

# Synthesis and characterization of a novel titanium aluminophosphate molecular sieve with ATS structure: TAPO-36

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An attempt is made to synthesize hydrothermally a titanium aluminophosphate molecular sieve with ATS structure (TAPO-36); successful synthesis established the range of titanium incorporation  $0.04 < x < 0.12$  where  $x$  is the Ti:P ratio in the gel which has the composition  $2\text{Pr}_3\text{N}:2x\text{TiO}_2:\text{P}_2\text{O}_5:(1-x)\text{Al}_2\text{O}_3:40\text{H}_2\text{O}$ .

Recently, increasing attention has been devoted to the synthesis, characterization and catalytic activity of titanium containing molecular sieves by virtue of their unique structural and physicochemical properties. Although titanium substitution is well documented in various topologies,<sup>1-3</sup> little information on the insertion of titanium in aluminophosphate molecular sieves has been published. Excluding the original patent on synthesis of some titanium containing ALPOs,<sup>4</sup> only the synthesis and catalytic investigation of TAPSO-5,<sup>5</sup> and more recently of TAPO-5 and TAPO-11,<sup>6</sup> have been published. Now we are reporting, for the first time, the synthesis of a titanium containing aluminophosphate molecular sieve with ATS structure which has no ALPO analogue. The structure type 36 aluminophosphate-based molecular sieve has an elliptical channel with staggered annular side pockets. These side pockets produce a stereospecificity that is quite different from that in the cylindrical channels of ALPO<sub>4-5</sub> and is responsible for the greater adsorption capacity of structure type 36 molecular sieve for H<sub>2</sub>O, O<sub>2</sub>, *n*-butane and neopentane than that of ALPO<sub>4-5</sub>.<sup>7</sup> The peculiar structure of MeAPO-36 may also be partly responsible for their higher potentiality in cracking, among all ALPOs and metal substituted ALPOs possessing a 12-membered ring structure.<sup>8</sup> In order to make it an effective catalyst for selective oxidation, hydroxylation and epoxidation reactions, attempts were made to incorporate titanium in the framework position of the ATS structure by direct hydrothermal synthesis.

Table 1 XRD data of calcined TAPO-36 and MAPO-36

TAPO-36		MAPO-36 <sup>a</sup>	
<i>d</i> /Å	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> /Å	<i>I</i> / <i>I</i> <sub>0</sub>
11.24	100	11.2	100
10.83	33	10.8	31
6.56	11	6.54	4
5.60	4	5.59	11
5.37	35	5.39	31
4.60	38	4.64	13
4.28	20	4.24	34
4.07	6	4.10	15
—	—	4.03	13
3.95	39	3.95	14
3.74	10	3.72	5
3.28	21	3.27	12
3.15	7	3.15	7
3.06	5	3.08	6
2.92	3	—	—
2.80	8	2.80	7
2.57	2	2.58	5

<sup>a</sup> Data for MAPO-36 are from ref. 8.

Tripropylamine (Pr<sub>3</sub>N) was used as the templating agent in the present studies. From preliminary synthesis runs, it was observed that it is necessary to modify the gel composition and method of preparation to crystallize a pure TAPO-36 phase with no contribution due to either TAPO-5 and/or anatase phases. Pure TAPO-36 was prepared from a gel with molar composition  $2\text{Pr}_3\text{N}:2x\text{TiO}_2:\text{P}_2\text{O}_5:(1-x)\text{Al}_2\text{O}_3:40\text{H}_2\text{O}$ . Titanium acetyl acetonate, phosphoric acid and pseudoboehmite (catapal B) were used as the sources of titanium, phosphorus and aluminium, respectively.

In a typical gel preparation ( $x = 0.06$ ), 4.15 g titanium acetyl acetonate solution (75 mass%) was added dropwise to 16.47 g phosphoric acid diluted with 51.5 g water. The mixture was blended for 30 min and to it 9.64 g pseudoboehmite was added gradually with stirring and was stirred for 2 h until a homogeneous mixture was obtained. Finally 20.47 g of Pr<sub>3</sub>N was introduced slowly and slurry blended for 30 min. The gel was then transferred to a Teflon-coated autoclave and subjected to hydrothermal treatment under autogenous pressure initially at 373 K for 24 h, followed by further heating at 408 K for 48 h. After separating, washing and drying, the product was calcined at 803 K in air for 18 h.

TAPO-36 was characterized by XRD, N<sub>2</sub> and *n*-butane adsorption, elemental analysis, diffuse reflectance UV-VIS spectroscopy, TG-DTG-DTA, SEM, MAS NMR and XPS.

Under the present experimental conditions, the concentration of titanium in the gel was found to influence the nature of the crystalline phases produced. Pure TAPO-36 was obtained only from the gels with  $0.04 < x < 0.12$ , whereas most of the time TAPO-5 co-crystallized with other gel compositions. XRD *d*-spacing values and relative intensities of a calcined product obtained from the gel with  $x = 0.06$  are presented and compared with similar data reported for MAPO-36<sup>8</sup> in Table 1. This comparison allows us to confirm that the crystallization product is pure TAPO-36 without TAPO-5 or other crystalline phases. The scanning electron micrographs (Fig. 1) reveal the needle-

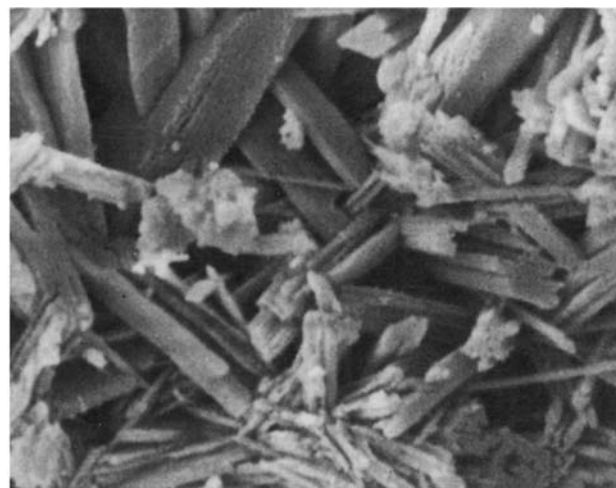
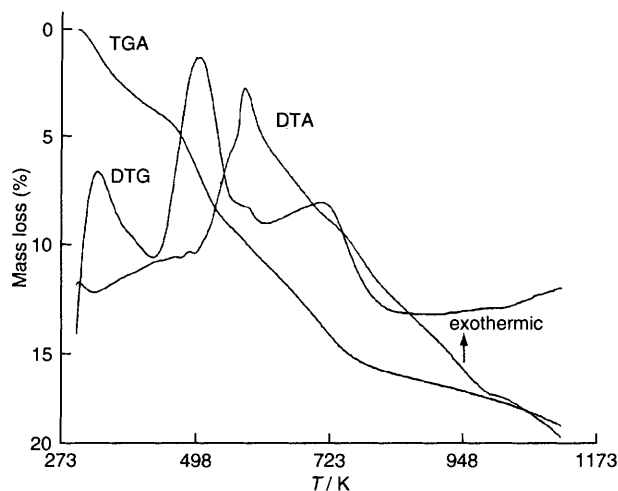


Fig. 1 Scanning electron micrograph of TAPO-36

**Table 2** XPS binding energies and elemental analysis of TAPO-36

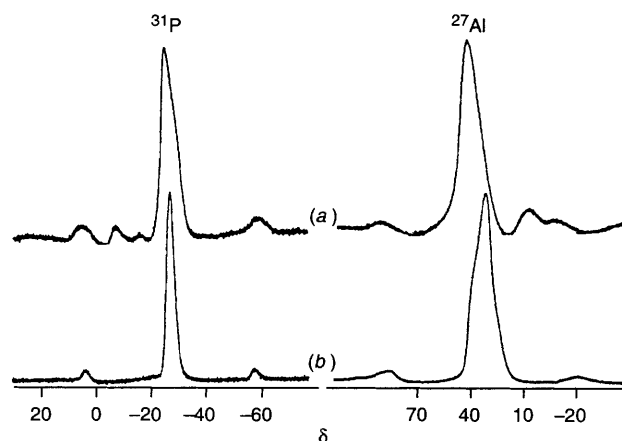
Binding energy/eV <sup>a</sup>				Atomic ratio			
				Ti:Al		Al:P	
O <sub>1s</sub>	Al <sub>2p</sub>	P <sub>2p</sub>	Ti <sub>2p</sub>	Bulk	Surface	Bulk	Surface
532.3 (3.2)	74.9 (2.9)	134.7 (2.9)	459.0 (2.5)	0.07	0.07	1.33	1.51

<sup>a</sup> Full width at half maximum (eV) in parentheses.



**Fig. 2** TGA-DTG-DTA curves of TAPO-36 in air

like morphology of TAPO-36 crystals and the absence of any amorphous material. The absence of pore plugging or extraneous phases was also checked by N<sub>2</sub> and *n*-butane adsorption. N<sub>2</sub> sorption showed a BET surface area of 380 m<sup>2</sup> g<sup>-1</sup> and void volume of 0.12 ml g<sup>-1</sup>. The amount of *n*-butane adsorbed at 296 K and 715 Torr is 8.5 mass% which is comparable to the 7.3% value reported for MAPO-36.<sup>9</sup> Diffuse reflectance UV-VIS spectra indicate a single peak at 230.7 nm for as-synthesized TAPO-36 which was shifted to 236 nm after calcination. The absence of any shoulder around the anatase peak position (300 nm) showed that TAPO-36 is free from any extra-framework titanium oxide (anatase) which supports the BET and *n*-butane adsorption results. Thermal analysis of TAPO-36 in air is presented in Fig. 2. A two-step mass loss was observed in the temperature ranges 298–423 and 423–615 K which was assigned to desorption of water and complete cracking and combustion of the template, respectively. XPS binding energies and apparent relative atomic concentration for the sample with  $x = 0.06$  are summarized in Table 2. The binding energy of Ti<sub>2p</sub> is close to the value reported for tetrahedrally coordinated titanium.<sup>10</sup> Fig. 3 illustrates the <sup>27</sup>Al and <sup>31</sup>P MAS NMR spectra of as-synthesized and calcined forms of TAPO-36, recorded at ambient temperature. <sup>27</sup>Al MAS NMR spectrum of as-synthesized TAPO-36 show two peaks at  $\delta$  40.2 and 6.6 [relative to Al(NO<sub>3</sub>)<sub>3</sub> (aq.), pH  $\approx$  1] which were assigned<sup>11–14</sup> to AlO<sub>4</sub> tetrahedra and aluminium in interaction with adsorbed/occluded water and/or template molecules, respectively. Upon calcination, the disappearance of the peak at  $\delta$  6.6 suggests the direct influence of adsorbed and/or occluded template and/or water molecules on the Al environment and absence of octahedral aluminium in an amorphous environment such as in pseudoboehmite.<sup>15</sup> The <sup>27</sup>Al MAS NMR spectrum of the calcined form exhibited a main peak at  $\delta$  32.3 with a shoulder at *ca.*  $\delta$  40, indicating alteration in the coordination environment of aluminium atoms due to adsorbed and/or occluded water and/or template molecules. Similar results were obtained from <sup>31</sup>P MAS NMR spectra. The spectrum of the as-synthesized form showed a main peak at  $\delta$  -26.7 [relative to H<sub>3</sub>PO<sub>4</sub> (85 mass%)] which is ascribed<sup>12</sup> to PO<sub>4</sub> tetrahedra and



**Fig. 3** <sup>27</sup>Al and <sup>31</sup>P MAS NMR spectra of as-synthesized (a) and calcined (b) TAPO-36

shifted to  $\delta$  27.4 after calcination. The as-synthesized TAPO-36 material present additional peaks at  $\delta$  -7.5 and -15.9 which were not visible after calcination, suggesting that it arises from the framework phosphorus adjacent to occluded organic template and/or water molecules.

The overall characterization results lead to the conclusion that a novel titanium containing aluminophosphate molecular sieve with ATS structure (TAPO-36) which has no ALPOs counterpart has been synthesized and pure TAPO-36 can be obtained only from the gel with Ti:P ratio in the range of 0.04–0.12:1 after hydrothermal crystallization.

Investigations on the catalytic behaviour of TAPO-36 catalysts in various hydrocarbon conversion reactions, *viz.* selective oxidation, hydroxylation and epoxidation, are in progress.

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