Microporous vanadyl-arsenate with the template incorporated exhibiting sorption and catalytic properties†

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$(C_5H_{14}N_2)[(VO)_3(AsO_4)(HAsO_4)_2(OH)]\cdot 3H_2O$ behaves as a microporous organically templated compound, with reversible adsorption and desorption of N_2 at 77 K, and as an extremely efficient catalyst that catalyzes selective sulfoxide formation from organic sulfides, under mild conditions.

It is known that the silica-based and aluminophosphate-based zeolite materials yield crystalline porous compounds after heating. In this way, since the discovery of organically templated compounds,[1] many researches have devoted their efforts to the syntheses of this type of porous materials exhibiting sorption and catalytic properties. The attempts directed in this direction, based on the organically templated transition metal phosphates, phosphites and arsenates, have mainly focused on elimination by heating of the organic templates, with the aim of obtaining true microporous phases where catalytic activity can take place. However, the compounds obtained after calcination of the organic template were always amorphous phases.[2] This is due to the strong ionic and hydrogen bonding forces that maintain the linking between the templates and the inorganic frameworks, the elimination of which always leads to the collapse of the crystal structure, precluding the attainment of true microporous compounds.

We have synthesized the $(C_5H_{14}N_2)[(VO)_3(AsO_4)(HAsO_4)_2(OH)]\cdot 3H_2O$ phase,‡ that exhibits channels with a maximum diameter of *ca.* 14.0 Å. In this compound, the 2-methylpiperazine template is located inside the channels and near to their walls. This unusual disposition of the template allows the existence of an empty space inside the channels which makes possible the use of this compound as a true microporous phase, without eliminating the organic counterpart by calcination. Thus the inorganic framework retains its original structure so preventing a collapse of the structure. Other organically templated compounds referred in the literature, based on vanadyl-arsenates[3] and vanadyl-phosphates,[4] do not exhibit sorption and/or catalytic activity. However, our compound exhibits reversible adsorption and desorption of N_2 at 77 K, and catalytic oxidation activity on organic sulfides, terpenes and alcohols. As far as we are aware, $(C_5H_{14}N_2)[(VO)_3(AsO_4)(HAsO_4)_2(OH)]\cdot 3H_2O$ is the first microporous compound with the template incorporated exhibiting simultaneously sorption and catalytic properties.§

The crystal structure of $(C_5H_{14}N_2)[(VO)_3(AsO_4)(HAsO_4)_2(OH)]\cdot 3H_2O$ is built from $[V_3O_{19}As_3]$ SBU-6 (secondary building unit) units formed by trimers of edge-sharing vanadyl, $(VO)^{2+}$, octahedra which are interconnected through arsenate, $(AsO_4)^{3-}$, and hydrogenarsenate, $(HAsO_4)^{2-}$, tetrahedra (see Fig. 1(a)) giving rise to a three-dimensional inorganic framework.¶ In this 3D skeleton channels exist along the [100] and [001] directions. The channels along the [100] direction have a diameter of *ca.* 8.0 Å, delimited by six SBU-6 units. Along the [001] direction, two type of channels can be observed (see Fig. 1(b)). One of them, delimited by three SBU-6 units, is empty with a diameter of *ca.* 5.0 Å. The other channels exhibit a greater diameter of *ca.* 14.0 Å, and are delimited by twelve SBU-6 units, containing the template. The 2-methylpiperazinium template is located near the walls of these channels, increasing the effectiveness of the hydrogen bond and electrostatic interactions with the inorganic framework. In this way, an empty space of about 10.0 Å is generated along the channels.

Sorption isotherm measurements of $(C_5H_{14}N_2)[(VO)_3(AsO_4)(HAsO_4)_2(OH)]\cdot 3H_2O$, without previous elimination of the template molecule, carried out at 77 K, show reversible

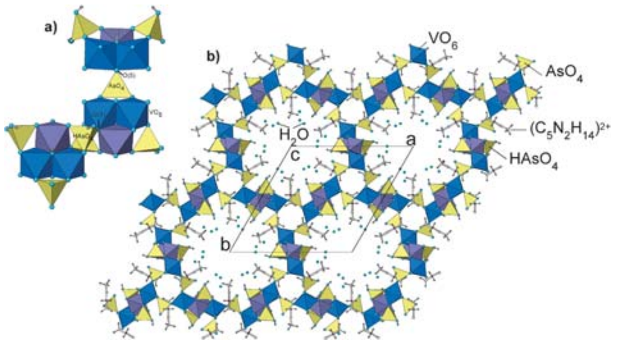

Fig. 1 (a) Polyhedral view of the SBU-6 unit of $(C_5H_{14}N_2)[(VO)_3(AsO_4)(HAsO_4)_2(OH)]\cdot 3H_2O$. (b) Polyhedral view of the crystal structure showing the channels along the [001] direction.

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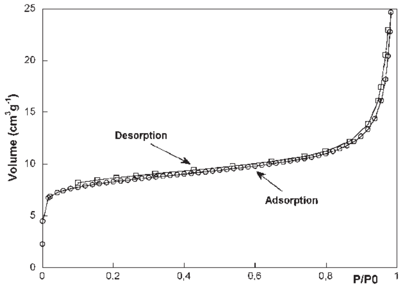


Fig. 2 Adsorption and desorption isotherms of N_2 at 77 K for $(C_5H_{14}N_2)[(VO)_3(AsO_4)(HAsO_4)_2(OH)]\cdot 3H_2O$.

adsorption and desorption of N_2 liquid, as can be seen in Fig. 2, which reveals type IV behaviour.[5] The values obtained of the BET surface area is 30.4(1) $m^2\ g^{-1}$ and the average pore diameter, 11.7(1) Å. This latter value is in the range (3–20 Å) usually found for microporous compounds.[6]

$(C_5H_{14}N_2)[(VO)_3(AsO_4)(HAsO_4)_2(OH)]\cdot 3H_2O$ was tested as a catalyst for the oxidation of organic sulfides, and terpenes using methyl phenyl sulfide (**1**) and linalool (**2**) as model substrates.¶ H_2O_2 was employed as oxygen source, always in excess with respect to the substrate (10%). Reactions were carried out at 313 K. Higher reaction temperatures lead to a dramatic decrease in the selectivity to sulfoxide. The outcome of the reaction was followed by GC and results are summarised in Tables 1 and 2 and Fig. 3. Blank experiments with both substrates under identical test conditions were carried out. No reaction was observed and conversions lower than 3% after 2 h were obtained, even at room temperature, in the presence of H_2O_2.

The new material is extremely efficient (turnover frequency: mmol product/mmol cat. min.: 3780 min^{-1}) in comparison with other metal–organic frameworks,[7] and catalyzes selective sulfoxide formation at a concentration of 0.005 mmol of the V-compound under mild conditions. Total conversion was reached with most of the catalysts after 1 h of reaction. However, at high conversion of sulfide (>90%), the oxidation does not stop at the sulfoxide level and proceeds yielding overoxidized products, such as sulfone. The selectivity analysis shows that the sulfoxide is a primary and unstable product, while the corresponding sulfone appears as a secondary and stable product at high conversion. The selectivity depends on the reaction conditions (see Table 1). At 40 °C, the sulfone is the main product when 2.5 mmol of the oxidant agent are used. If the reaction is carried out at room temperature, only sulfoxide is obtained. In this process, it is worth mentioning that the controlled addition of 1.1 mmol of H_2O_2, instead of 2.5 mmol, allows significant improvement of the selectivity of the oxidation reaction, the sulfoxide being the only product obtained. The kinetic profile of the reaction at room temperature (1% of catalyst and 2.5 mmol of H_2O_2) is shown in Fig. 3(a). It can be observed that, after 25 min of reaction the total conversion of the substrate takes place, with a 90% of selectivity towards the formation of the sulfoxide. The evolution of the selectivity of the reaction *vs.* the degree of conversion is illustrated in Fig. 3(b).

Table 2 Epoxidation of linalool catalyzed by $(C_5H_{14}N_2)[(VO)_3(AsO_4)(HAsO_4)(OH)]\cdot 3H_2O$ (1%), 70 °C

t/h	Conv. (%)	Furan	Pyran	Furan/pyran
1	63	43	20	2.2
2	75	52	23	2.3
3	90	63	27	2.3
4	96	68	29	2.3

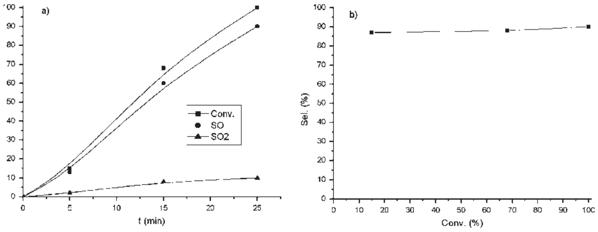
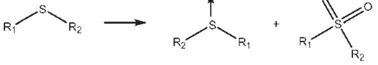


Fig. 3 (a) Kinetic profile of the catalytic reaction and (b) evolution of the selectivity *vs.* degree of conversion.

The major advantage of heterogeneous catalysis over its homogeneous counterpart is the ease of recovery and recycling of the catalyst and the easier work up procedure that permits removing catalysts from reaction media through a simple filtration. The lifetime of the heterogenized catalyst was examined by using it in several reaction cycles. The solid was separated from the reaction medium by filtration and washed with dichloromethane before reusing. The heterogenized catalyst could be reused at least four times without neither loss of activity nor selectivity with catalyst loading as low as 1.5 mol%. The slight decrease of the rate observed for the consecutive runs is due to the small amount of catalytic material lost upon filtration. While the oxidation of sulfide continued in presence of the catalyst, there was no further

Table 1 Oxidation of methyl phenyl sulfide catalyzed by $(C_5H_{14}N_2)[(VO)_3(AsO_4)(HAsO_4)(OH)]\cdot 3H_2O$[a]



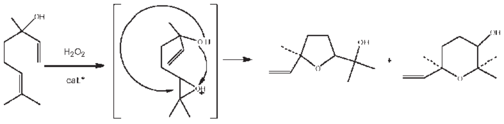
Conditions	Conversion (%) (min)	Selectivity[b] (%)
10% cat., 40 °C, H_2O_2 (2.5 mmol)	100 (10)	18
1% cat.., 40 °C, H_2O_2 (2.5 mmol)	100 (15)	71
1% cat., RT, H_2O_2 (2.5 mmol)	100 (25)	90
1% cat., RT, H_2O_2 (1.1 mmol)	100 (60)	99

[a] Reactions were performed in acetonitrile. [b] Selectivity referred to the sulfoxides.

significant conversion when the catalyst was removed from the reaction media.

This new material offers the possibility of combining the catalytic properties of transition metal ions with the advantages of a solid catalyst. The small size of the pore in this structure avoids the accessibility of the substrates to the metallic centres and the catalytic reactions take place on the surface. Accordingly, the reaction rates are quite similar, not showing any dependence on the volume of the substrate.

The title compound also acts as a homogenous catalyst for the oxidation of linalool (**2**) at temperatures higher than 373 K, to give rise to furans and pyrans, with a greater degree of conversion when increasing the reaction time (see Table 2). In this case the catalyst acts as a bifunctional system (redox-acid). The proposed reaction pathway is as shown:



It seems, thus, quite plausible that the process involves first the epoxidation at the metal site of the 2,3 double bond followed by the intramolecular opening of the epoxide ring by the hydroxy group at positions 6 or 7, the latter reaction being catalyzed by the acid sites.

The limit of thermal stability of this compound is 220 °C, as can be deduced from thermodiffractometric and thermogravimetric studies (see ESI†) and so this phase can be used as an effective catalyst above room temperature. $(C_5H_{14}N_2)[(VO)_3(AsO_4)(HAsO_4)_2(OH)]\cdot 3H_2O$ also exhibits magnetic properties. ESR spectra, recorded on a powdered sample at X-band between 4.2 and 300 K, show isotropic signals with a mean g-value of 1.96 (see ESI†). This value is characteristic of the octahedrally coordinated $(VO)^{2+}$ vanadyl cation.[8] The compound is antiferromagnetic and the effective magnetic moment decreases from 2.78 μ_B at room temperature to 1.76 μ_B at 5.0 K (see ESI†).

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Notes and references

‡ *Synthesis*: Mild hydrothermal synthesis (443 K, 5 days) was carried out in a PTFE-lined stainless steel vessel in which a previously stirred mixture of As_2O_5 (3.0 mmol), VCl_3 (1.9 mmol), $C_5H_{12}N_2$ (8.5 mol) in 30 mL of water was placed. The initial pH = 6.0 does not show any appreciable change during the hydrothermal reaction. The elemental percentages in the product were calculated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and elemental analysis. Calc. (%) for $(C_5H_{14}N_2)[(VO)_3(AsO_4)(HAsO_4)_2(OH)]\cdot 3H_2O$: C 7.2, H 3.3, N 3.4, V, 18.4, As 27.1. Found: C 7.1, H 3.1, N 3.3, V 18.3, As 27.0.

§ *Physical measurements*: A Bruker D8 Advance diffractometer (Cu-Kα radiation) equipped with, a variable-temperature stage (Paar Physica TCU2000), a Pt sample heater and a Vanter high-speed one-dimensional detector with angular aperture of 3°, was used in the thermodiffractometric experiment. Sorption measurements of N_2 were carried out using an ASAP 20010 MICROMETRICS system. Gas chromatography (GCMS) analysis was performed using a Hewlett-Packard 5890 II in a cross-linked methylsilicone column. A Bruker ESP 300 spectrometer, operating at X band, was used to record the ESR polycrystalline spectra between 4.2 and 300 K. The temperature was stabilized by an Oxford Instrument (ITC 4) regulator. The magnetic field was measured with a Bruker BNM 200 guassmeter and the frequency inside the cavity was determined using a Hewlett-Packard 5352B microwave frequency counter. Magnetic measurements on a powdered sample were carried out in the 5.0–300 K range, using a Quantum Design MPMS-7 SQUID magnetometer. The magnetic field was 0.1 T, a value in the range of linear dependence of magnetization *vs.* magnetic field, even at 5.0 K. Oxidation reactions were carried out in a 25 ml flask equipped with a magnetic stirrer. The flask was charged with: (i) 5 ml of a suspension of the catalyst (0.005 mmol) in acetonitrile; (ii) a solution of the corresponding substrate [methyl phenyl sulfide or linalool, 1 mmol]. The oxidant, H_2O_2 (30%, 1.5 mmol or 1.1 mmol) was added dropwise while the overall suspension which was heated at 313 K. Samples were taken at regular intervals and analyzed after filtration.

¶ *Crystal data*: Structure determination of $(C_5H_{14}N_2)[(VO)_3(AsO_4)(HAsO_4)_2(OH)]\cdot 3H_2O$: 0.1 × 0.01 × 0.01 mm (blue colour), M_r = 792.83 g mol^{-1}, hexagonal, space group $P6_3/m$ (no. 176), a = 19.0945(16), c = 11.0133(9) Å, γ = 120.0°, Z = 6, μ = 5.519 mm^{-1}, D_m = 2.22(1) g cm^{-3}, D_c = 2.272 g cm^{-3}, $F(000)$ = 2322 The X-ray crystal data were collected on an BRUKER-SIEMENS APEX automated diffractometer (graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, T = 293(2) K). Of 30908 measured reflections ($2.82 \leq \theta \leq 25.98^\circ$), 2367 were independent (R_{int} = 0.1566) and 1673 observed ($I > 2\sigma(I)$). The structure was solved by direct methods with the SHELXS97 computer program,[9] and refined by the least-squares method based on F^2, using the SHELXL97 program[10] of the WINGX V1.63.02 software package.[11] Scattering factors were taken from International Tables for X-ray Crystallography. Anisotropic thermal parameters were used to refine all the atoms, except the hydrogen ones. Final R-factors were $R1$ = 0.0693 (all data) ($wR2$ = 0.0725). Maximum and minimum peaks in the final difference synthesis were 1.331, −0.617 e $Å^{-3}$. Goodness of fit on F^2 = 0.876. A simulation based on the single-crystal structure of $(C_5H_{14}N_2)[(VO)_3(AsO_4)(HAsO_4)_2(OH)]\cdot 3H_2O$ was in excellent agreement with the X-ray powder data, indicating purity and high crystallinity.

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