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# Introduction

The interest in finding suitable catalysts for higher selectivity in chemical reactions has resulted in the ongoing development of new synthetic pathways. At first, aluminosilicate zeolites, which show chemical stability and high selectivity for molecular shape through their well-defined pores and cages, were extensively studied. Subsequent work has focused on combining the well-known catalytic properties of transition elements with the shape-selective capacity of zeolites.<sup>1</sup>

Among microporous solids, open-framework metal phosphates also constitute an important class of materials due to their potential applications in catalysis, gas separation and storage.<sup>2–4</sup> The wide variety of structural architectures, one-, two- and three-dimensional, shown by the family of

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# Amine templated open-framework vanadium(III) phosphites with catalytic properties†

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Four novel amine templated open-framework vanadium(III) phosphites with the formula  $(C_5N_2H_{14})_{0.5}$ - $[V(H_2O)(HPO_3)_2]$ , **1**  $(C_5N_2H_{14} = 2$ -methylpiperazinium), and  $(L)_{4-x}(H_3O)_x[V_9(H_2O)_6(HPO_3)_{14-y}(HPO_4)_y(H_2PO_3)_{3-z}(H_2PO_4)_2]$ · $H_2O(2$ , L = cyclopentylammonium, x = 0, y = 3.5, z = 3, n = 0; **3**, L = cyclohexylammonium, x = 1, y = 0, z = 0, n = 2.33; **4**, L = cycloheptylammonium, x = 1, y = 0, z = 0, n = 2.33) were synthesized employing solvothermal reactions and characterized by single-crystal X-ray diffraction, ICP-AES and elemental analyses, thermogravimetric and thermodiffractometric analyses, and IR and UV/vis spectroscopy. Single-crystal data indicate that **1** crystallizes in the triclinic system, space group  $P\overline{1}$ , whereas **2**, **3** and **4** crystallize in the hexagonal space group  $P6_3/m$ . Compound **1** has a two-dimensional motif with anionic sheets of  $[V(H_2O)(HPO_3)_2]^-$  formula, whose charge is compensated by the 2-methylpiperazinium cations embedded between the layers. In contrast, **2**, **3** and **4** present a pillar-layer network giving rise to a three-dimensional framework containing intersecting 16-ring channels with the primary amine templates and the crystallization water molecules enclosed in them. **1**, **2**, **3** and **4** behave as heterogeneous catalysts for the selective oxidation of alkyl aryl sulfides, with *tert*-butylhydroperoxide (TBHP) as the oxidizing agent, being active, selective and recyclable for several successive cycles of reaction.

phosphates and related compounds with open structures, is mainly derived from the use of organic compounds that act as structure directing agents (SDAs)<sup>5</sup> and the substitution of transition metal ions, which are able to occur in different oxidation states and/or different coordination numbers.

In contrast to the four coordinated phosphate oxoanion, the phosphite group has only three oxygen atoms. This feature can give rise to new topologies often with lower connectivities.<sup>6</sup> Since the first organically templated phosphite was synthesized,<sup>7</sup> this family of compounds has rapidly grown, highlighting those with a Zn transition metal cation.<sup>8</sup> Open-framework phosphites of V,<sup>9</sup> Mn,<sup>10</sup> Fe,<sup>11</sup> Co,<sup>12</sup> Ga<sup>13</sup> and even of Cr,<sup>14</sup> Be,<sup>15</sup> In<sup>16</sup> and U<sup>17</sup> have been prepared, but they are still less numerous than those reported with Zn.

Vanadium is an interesting reactive element that can easily adopt different coordination environments due to its numerous oxidation states, in minerals 3+, 4+, and 5+. The most dominant non-metallurgical use of vanadium is in catalysis.<sup>18</sup> Synthesis of compounds containing vanadium increased substantially after the work of Centi *et al.*<sup>19</sup> Nowadays, one of the most well studied heterogeneous mixed oxide catalyst systems are vanadium phosphates (V–P–O) which are commercially used for the selective oxidation of *n*-butane to maleic anhydride (MA).<sup>20–26</sup>

On the other hand, organic sulfoxides and sulfones are useful synthetic intermediates for the construction of various

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chemically and biologically active molecules.<sup>27</sup> The sulfoxides are obtained by oxidation of thioethers by peracids, peroxides and alkyl peroxides using transition metal catalysts.<sup>28</sup> Depending on the catalyst selectivity and the reaction conditions, that is, time, temperature and the relative amount of oxidants, different proportions of sulfoxide and sulfone are produced.<sup>29,30</sup> When using vanadyl compounds, the catalytically active oxo-peroxo intermediate is formed in situ by oxidation of V(IV) to V(V) with an excess of the oxidizing agent.<sup>31</sup> The use of heterogeneous catalysts in the liquid phase has the inherent advantages of easier handling, separation, recovery and recycling, and enhanced stability. In addition, from an environmental and economic standpoint, classical stoichiometric oxidants, such as dichromate or permanganate, should be replaced by new environmentally friendly catalytic processes using clean oxidants.<sup>32</sup> Oxidants such as hydrogen peroxide and tert-butyl hydroperoxide are ideal, as they are environment-friendly reagents with water and tert-butyl alcohol as the respective by-products.

According to the results of our literature research, catalytic studies on phosphite group containing materials are scarce. A purely inorganic layered zirconium phosphite was evaluated as an acidic catalyst in dehydration of ethanol reactions.<sup>33</sup> Recently, Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate was carried out with open-framework zinc phosphites as the base catalytic support.<sup>34</sup> As far as we are concerned, this is the first report of the catalytic properties of vanadium phosphites. There are some studies of related materials, such as amine-templated vanadyl arsenates<sup>35</sup> or hybrid vanadates<sup>36</sup> as well as of vanadium containing heteropolycompounds.<sup>30</sup>

In the present work we report on the catalytic properties of four new amine templated open-framework vanadium(III) phosphites,  $(C_5N_2H_{14})_{0.5}[V(H_2O)(HPO_3)_2]$ , **1**  $(C_5N_2H_{14} = 2 - methylpiperazinium)$ , and  $(L)_{4-x}(H_3O)_x[V_9(H_2O)_6(HPO_3)_{14} -_y(HPO_4)_y(H_2PO_3)_{3-z}(H_2PO_4)_z] \cdot nH_2O$  (2, L = cyclopentylammonium, x = 0, y = 3.5, z = 3, n = 0; **3**, L = cyclohexylammonium, x = 1, y = 0, z = 0.6, n = 2.33; **4**, L = cycloheptylammonium, x = 1, y = 0, z = 0, n = 2.33). Moreover, the hydrothermal synthesis, crystal structure determination, as well as the thermal and spectroscopic behaviour of these phases are described.

### **Results and discussion**

#### Structures description

The asymmetric unit of  $(C_5N_2H_{14})_{0.5}[V(H_2O)(HPO_3)_2]$ , 1, contains 15 non-hydrogen atoms, of which two vanadium atoms situated in inversion centres and two phosphorus atoms occupying general positions are crystallographically independent (ESI, Fig. S2.1<sup>†</sup>).

The two-dimensional crystal structure of compound **1** is composed of anionic sheets of  $[V(H_2O)(HPO_3)_2]^-$  formula placed in the *ab* plane (Fig. 1(a)).

The inorganic sheets consist of octahedral  $[VO_6]$  and  $[VO_4(H_2O)_2]$  units joined by bridging HPO<sub>3</sub> pseudopyramids



**Fig. 1** (a) Polyhedral view of the two-dimensional crystal structure along the [100] direction. (b) Topological simplification of the inorganic sheets.

through oxygen vertices. Each  $[V(1)O_6]$  octahedron is linked to four  $[HP(1)O_3]$  and two  $[HP(2)O_3]$  units, while  $[VO_4(H_2O_2)]$ octahedra are exclusively coordinated to  $[HP(2)O_3]$  units. The water molecule coordinated to the  $[VO_4(H_2O)_2]$  polyhedron establishes the intralayer H-bonding scheme given in ESI, Table S2.1 and Fig. S2.2.<sup>†</sup> The topological analysis of the inorganic sheets of compound 1 was performed using the TOPOS 4.0<sup>37</sup> program. Considering the two P and two V crystallographically independent atoms as nodes of a simplified network, a tetranodal net  $(2-c)_2(3-c)_2(4-c)(6-c)$  is obtained. The complexity of this net is the result of coordination of four types of structural subunits: hexa-connected [V(1)O<sub>6</sub>], tetra-connected  $[V(2)O_4(H_2O)]$ , tri-connected  $[HP(2)O_3]$  and di-connected  $[HP(1)O_3]$  (Fig. 1(b)). In order to construct the underlying net of the sheets and to relate this structure to other ones registered in the topological databases, it is necessary to replace 2-connected nodes by edges. After this simplification a trinodal net with known topology type 3,4,4L13<sup>38,39</sup> is obtained (ESI, Fig. S2.3<sup>†</sup>).

The 2-methylpiperazinium cations are located in the interlayer space stabilizing the inorganic framework through hydrogen bonding interactions (ESI, Table S2.1<sup>†</sup>) with the three oxygen atoms belonging to the [HP(1)O<sub>3</sub>] group (ESI, Fig. S2.4<sup>†</sup>). This organic molecule, which adopts a chair conformation, is located over a symmetry centre causing a positional disorder of the methyl group with an occupation factor of 0.5. Therefore, the organic molecule looks like a 2,4dimethylpiperazine molecule due to the statistical distribution of the methyl group on two sites. This type of disorder was observed in the  $P2_1/n$  and C2/c polymorphs of the monodimensional  $[C_5N_2H_{14}][Co(HPO_4)_2]^{40,41}$  hydrogen phosphate.

The asymmetric units of  $(L)_{4-x}(H_3O)_x[V_9(H_2O)_6(HPO_3)_{14-y}-(HPO_4)_y(H_2PO_3)_{3-z}(H_2PO_4)_z]\cdot nH_2O$  (2, L = cyclopentylammonium, x = 0, y = 3.5, z = 3, n = 0; 3, L = cyclohexylammonium, x = 1, y = 0, z = 0.6, n = 2.33; 4, L = cycloheptylammonium, x = 1, y = 0, z = 0, n = 2.33) contain three crystallographically independent V atoms and four crystallographically distinct P atoms (ESI, Fig. S2.5<sup>+</sup>).

The structural analyses show that compounds 2, 3 and 4 are isostructural crystallizing in the hexagonal space group  $P6_3/m$ , with very similar cell parameters. These compounds present



Fig. 2 Polyhedral view of the three-dimensional crystal structures of phases 2, 3 and 4 along the  $a_2$  axis.

differences in the phosphorous anionic group types and in the organic templates, as well as in the crystallization water molecules content. Their inorganic buildings are isostructural with the compounds  $(Hcha)_3(H_3O)_{1+x}[V_9(H_2O)_6(HPO_3)_{14-x}-(BO_3)_x(H_2PO_3)_3]\cdot 2H_2O$  (cha = cyclohexylamine and  $x = 0.1-1.2)^{64}$  and  $[In_9(H_2O)_6(HPO_3)_{13}(H_2PO_3)_2(PO_4)(HPO_4)]-[(C_6N_2H_{18})_3]$  ( $C_6N_2H_{18} = 2$ -methyl-1,5-pentanediamine).<sup>42</sup> However in the last two compounds, the extra-framework species were not located by single-crystal X-ray diffraction.

Compounds 2, 3 and 4 are based on a pillar-layer network giving rise to a three dimensional framework containing intersecting 16-membered ring channels along the [100], [010] and [110] directions with the primary amine templates and the crystallization water molecules enclosed in them (Fig. 2). The approximate sizes of the channel windows are  $13 \times 7 \text{ Å}^2$  (ESI, Fig. S2.6†). A detailed structural description of the inorganic buildings of compounds 2, 3 and 4 is given as ESI (S2†).

The interlayer spaces of compounds 3 and 4 are complicated by disordered water molecules located in positions similar to those of the organic cations (ESI, Fig. S2.10<sup>+</sup>). Taking into account the general positions for the organic cations and the O(W1) and O(W2) oxygen atoms, the total occupancy factors for cyclohexylamine or cycloheptylamine + O(W1) + O(W2) must be equal to 1. Based on the elemental analyses, for the organic cations an occupancy factor of 0.5 was estimated. For compound 4, the occupancy factor of the cycloheptylammonium cation is imposed by symmetry. For the O(W1) and O(W2) occupancy factors calculations, electronic density values and similar isotropic thermal parameters after the final refinement were considered (Occ. O(W1) = 0.30; Occ. O(W2) = 0.20). Besides, for charge balance an additional proton should be distributed over one crystallization water molecule with a site occupancy of 1/6. Although hydronium cations and water molecules cannot be distinguished in the X-ray refinement, short contacts between O(W1) and O(10) atoms of 2.46(2) and 2.52(2) Å for compounds 3 and 4, respectively, could indicate the location of the protonated water molecules.43 The O(W3) water molecule is located at logical distances of the organic cations, coexisting with them. For compound 2, there are no extra framework water molecules, so the cyclopentylammonium cations present an occupancy

factor of 4/6 balancing the total negative charge of the inorganic framework but they are disordered in two positions in order to occupy more interlayer space (ESI, Fig. S2.10<sup>†</sup>).

The amount of potential-free volume was estimated by the program PLATON<sup>44</sup> assuming that the guest molecules could be removed from the channels, being 39.8, 45.0 and 46.0% of the total volume for phases 2, 3 and 4, respectively. The analysis of these voids was performed using the TOPOS 4.0 program<sup>37</sup> by means of Voronoi–Dirichlet polyhedra (VDP)<sup>45-47</sup> (ESI, Fig. S2.12†). Taking into account the real occupancy factors of the solvent species, we have estimated the real percentages of free voids volumes, obtaining 13.7, 17.8 and 19.2% for phases 2, 3 and 4, respectively. These data suggest an increase of free space associated with the increase of the organic guests size.

Discussions about the bond distances and angles and polyhedral distortion study are included in the ESI  $(S2(a)^{\dagger})$ .

#### Thermal study

The thermogravimetric curves of the four phases show small initial mass losses attributed to the elimination of the water adsorbed by the compounds. For compound 1, between 100 and 285 °C, there are two slopes in the TG curve (6.44%), the first of them very soft and possibly related to the breaking of some bonds of water molecules coordinated to the  $V(2)O_4(H_2O)_2$  polyhedron. And the second one, rather more sharply, from about 210 °C, assigned to the total elimination of all coordinated water molecules (6.42% calculated) and coincident with the beginning of the destruction of the crystal structure of the compound observed by thermodiffractometry. In the 330-525 °C temperature range there is a weight loss of 9.35%, which corresponds to a half of the 2-methylpiperazinium molecule present in the compound  $((C_5N_2H_{14})_{0.25} =$ 9.125%). The remaining organic matter is lost in two stages from 525 °C to 900 °C (ESI, Fig. S3.1<sup>†</sup>).

For compounds 2, 3 and 4, the total weight losses observed in the TG curves are 21.2%, 25.1% and 20.7% respectively (ESI, Fig. S3.2<sup>†</sup>). The decomposition of the phases takes place in several overlapped steps beginning from nearly room temperature, with the removal of the corresponding crystallization and coordinated water molecules. Subsequently, from approximately 100 °C for 3 and 150 °C for 2 and 4 the beginning of the organic molecules calcination takes place, in two processes that are related to two exothermic peaks around 260 °C and 350 °C in the DTA and DSC curves due to the breakage of C–C and C–N bonds. Finally, at around 750 °C–800 °C of temperature, DTA and DSC curves show an exothermic peak associated with the crystallization of the inorganic residue.

The thermal behaviour of the compounds was also studied by time-resolved X-ray thermodiffractometry in air. The diffraction maxima of phase 1 remain unchanged up to 210 °C, with temperature considered as the thermal stability limit of the compound (ESI, Fig. S3.3†). The thermal evolution of the cell parameters was studied by Pattern Matching refinement using the FULLPROF<sup>48</sup> program (ESI, Fig. S3.4†). A trend change in all of the cell parameters evolution is observed at



approximately 195 °C, related to the onset of degradation of the initial phase structure. The parameters *b*, *c* and *a* show a continuous increase with increasing temperature up to 195 °C, attributed to an increase in interlayer space and a slight displacement between the inorganic layers. The phase volume exhibits a constant increase in the whole temperature range. The thermal expansion coefficients of the *b*, *c* and volume cell parameters were qualitatively calculated using the expression  $V(T) = V_{\rm Tr} \exp[\alpha_0(T - {\rm Tr})]$ ,<sup>49</sup> where  $V_{\rm Tr}$  is the parameter value at room temperature and  $\alpha_0$  the thermal expansion coefficient.

For compounds **2**, **3** and **4**, the diffraction maxima are observed in the thermodiffractograms until 165 °C, 120 °C and 105 °C, respectively. At these temperatures, the compounds become amorphous, marking the limits of thermal stability. For compounds **2** and **3**, at 630 °C and 675 °C, respectively, the vanadyl phosphate, VO(PO<sub>3</sub>)<sub>2</sub><sup>50</sup> (*I*42*d* (122), *a* = 10.9900 Å, *c* = 4.2580 Å) crystallizes. This phase undergoes a structural transformation to the space group *C*2/*c* (15)<sup>51</sup> (*a* = 15.1400 Å, *b* = 4.1950 Å, *c* = 9.5730 Å,  $\beta$  = 126.54°) with increasing temperature (ESI, Fig. S3.5†).

The thermal evolution of the cell parameters was also studied by Pattern Matching refinements. For compounds 2, 3 and 4, the *a* parameter increases with the temperature until their stability limit, except for compound 2, whose *a* parameter increases until 135 °C and then decreases until 165 °C (ESI, Fig. S3.6<sup>†</sup>). Fig. 3 shows the thermal evolution of the (013), (004), (110) and (111) reflections. The (004) reflection of compounds 3 and 4 shifts continuously and progressively towards higher  $2\theta$  angles with increasing temperature, suggesting a decrease of the *c* parameter. For compound 2, a very slight shift towards higher angles takes place only until 120 °C. From this temperature to 165 °C, this shift tends towards smaller  $2\theta$  angles (see ESI, Fig. S3.6<sup>†</sup>).

Note that, in spite of the similarities between the three inorganic buildings, they behave differently with the heating. In compounds 3 and 4, the removal of the crystallization and coordinated water molecules causes the positive thermal expansion of the *a* axis, being negative in the case of the *c* axis until the collapse of the structures. Compound 2 behaves in a similar way to compounds 3 and 4 until 120 °C and 135 °C. However, from these temperatures, the thermal evolution of the parameters reverses, resulting in the contraction and expansion of the *a* and *c* axis, respectively. Therefore, it seems that the removal of the protonated water molecules, that compensate partially the negative charge of the inorganic building, involves the direct destruction of the structures of compounds 3 and 4. In contrast, for compound 2 the beginning of the destruction of the cyclopentylammonium cations at 150 °C gives rise to an unsuccessful attempt of reorganization of the crystal structure to maintain the stability.

#### Infrared and UV-Vis spectroscopy

In the infrared spectra of the four compounds (ESI, Fig. S4.1<sup>†</sup>), from 3100 to 2500 cm<sup>-1</sup> a group of overlapped bands corresponding to stretching vibrations ( $\nu$ ) of N–H and C–H bonds of the different organic molecules appears. The deformation ( $\delta$ ) 4

Table 1 Conversion (C<sub>T</sub>), selectivity towards sulfoxides formation (S<sub>SO</sub>) and turnover frequency (TOF) data of oxidation of alkyl aryl sulfides catalyzed by 1, 2, 3 and

Catalyst	Substrate	Oxidizing agent	Solvent	Temp.	$C_{\mathrm{T}}$ (%) ( $t$ , min)	$S_{\rm SO}$ (%)	$TOF(min^{-1})$
1	MeSPh	TBHP (2.2 equiv.)	CH <sub>2</sub> Cl <sub>2</sub>	50 °C	94(120)	100	2
	MeSPh	$H_2O_2$ (1.5 equiv.)	CH <sub>3</sub> CN	r.t.	99(60)	100	4.9
	EtBuSPh	$H_2O_2$ (1.5 equiv.)	CH <sub>3</sub> CN	r.t.	14(270)	100	0.1
	ClPhSMe	$H_2O_2$ (1.5 equiv.)	CH <sub>3</sub> CN	r.t.	24(270)	100	0.5
	MeSMePh	$H_2O_2$ (1.5 equiv.)	CH <sub>3</sub> CN	r.t.	19(270)	100	1
2	MeSPh	TBHP (1.5 equiv.)	$CH_2Cl_2$	50 °C	92(60)	100	3.6
	MeSPh	$H_2O_2$ (1.5 equiv.)	CH <sub>3</sub> CN	r.t.	85(60)	100	5.5
3	MeSPh	TBHP (1.5 equiv.)	$CH_2Cl_2$	50 °C	70(60)	100	1.5
	MeSPh	$H_2O_2$ (1.5 equiv.)	CH <sub>3</sub> CN	r.t.	60(60)	100	4.0
4	MeSPh	TBHP (1.5 equiv.)	CH <sub>2</sub> Cl <sub>2</sub>	50 °C	100(60)	92	8
	MeSPh	$H_2O_2$ (1.5 equiv.)	$CH_3CN$	r.t.	77(60)	100	2.8

mode of  $(NH_3^+)$  groups, for 2, 3 and 4, and of  $(NH_2^+)$  groups, for 1, appears split into two close bands at 1630 and 1615 cm<sup>-1</sup>, indicating that the organic molecules are protonated and not coordinated to the inorganic skeleton. With regard to the inorganic part, around 2400 cm<sup>-1</sup> a narrow band split into two ones, corresponding to the stretching vibrational mode of the P–H bond from the phosphite, can be observed in the spectra. At lower frequencies, in the 1100–400 cm<sup>-1</sup> range, the bands corresponding to the P–O bonds vibrations of the phosphite/phosphate groups are observed.

The diffuse reflectance spectra (ESI, Fig. S4.2(a)<sup> $\dagger$ </sup>) show two d-d bands, at 14700 and 22800 cm<sup>-1</sup> for 1 and at approximately 15 010 and 22 600  $\text{cm}^{-1}$  for 2, 3 and 4. These bands are characteristic of the octahedrally coordinated V<sup>3+</sup> cations, which correspond to transitions from the  ${}^{3}T_{1g}({}^{3}F)$  ground state to  ${}^{3}T_{2g}({}^{3}F)$  and  ${}^{3}T_{1g}({}^{3}P)$  terms and are responsible for the light green colour observed in these phases. The Dq and Racah parameters have been calculated by fitting the experimental frequencies obtained from the diffuse reflectance spectra to an energy level diagram for an octahedral d<sup>2</sup> system.<sup>52</sup> For 1,  $Dq = 1620 \text{ cm}^{-1}$ ,  $B = 585 \text{ cm}^{-1}$ , 68% of the free ion  $(B_0(V^{3+}) = 861 \text{ cm}^{-1})^{53}$  and  $C = 3380 \text{ cm}^{-1}$ . For 2, 3 and 4,  $Dq = 1594 \text{ cm}^{-1}$ ,  $B = 623 \text{ cm}^{-1}$ , 72% of the free ion<sup>53</sup> and  $C = 3377 \text{ cm}^{-1}$ . These values are in the range usually found for octahedrally coordinated V(III) compounds<sup>52,54</sup> but are lower than those observed for the free ion, indicating a noticeable degree of covalency between the V<sup>3+</sup> cations and the surrounding oxygen ions.52

#### Catalytic behaviour

Vanadium peroxides are known as very effective oxidants of different organic and inorganic substrates such as sulfides, alkenes, alcohols, aromatic and aliphatic hydrocarbons, halides and sulfur dioxide.<sup>55</sup> These reactions, either stoichiometric or catalytic, where the terminal oxidant is normally hydrogen peroxide or an alkylhydroperoxide, are carried out, on average, in mild conditions and associated with good product yield and selectivity.

The activity of the vanadium catalysts 1-4 was probed towards oxidation of sulfides (eqn (1)). To note, this reaction is interesting both for the preparation of sulfoxides and sulfones,<sup>55</sup> as well as for desulfurization of fuels.<sup>56</sup> The scope of the reaction was studied with various substrates (methyl phenyl sulfide, ethylbutyl phenyl sulfide, *p*-chlorophenyl methyl sulfide and methyl *p*-tolyl sulfide) and two oxidizing agents ( $H_2O_2$  and TBHP) (Table 1).



In the proposed mechanism for the oxidation of thioethers<sup>57</sup> the first stage consists of the activation of the hydroperoxide by coordination with the metallic centre in order to obtain the peroxo species. The oxygen atom coordinated to the metal has high electrophilic character, so it could be easily attacked by the sulfide, giving rise to a transition state shown in eqn (2). Once the sulfoxide is formed, the sulphur atom already has a pair of electrons for another nucleophilic attack to the peroxidic oxygen, originating the corresponding sulfone, which is the main reaction by-product.



**Catalytic reactions with H\_2O\_2 as the oxidant.** The catalysts were first tested for the oxidation of methyl phenyl sulfide (MeSPh) with  $H_2O_2$  as the oxidizing agent. The catalysts overcome a transformation due to the effect of the oxidizing agent. Compound **1**, with a 2D crystal structure, suffers a colour change, from light green to orange-yellowish getting partially solved, as can be seen by the colour change of the solution. Catalysts with 3D crystal structure, **2**, **3** and **4**, get totally solved by the action of  $H_2O_2$ , giving rise to orange solutions. Therefore, the reactions take place in homogeneous media. If the

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Fig. 4 Conversion of methyl phenyl sulfide (MeSPh) over the four catalysts with  $H_2O_2$  as the oxidizing agent after 15 and 60 minutes of reaction.

catalysts are not treated with the oxidant previously (activation stage) the reaction runs out of oxidant because of the transformation of the catalysts, and very low conversions are obtained. The colour changes indicate the oxidation of vanadium from V(m) to V(v).<sup>58</sup>

Total conversion was achieved in less than 60 minutes with a selectivity towards sulfoxide formation of 100% (Fig. 4).

In order to study the effect of the temperature we performed the reaction of 2 at 0 °C. The conversion and selectivity rates did not show differences with those of the reactions at r.t. On the other hand, we have reduced the catalyst: substrate ratio to study the effect of the catalyst concentration. When a 1:1000 ratio is used, the conversion rate of 80% was reached at 20 minutes of the reaction, so there is no activity loss. However, when a 1:5000 ratio is used the conversion rate is a little bit lower, 68%, reaching it in 60 minutes of the reaction (Fig. 5).

The scope of the reaction with various alkyl aryl sulfides was studied over catalyst **1**. The oxidation reactions were carried out with ethylbutyl phenyl sulfide (EtBuSPh), *p*-chlorophenyl methyl sulfide (ClPhSMe) and methyl *p*-tolyl sulfide (MeSMePh) at room temperature. The kinetic profiles of these reactions are shown in ESI, Fig. S5.1.<sup>†</sup> A drastic decrease of the catalytic activity is observed when electron donor or acceptor groups are introduced or when the steric hindrance is increased, with conversions between 24 and 14%, and TOF between 1 and 0.1 min<sup>-1</sup>. All the reactions are 100% selective towards sulfoxides formation.

After the oxidation reactions, compound 1 recovers a green colour, but darker than the original one. The powder X-ray diffraction patterns of this dark-green compound show only one maximum, corresponding to the (001) reflection, displaced from 9.1° in  $2\theta$  before the reaction to 8.9° after the reaction with MeSPh, and to 9.3° in the case of the other substrates. This peak is associated with the layer stacking direction, therefore, the transformation that takes place



Fig. 5 Kinetic profiles of 2 for the oxidation reaction of methyl phenyl sulfide with  $H_2O_2$  with catalyst : substrate ratios of 1 : 1000 and 1 : 5000.

**Table 2** Reutilization data for oxidation of MeSPh with  $H_2O_2$  over catalyst **1**. Conversion ( $C_T$ ) and selectivity towards the sulfoxide formation ( $S_{SO}$ ) results at 60 min of reaction at each cycle (T = 298 K)

Catalyst	Cycle	Cat/substr	$C_{\mathrm{T}}$ (%)	$S_{\rm SO}$ (%)
1	1	1/100	99	100
	2	1/100	100	97
	3	1/100	56	100

produces an increase in the interlayer space in the reaction with MeSPh and a contraction when reacting with the substituted substrates, explaining the loss of activity observed (ESI, Fig. S5.2<sup>†</sup>). The IR spectra of the recovered solids show the same vibration modes of the fresh catalyst, with a broadening of the bands due to the loss of crystallinity (ESI, Fig. S5.3<sup>†</sup>). This indicates that the reactive species has a similar chemical composition as **1**.

**Recycling and heterogeneity test.** Recycling tests were carried out over **1** in the MeSPh-oxidation, because it is the only reaction where the catalyst can be recovered. During the successive cycles a decrease in the solid amount is observed, due to the partial decomposition of the catalyst by the effect of  $H_2O_2$ . After the second cycle a decrease in the activity is observed (Table 2).

Leaching tests were made for the same reaction after the third cycle. Thus, at a conversion of about 15%, the solid was separated from the reaction media by centrifugation. The supernatant was then allowed to react, detecting a slight increase in the conversion, up to 35% after 60 minutes. Although the effect of introducing different substituents in the substrates and the X-ray powder diffraction analysis of the recovered catalyst indicate that the reaction is catalyzed by the solid phase, there seems to be some leaching. This may be because some of the solid gets dissolved by the action of  $H_2O_2$ , this solution also being able to catalyze the oxidation reaction.

**Catalytic reactions with TBHP as the oxidant.** When TBHP is the oxidizing agent, all the materials behave as heterogeneous catalysts, and the reactions take place at 50 °C, achieving 100% conversion rates in short times. The kinetic profiles of these reactions are shown in Fig. 6.

The most remarkable feature of these kinetic profiles is that when using 1 with TBHP (2.2 equiv.), the kinetic profile shows a long induction period. Another test was made adding the same quantity of TBHP gradually, 1.5 equiv. at the beginning and 0.35 equiv. twice at 40 and at 90 minutes. In this case, the kinetic profile is almost linear (ESI, Fig. S5.4<sup>†</sup>). It seems that



Fig. 6 Kinetic profiles of 1, 2, 3 and 4 for the oxidation reaction of methyl phenyl sulfide with TBHP.

the active centres on the surface get blocked when an excess of TBHP is added, obstructing the substrate to get them. However, if the oxidizing agent is added gradually the substrate could reach the active centres and the reaction takes place more gradually.

After the reactions, the catalysts were filtered and characterized by X-ray powder diffraction and IR spectroscopy. The powder patterns of the catalysts 2-4 after the reactions with TBHP did not show significant changes with respect to those obtained before them (Fig. 7a). However, the pattern of catalyst 1 after the reaction with TBHP added in one go shows the splitting of some maxima. For these reasons, the reactions have been monitored by means of X-ray powder diffraction (Fig. 7b). Comparing the X-ray diffractograms of as-synthesized 1, 1 after the activation stage, 1 after the reaction with TBHP added in one go and 1 after the reaction with TBHP added in three goes, a evolution on the (001) reflection can be observed. It seems that this maximum suffers a gradual displacement to higher  $2\theta$  angles in the activation stage, gaining intensity after the reaction with TBHP added in one go. When TBHP is added in three times, the maximum displacement is smaller, observing it as a shoulder. The same behaviour is observed for some less intense diffraction maxima in all cases.

These maxima shifts should be the result of the oxidation of **1** not only at the particle surface, but also at the structural level. The unit cell of the oxidized compound is very similar to the as-synthesized **1**, with a decrease of the *c* parameter, associated with a reduction of the interlayer space. Judging by the powder X-ray diffraction, catalysts 2-4 are only oxidized superficially by the action of TBHP.



Fig. 7 Powder X-ray diffraction patterns of (a) catalysts 2–4 before and after the oxidation reaction of MeSPh with TBHP and (b) catalyst 1 before the reaction, after the activation stage and after the reaction adding TBHP in one go and in three goes.

**Table 3** Reutilization data for oxidation of MeSPh with TBHP over catalyst **4**. Conversion ( $C_T$ ) and selectivity towards the sulfoxide formation ( $S_{SO}$ ) results at 60 min of reaction at each cycle (T = 323 K)

Catalyst	Cycle	Cat/substr	$C_{\mathrm{T}}$	$S_{\rm SO}$
4	1	1/100	100	92
	2	1/100	100	95
	3	1/100	96	93

The IR spectra obtained after the reactions are very similar to those of the fresh catalysts. However, there are some bands that are less intense. These bands are related to the torsional vibration modes ( $\gamma$ ) of the (NH<sub>n</sub><sup>+</sup>) and (CH<sub>2</sub>) groups.

Taking into account that the inorganic frameworks of 1-4 contain no residual solvent accessible voids because their pores are occupied by guest molecules (organic amine cations and water molecules), the catalytic activity of these materials should be attributed to the vanadium centres on the surface. In order to corroborate this hypothesis, the oxidation reactions have been reproduced using crystals instead of powder. The kinetic profiles of these reactions are summarized in ESI, Fig. S5.5.<sup>†</sup> For catalysts 2–4, the conversion rates are almost zero until a certain reaction time when the conversion increases abruptly, almost to a 100%. After the reaction, the particle size of the recovered catalysts has been reduced drastically, probably due to the action of the magnetic stirrer (ESI, Fig. S5.5<sup>†</sup>). This fact suggests that it is necessary to increase the surface area in order for the catalyst to have enough active centres for the reaction to take place. The kinetic profiles of catalyst 1 both with powder and crystals are very similar. The catalyst has been recovered as a powder and the DRX pattern is the same as that observed when using powder of assynthesized 1.

In all cases the phases start to catalyze approximately at 80 minutes, probably because this is the time when there is enough catalyst in the reaction media with the appropriate particle size.

**Recycling and heterogeneity test.** Reutilization is one of the greatest advantages of heterogeneous catalysts, and can also provide useful information about the anchoring process and catalyst stability along the catalytic cycle. Recycling tests were carried out over 4. The catalyst was recycled for at least 3 runs maintaining its activity and selectivity (Table 3).

The heterogeneity of the reaction was probed by a leaching test with catalyst 2. When the reaction reached a conversion rate of 5%, the solid was separated from the liquid by filtration. The supernatant was then allowed to react. After 1 hour without the catalyst the conversion rate was 12% (Fig. 8). This fact confirms the heterogeneity of the reactions.

# **Experimental section**

#### Synthesis and characterization

1, 2, 3, and 4 were synthesized under mild hydrothermal conditions and autogenous pressure.  $H_3PO_3$  (7.50 mmol for 1 and



**Fig. 8** Kinetic profile of oxidation of MeSPh over **2**, and after hot filtering, with TBHP.

15 mmol for 2, 3 and 4) and VCl<sub>3</sub> (0.3 mmol for 1 and 0.6 mmol for 2, 3 and 4) were dissolved in different mixtures of distilled water and organic solvents (5 ml H2O-25 ml ethanol for 1, 10 ml  $H_2O-20$  ml 1-butanol for 2, 10 ml  $H_2O-$ 20 ml methanol for 3 and 4). The pH of the resulting solutions was increased to the desired value with the corresponding organic amines (pH 4.5 with 5.09 mmol of 2-methylpiperazine for 1, pH 2-2.5 with 13.94 mmol of cyclopentylamine for 2, 11.40 mmol of cyclohexylamine for 3 and 10.06 mmol of cycloheptylamine for 4). These reaction mixtures were sealed in PTFE-lined stainless steel pressure vessels. After 3 days at 200 °C for 1 and 2 and at 170 °C for 3 and 4, the vessels were slowly cooled to room temperature. Fibrous radial crystalline growth and prismatic crystals for 1 and hexagonal tabular and plate crystals for 2, 3 and 4 were obtained, and then they were isolated by filtration, washed with water and acetone and dried at ambient temperature.

The pH value range in which 2, 3 and 4 are obtained as single phases in the synthesis is very limited, such that below pH 2  $V_2$ (HPO<sub>3</sub>)<sub>3</sub><sup>59</sup> appears and above pH 2.5 V(PO<sub>4</sub>)·H<sub>2</sub>O<sup>60</sup> crystallizes.

According to the literature, until now, there were six organically templated phosphites with V(III) as the single-valence cation centre. Among them,  $[C_4N_2H_{14}][VF(HPO_3)_2]\cdot H_2O_1^{61}$   $(C_4H_8N_2H_4)_{0.5}(C_4H_8N_2H_3)[V_4(HPO_3)_7(H_2O)_3]\cdot 1.5H_2O^{62}$  and  $(C_2H_{10}N_2)[V(HPO_3)F_3]^{63}$  compounds were typically prepared from a metal source containing pentavalent vanadium, V<sub>2</sub>O<sub>5</sub>. However, a tetravalent vanadium reactant, VOSO<sub>4</sub>, was employed to achieve  $(Hcha)_3(H_3O)_{1+x}[V_9(H_2O)_6(HPO_3)_{14-x}^{-1}(BO_3)_x(H_2PO_3)_3]\cdot 2H_2O$  (x = 0.1-1.2, cha = cyclohexylamine)^{64} and  $[C_3N_2H_5]_2[V_4(H_2O)_3(HPO_3)_4(HPO_4)_3]^{61}$  compounds. In this research,  $^{65}$  as in the obtaining of the  $(C_2H_{10}N_2)_{0.5}[M(HPO_3)_2]^{66}$  phase, a direct V<sup>3+</sup> source, VCl<sub>3</sub>, was used.

Huang and  $Wang^{64}$  proposed the  $VOSO_4$ -H<sub>3</sub>BO<sub>3</sub>-H<sub>3</sub>PO<sub>3</sub>-cyclohexylamine-H<sub>2</sub>O reaction system, with a 1:1.5:6:5:278 molar ratio, heated at 180 °C for 3 days, in order to obtain the compound with  $(Hcha)_3(H_3O)_{1+x}$ -

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 $[V_9(H_2O)_6(HPO_3)_{14-x}(BO_3)_x(H_2PO_3)_3]\cdot 2H_2O$  (cha = C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub> and x = 0.1-1.2) formula. The inorganic framework of this phase is very similar to that presented by compounds 2, 3 and 4. The authors suggest that the boric acid is essential for the formation of this compound. However, we have proved that it is possible to achieve compounds 2, 3 and 4 without borate incorporation, using a direct V<sup>3+</sup> source instead of a V<sup>4+</sup> reactant.

The amounts of vanadium in compounds **1**, **2**, **3** and **4** were measured by ICP-AES spectroscopy and the amounts of C, N and H by elemental analysis. Calculated for **1** (%): V, 18.2; C, 10.7; N, 5.0; H, 4.0. Found (%): V, 18.4(3); C, 10.7(4); N, 4.3(5); H, 4.0(2). Calculated for **2** (%): V, 19.3; C, 10.1; N, 2.4; H, 3.4. Found (%): V, 19.5(5); C, 9.9(5); N, 2.2(5); H, 3.2(4). Calculated for **3** (%): V, 19.9; C, 9.4; N, 1.8; H, 3.7. Found (%): V, 19.7(4); C, 9.1(4); N, 1.8(4); H, 3.8(5). Calculated for **4** (%): V, 19.6; C, 10.8; N, 1.8; H, 3.9. Found (%): V, 19.4(4); C, 10.3(5); N, 1.7(4); H, 3.7(4). The densities of the four phases were measured by flotation<sup>67</sup> using a mixture of  $CH_2I_2$  and  $CHCl_3$ , being 1.931(2) g cm<sup>-3</sup> for **1**, 1.81(3) g cm<sup>-3</sup> for **2**, 1.77(4) g cm<sup>-3</sup> for **3** and 1.79(3) for **4**.

#### Single crystal X-ray diffraction study

An elongated prismatic single-crystal with dimensions  $0.55 \times 0.11 \times 0.08$  mm of 1 and hexagonal plates for 2, 3 and 4 with dimensions  $0.48 \times 0.34 \times 0.06$  mm,  $0.42 \times 0.35 \times 0.07$  mm and  $0.13 \times 0.10 \times 0.03$  mm, respectively, were selected under a polarizing microscope and mounted on a glass fibre.

Intensity data were collected at 100 K on an Oxford Diffraction XCALIBUR 2 diffractometer for 1 and 2, and on a STOE IPDS 2T diffractometer for 3, fitted with a Sapphire 2 CCD detector and an image plate detector (34 cm diameter), respectively, using in both cases graphite monochromated Mo-K $\alpha$  radiation = 0.71073 Å. Data collection for 4 was performed at 100 K on an AGILENT SUPERNOVA diffractometer (Cu-K $\alpha$ radiation = 1.5418 Å; omega scan mode) using a CCD (Atlas) detector. Data frames were processed (unit cell determination, intensity data integration, correction for Lorentz and polarization effects,<sup>68</sup> and analytical absorption correction<sup>69</sup> taking into account the size and shape of the crystals) using the corresponding diffractometer software package.<sup>70</sup>

The structures were solved by direct methods, the SHELXS 97 computer program,<sup>71</sup> in the triclinic space group  $P\overline{1}$  for **1** and, in the hexagonal space group  $P6_3/m$  for **2**, **3** and **4**, and then refined by the full matrix least-squares procedure based on  $F^2$ , using the SHELXL 97 computer program<sup>72</sup> belonging to the WINGX software package.<sup>73</sup> This procedure allowed us to find the positions of the vanadium and phosphorus atoms, and all the other non-hydrogen atoms (O, C, N) were placed from subsequent Fourier-difference map calculations.

During the structure refinement, two types of disorder, positional and chemical, were found. In the ESI (S1<sup> $\dagger$ </sup>), the study of the different positional disorders of the phosphorous anionic groups and the chemical disorders between the crystallization water molecules and the organic cations is presented. Other features about the refinement are also included there.

Details of crystal data, data measurement and reduction, structure solution and refinement of the phases **1**, **2**, **3** and **4** are reported in Table 4. The selected bond distances and angles are reported in ESI, Tables S1.1 to S1.4.<sup>†</sup> All structure drawings were made using the ATOMS program.<sup>74</sup>

#### Physicochemical characterization techniques

Thermogravimetric analyses were performed on an SDT 2960 simultaneous DSC-TGA TA instrument for 1, 2 and 3 and on a Netzsch STA 449C one for 4. Crucibles containing 20 mg of each sample were heated at a rate of 5  $^{\circ}$ C min<sup>-1</sup> from room temperature to 900 °C. Temperature dependence X-ray diffraction experiments for all these compounds were carried out in air on a Bruker D8 Advance diffractometer (Cu Ka radiation) equipped with a variable-temperature stage (HTK2000), a Pt sample heater and a Vantec high-speed one dimensional detector with six degrees of angular aperture. The powder patterns were recorded in the  $8 \le 2\theta \le 30^\circ$  range (step size = 0.033° and time per step = 0.2 s) for 1 and in the  $5 \le 2\theta \le 38^\circ$ range (step size =  $0.033^\circ$  and time per step = 0.4 s) for 2, 3 and 4, in all cases at intervals of 15 °C, increasing the temperature at a 9 °C min<sup>-1</sup> rate from room temperature to 795 °C, except for 4, which was heated until 300 °C. The IR spectra (KBr pellets) were obtained with a JASCO FT/IR-6100 spectrophotometer in the 400-4000 cm<sup>-1</sup> range. UV-vis diffuse reflectance spectra were registered at room temperature on a Varian Cary 5000 (version 1.12) spectrometer in the 250-2500 nm range for all the compounds.

#### Catalytic activity

Oxidation of organic sulfides was carried out in a batch reactor at atmospheric pressure, using acetonitrile or dichloromethane as solvents (2 ml). Before the reactions, the materials (0.02 mmol) were activated by stirring them with the oxidizing agent, H<sub>2</sub>O<sub>2</sub> or *tert*-butyl hydroperoxide (TBHP), in the corresponding solvent, acetonitrile or dichloromethane, for 30 min at r.t. or 50 °C, respectively. After this activation stage, the catalysts were separated from the liquid media. The reactor with the activated catalyst was then charged with 2 mmol of the corresponding sulfide (methyl phenyl sulfide, 4-chlorophenyl methyl sulfide, methyl *p*-tolyl sulfide and 1-ethylbutyl phenyl sulfide) (ratio V: substrate = 1:100, 1:1000 and 1:5000) in 2 ml of solvent. The oxidizing agent was added dropwise and then the suspension was maintained at r.t. or 0 °C, when using H<sub>2</sub>O<sub>2</sub>, and heated to 50 °C, with TBHP. Experiments under the same reaction conditions without a catalyst have been also conducted and no appreciable amount of product was detected. Reaction samples were taken at regular times and analyzed on a Hewlett-Packard 5890 II GC-MS. After the reaction, the catalysts were filtered and characterized by X-ray powder diffraction and IR spectroscopy.

Blank experiments were carried out in order to determine the extension of the uncatalyzed reaction. At 315 K, using acetonitrile as the solvent (10 ml), 1 mmol of methyl phenyl sulfide and 3 equiv. of 30% H<sub>2</sub>O<sub>2</sub>, the reaction accounted for a conversion of 5 and 15% after 20 min and 1 h of reaction time

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Table 4	Crystallographic data and structure	efinement parameters for phases 1, 2, 3 and	4 obtained by single crystal X-ray diffraction
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Phase	1	2	3	4
Molecular weight (g mol <sup><math>-1</math></sup> )	280.0	2377.9	2300.4	2332.9
Crystal system	Triclinic	Hexagonal	Hexagonal	Hexagonal
Space group	$P\bar{1}$	$P6_3/m$	$P6_3/m$	$P6_3/m$
a, b, c (Å)	5.2403(1)	13.4107(3)	13.4578(2)	13.41250(10)
	9.2240(3)	13.4107(3)	13.4578(2)	13.41250(10)
	10.8060(4)	27.5678(7)	27.6928(7)	27.8003(3)
$\alpha, \beta, \gamma$ (°)	112.901(4)	90	90	90
	95.506(2)	90	90	90
	90.995(2)	120	120	120
$V(\text{\AA}^3)$	478.08(3)	4293.74(17)	4343.56(14)	4331.11(7)
Z	2	12	12	12
$\rho_{\rm obs}, \rho_{\rm calc} (\rm g \ cm^{-3})$	1.931(2), 1.942	1.81(3), 1.838	1.77(4), 1.753	1.79(3), 1.778
Crystal size	$0.55 \times 0.11 \times 0.08$	$0.48 \times 0.34 \times 0.06$	$0.42 \times 0.35 \times 0.07$	$0.13 \times 0.10 \times 0.03$
F(000)	283	2395	2305	2331
Temperature (K)	298(2)	100(2)	100(2)	100(2)
Diffractometer	Xcalibur 2	Xcalibur 2	Stoe IPDS 2T	Supernova
$\mu ({\rm mm^{-1}})$	1.378	1.357	1.338	11.695
$T_{\min}/T_{\max}$	0.679/0.913	0.633/0.926	0.654/0.913	0.371/0.694
Radiation (Å)	$\lambda$ (Mo K $\alpha$ ) = 0.71073	$\lambda$ (Mo K $\alpha$ ) = 0.71073	$\lambda$ (Mo K $\alpha$ ) = 0.71073	$\lambda$ (Cu K $\alpha$ ) = 1.54184
Limiting indices h, k, l	$h \pm 6$	$h \pm 16$	$-18 \le h \le 17$	$-15 \le h \le 16$
6 , ,	$k \pm 11$	$k \pm 16$	$-16 \le k \le 17$	$-15 \le k \le 16$
	$l \pm 13$	$l \pm 33$	$l \pm 37$	$l \pm 33$
Theta range (°); Completeness (%)	3.73-26.73; 98.7	2.83-25.68; 99.2	1.90-28.50; 99.7	3.81-70.04; 99.7
No. of reflections (measured/independent/observed)	13 363/2012/1730	32 685/2769/2368	54 238/3741/3184	24 685/2810/2740
$R(int)/R(\sigma)$	0.0287/0.0171	0.0289/0.0188	0.0441/0.0185	0.0582/0.0274
Parameters/restrictions	146/4	207/44	192/16	188/14
$R\left[I > 2\sigma(I)\right]$	$R_1 = 0.0327$	$R_1 = 0.0479$	$R_1 = 0.0613$	$R_1 = 0.0438$
	$wR_2 = 0.0919$	$wR_2 = 0.1355$	$wR_2 = 0.1749$	$wR_2 = 0.1278$
R [all data]	$R_1 = 0.0382$	$R_1 = 0.0555$	$R_1 = 0.0705$	$R_1 = 0.0449$
	$wR_2 = 0.0968$	$wR_2 = 0.1393$	$wR_2 = 0.1816$	$wR_2 = 0.1296$
Weight factor	x = 0.0671	x = 0.0747	x = 0.1060	x = 0.0835
-	<i>y</i> = 0.1791	<i>y</i> = 18.9021	<i>y</i> = 10.0529	<i>y</i> = 7.9489
G.O.F.	1.087	1.057	1.077	1.096
Max. and min. e. density (e $Å^{-3}$ )	0.902, -0.366	1.09, -0.898	1.454, -1.901	1.302, -0.704

 $R_{1} = \frac{\sum ||F_{0}| - |F_{c}||}{\sum |F_{0}|}, \quad wR_{2} = \sqrt{\frac{\sum w(||F_{0}| - |F_{c}||)^{2}}{\sum w|F_{0}|^{2}}}, \quad w = \frac{1}{\sigma^{2}(|F_{0}|^{2}) + (xp)^{2} + yp}, \quad p = \frac{|F_{0}|^{2} + 2|F_{0}|^{2}}{3}.$ 

respectively. Under the same conditions but using 1.5 mmol of TBHP instead of  $H_2O_2$ , the conversion after 5 h was 10%.

## Concluding remarks

The mild hydrothermal technique was used for the synthesis of four novel amine templated open-framework vanadium(m) phosphites. The crystal structure of **1** consists of a two-dimensional network formed by anionic sheets of  $[V(H_2O)(HPO_3)_2]^-$  formula, compensated by the 2-methylpiperazinium cations embedded between the layers. Phases **2**, **3** and **4** present a pillar-layer network giving rise to a three-dimensional framework containing intersecting 16-ring channels with the primary amine templates and the crystallization water molecules enclosed in them. Phases **2**, **3** and **4** behave differently from the heating due to the presence of crystallization water molecules in compounds **3** and **4** and the absence of them in compound **2**. The catalytic tests show that the phases are heterogeneous and active catalysts for the selective oxidation of

alkyl aryl sulfides with TBHP as the oxidizing agent, and can be recovered and reutilised after the reaction showing no important change in their chemical composition or crystal structure. However, the use of  $H_2O_2$  induces the dissolution of the catalysts, partial for **1** and total for **2**, **3** and **4**, giving rise to active species. Catalyst **1** is affected not only by the size of the substrate, but also by the size of the oxidizing agent.

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