthesised. Calcined TAPO₄-5 and CrAPO₄-11 also show the IR peak at 1040 cm^{-1} . Titanium and vanadium in silica environment give a distinct IR peak 960 cm^{-1} (refs. 11,15,19) which were assigned to M-O-Si vibrations. However in AlPO₄ environment, the substitution of Ti, V and Cr give peaks at different places, which are very close to the simple metal-oxo (M=O) vibrations^{19,20}. Pure titanyl occurs at 1087 cm^{-1} and hence the shoulder at 1040 cm^{-1} in TAPO₄ was assigned to Ti=O vibrations. Similar metal-oxo species could be present in VAPO₄ and CrAPO₄. In TAPO₄-5, the shoulder is not

clear due to the presence of template, which was evident from template peaks at 1384 and 1501 cm^{-1} .

The calcined TAPO₄-5 (Ti mol% = 0.94) and TAPO₄-11 (Ti mol% = 1.46) were analysed by ²⁷Al and ³¹P MAS-NMR and the spectra were recorded. ²⁷Al MAS-NMR of both samples show a single symmetric peak at 30.3 and 32.3 ppm respectively for TAPO₄-5 and TAPO₄-11 with side bands. ³¹P MAS-NMR spectra also showed single symmetric peak at -29.5 and -31.2 ppm respectively for TAPO₄-5 and TAPO₄-11 with side bands. These peaks suggest that aluminium and phosphorous in TAPO₄s are found to be in tetrahedral environment. The side bands changed their position on changing the spinning rate and they arise from dipolar-dipolar interaction of the metal ion. A close examination of ³¹P spectra show a small broadening at zero and -20 ppm, which suggest the presence of phosphorous pentoxide in trace amount. The as-synthesised Et₃-TAPO₄-5 and Pr₂NH-TAPO₄-11 were analysed by ¹³C MAS-NMR and the spectra was recorded. Et₃N-TAPO₄-5 show signals corresponding to -CH₃ and -CH₂-N- carbons at δ 9.14 and 47.48 ppm respectively. Pr₂NH-TAPO₄-11 show signals corresponding to -CH₃, -CH₂- and -CH₂-N- at δ 10.81, 19.05 and 49.46 ppm respectively, which confirms that the templates are found in the channels of TAPO₄s and is responsible for crystallisation with the concerned topologies.

To conclude the above discussion, anatase-free, highly crystalline TAPO₄-5 and TAPO₄-11 were synthesised by modified procedure. The unit cell constants of TAPO₄-5 and TAPO₄-11 were found to decrease and the extent of decrease is proportional to titanium content. Titanium is found to be present as titanyl species (Ti=O) in AlPO₄ environment. The presence of trace amount of P₂O₅ is confirmed to be in the channels of TAPO₄s.

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