Synthesis and Characterization of a Novel Vanadium Analogue of ALPO-31

N. Venkatathri, S. G. Hegde and S. Sivasanker*

National Chemical Laboratory, Pune 411 008, India

A new analogue of AlPO-31 molecular sieve (VAPO-31) is synthesized using secondary long chain alkylamines and characterized by physicochemical and catalytic oxidation properties.

Vanadium analogues of molecular sieves based on zeolites and aluminophosphates are potential catalysts for partial oxidation reactions.[1,2] The only V-analogues of 12MR molecular sieves reported so far are V-NCL-1, V-MCM-41 and VS-12 belonging to the zeolite family[3] and VAPO-5,[4–7] to the AlPO family.

AlPO-31 belongs to a novel structure type 'ATO' and space group $R\bar{3}$ with unit cell constants $a = b = 20.83$, $c = 5.0$ Å and $r = 109°$.[8] Studies on AlPO-31 structure type are also limited. In addition to the patent reports[9,10] there are only two publications, one on AlPO-31[8] and another on SAPO-31.[11] Only two templates, dipropylamine (DPA) and butylethylamine (BEA) were reportedly useful[9,10] in its synthesis. It should be noted that the dimension of these templates is 7.0 × 10.4 Å whereas the diameter of the main channel in AlPO-31 is 5.3 Å parallel to 'c' direction with repeat distance of only 5 Å.[8] It is an anomalous example of a structure template specificity. We report here our preliminary results on the synthesis and characterization of VAPO-31 using two different secondary alkylamines, DPA and dibutylamine (DBA), the latter being used for the first time as a template in the synthesis of 'ATO' type molecular sieves.

VAPO-31 was synthesized hydrothermally using a reactive gel of the following molar composition $Al_2O_3:P_2O_5:X\ V_2O_5:R:50\ H_2O$, where R is DPA, DBA or DPeA (dipentylamine), and X = 0.02 (for sample **2**) and 0.05 (for samples **3** and **4**). In a typical synthesis, pseudoboehmite (7.16 g, 74.2%, Vista Chemicals, USA) was mixed with water (10 ml), phosphoric acid (11.5 g, 85%, S.D. fine, India) was added dropwise with thorough mixing for 30 min. To this gel, vanadium pentoxide (0.475 g, 98%, Aldrich, USA) was added and thoroughly mixed. This gel was aged at 298 K for 12 h. Then DBA (7.58 g, 99%, Aldrich) with water (30 ml) was added slowly while stirring for 1 h. This reaction gel was crystallized in PTFE lined stainless steel autoclave at 473 K for 48 h. The product was then filtered, washed and dried at 373 K in air. The sample was calcined in air to remove the template by heating slowly (1.6 K min^{-1}) to 773 K, and holding for 8 h. The calcined sample was then treated with an aqueous ammonium acetate solution (1.0 mol dm^{-3}) for 24 h at 298 K, filtered and washed. This treatment removed the possible extraneous vanadium species from VAPO-31 pores. Pure AlPO-31 was similarly prepared without adding V_2O_5. VAPO-5 was prepared as per the reported method[4] for comparison purposes.

XRD patterns of the calcined samples (Fig. 1) are similar to those reported for AlPO-31[9] and show that they are highly crystalline. The samples prepared using DPeA were found to be dense phase materials. SEM photographs (Fig. 2) show

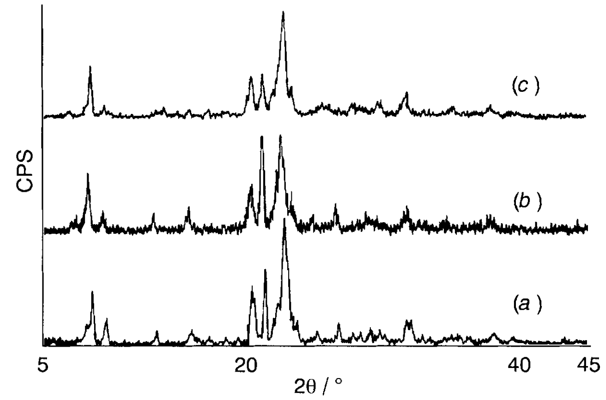

Fig. 1 XRD patterns of the samples. (*a*) ALPO-31 (sample **5**); (*b*) VAPO-31 (sample **3**); (*c*) VAPO-31 (sample **4**)

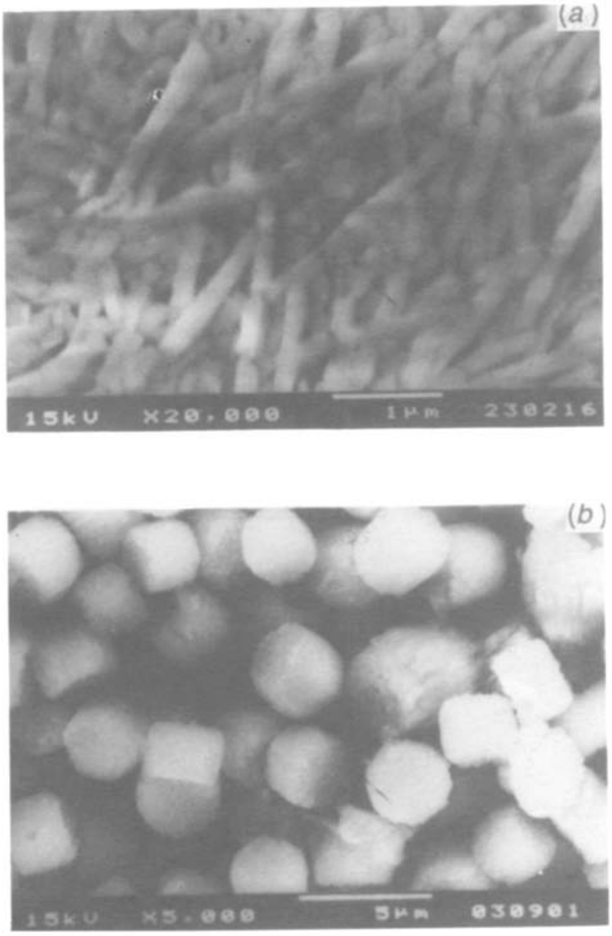

Fig. 2 SEM pictures of VAPO-31 samples. (*a*) VAPO-31 (sample **3**); (*b*) VAPO-31 (sample **4**)

Table 1 Catalytic properties of VAPO-31 (sample **3**)[a]

Sample	Substrate	Conversion (%TBHP)	Substrate selectivity[b] (mass%) 1	2	3	4
VAPO-5	Cyclohexene	45 (6 h)	70	8	15	7
VAPO-31	Cyclohexene	84 (6 h)	56	3	16	25
			A	B	C	D
VAPO-5	Toluene	27 (22 h)	12	18	70	—
VAPO-31	Toluene	44 (22 h)	24	6	65	5

[a] Reaction conditions: T 303 K; Chlorobenzene 20 g, Substrate 40 mmol, TBHP 20 mmol. [b] Cyclohexene epoxide; 2 cyclohexanone; 3 3-cyclohexenol; 4 2,3-epoxy cyclohexenol. A Benzyl alcohol; B benzaldehyde; C benzoic acid; D cresols.

interesting differences between VAPO-31 prepared by using DPA and DBA. Samples prepared from DBA consist of uniform rod shaped crystals of about 0.2 × 1–2 μm, whereas samples from DPA are uniform hexagonal crystallites, 2–3 μm in size. The absence of amorphous material in the picture shows the highly crystalline nature of the samples. The compositions of the samples based on chemical analysis are: **1** TPA–VAPO-5 $Al_2O_3 : 0.97\ P_2O_5 : 0.015\ V_2O_5$; **2** DBA–VAPO-31 $Al_2O_3 : 0.98\ P_2O_5 : 0.005\ V_2O_5$; **3** DBA–VAPO-31 $Al_2O_3 : 0.99\ P_2O_5 : 0.012\ V_2O_5$; **4** DPA–VAPO-31 $Al_2O_3 : 0.99\ P_2O_5 : 0.014\ V_2O_5$ and **5** DBA–AlPO-31; $Al_2O_3 : 0.99\ P_2O_5$.

The ESR spectra of the uncalcined sample (Fig. 3) are anisotropic with g and splitting parameters characteristic of atomically dispersed and immobile V^{4+} ions. The intensity of the ESR signal increased with V-content. The g values and hyperfine splitting constants are $g_{\parallel} = 1.932$, $g_{\perp} = 1.987$, $A_{\parallel} = 198.5$ and $A_{\perp} = 80$ G. They are characteristic of vanadyl (VO^{2+}) species present in distorted octahedral or square pyramidal structure. On calcination, all the V^{4+} ions were oxidized to V^{5+} ions and no ESR signal was observed. On reducing the calcined sample with hydrogen at 673 K or refluxing with toluene at 373 K (6 h) the ESR signals reappeared.

DTA/TGA studies reveal that the temperature of oxidative decomposition of the template for V-analogues is higher (673 and 705 K for samples **2** and **3**, respectively) than for AlPO-31 (623 K) suggesting strong interaction of the basic templates with V^{4+} (electron withdrawing) ions in the lattice. Similar results have also been reported in the case of VAPO-5.[6] After calcination in air and reduction in H_2 (773 K, 8 h), the NH_4^+ exchange capacity of AlPO-31 (sample **5**), VAPO-31 (sample **2**) and VAPO-31 (sample **3**) were 0.001, 0.008 and 0.014 mol fraction Al, respectively, suggesting the creation of exchange sites due to charge imbalance (V^{4+} in place of P^{5+}) in VAPO-31 samples. Montes *et al.*[4] have also reported the creation of exchange capacity in reduced VAPO-5 samples. Gravimetric adsorption of water, n-hexane (both at 298 K, $P/P\tilde{o} = 0.5$) and nitrogen (197 K, $P/P\tilde{o} = 0.5$) for VAPO-31 gave pore volume values of 0.18, 0.14 and 0.14 ml g^{-1} respectively, which are comparable to the reported value (0.17 ml g^{-1} for H_2O) for AlPO-31[12] indicating that the samples are free from extra lattice, occluded materials. DRS–UV–VIS spectra of VAPO-31 show two adsorption bands at 280 nm (strong) and 540 nm (weak) for the uncalcined material and a single band at 280 nm for the calcined sample. Jhung *et al.*[6] have also obtained similar UV–VIS spectra for uncalcined and calcined VAPO-5. they have attributed the 300 and 500 nm bands to V^{5+} and V^{4+} in Td symmetries suggesting that the V-ions reside in the lattice in both uncalcined and calcined samples.

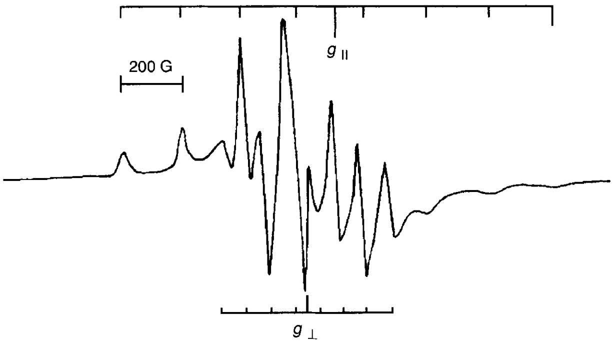

Fig. 3 ESR spectrum of VAPO-31 (sample **3**)

Cyclohexene and toluene oxidation activity by *tert*-butylhydroperoxide (TBHP) over VAPO-5 and VAPO-31 are compared in Table 1. In the oxidation of cyclohexene, the epoxide is the main product while the other products are cyclohexanone, cyclohexen-3-ol, and 2,3-epoxycyclohexanol. Conversion is greater over VAPO-31 than VAPO-5 (70% *vs.* 56%), where as selectivity for 2,3-epoxyhexanol is higher for VAPO-31 compared with VAPO-5 (40% *vs.* 25%). Conversion of toluene is also found to be greater over VAPO-31 than VAPO-5. Selectivity is also slightly different for the two catalysts.

In conclusion, a novel 12-membered ring molecular sieve, VAPO-31 has been synthesized and characterized by SEM, ESR and catalytic oxidation of cyclohexene and toluene. We have found that DBA is the largest secondary amine which can template AlPO-31 type molecular sieves and its use in the synthesis of the above molecular sieves is being reported for the first time. The hydroxylation activity of VAPO-31 using TBHP is attributed to the presence of framework vanadium cations.

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