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Synthesis of V-containing Keggin polyoxometalates: Versatile catalysts for the synthesis of fine chemicals?

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ABSTRACT

Vanadium-containing polyoxometalates (POM): $H_4PVMo_{11}O_{40}$, $H_5PV_2Mo_{10}O_{40}$ and $H_6PV_3Mo_9O_{40}$ were synthesized by two distinct procedures and characterised by XRD, ^{31}P MAS-NMR, FT-IR, BET, UV–vis and SEM. These vanadium-substituted POM were shown to be able to oxidize benzene into phenol with nearly 100% selectivity in the presence of H_2O_2. Furthermore, other aromatics were also oxidised to the corresponding phenols or ketones at appreciable degrees of conversion. However, the question of their stability toward leaching arises and has been investigated. While, there appears to be a correlation for liquid-phase reactions between the yields toward oxygenates and the vanadium content in the Keggin structure, we were also able to observe a decrease in the stability of these POM after successive catalytic runs. Furthermore, POM crystals having a regular size and shape, with peculiar orientation have been prepared and hence exhibited the highest catalytic activity.

1. Introduction

Heteropolyacids (HPA) have typical properties that are of valuable interest for catalysis, such as strong Brönsted acidity, ability to catalyse redox reactions under mild conditions and high solubility in water and organic solvents. Those bifunctional properties working cooperatively are a great challenge for tailoring new catalysts, either via introduction of a transition metal, or heteroatom (P, Si, Ge), or any combination, depending on the desired practical application. HPA are polyoxometalates (POM) incorporating anions having metal-oxygen octahedra as basic structural units, forming the Keggin structure [1,2]. This so-called primary structure results from the condensation of oxoanions as for instance:

$$12MoO_4{}^{2-} + HPO_4{}^{2-} + 23H^+ \rightarrow PMo_{12}O_{40}{}^{3-} + 12H_2O$$

where $PMo_{12}O_{40}{}^{3-}$ represents the Keggin unit. They are composed by oxides of addenda atoms (W, Mo, V, Nb, Ta) and heteroatoms like P, Si, or Ge. HPA and their salts are polyoxo compounds incorporating large counteranions having metal-oxygen octahedra (MO_6) as the basic structural unit. The hetero atoms (mostly P) are located at the centre of the structure (tetrahedrally coordinated with O atoms). The MO_6 units are linked together to form an extremely stable and compact matrix. The three dimensional arrangement of polyanions, counter cations and water builds the secondary structure. The tertiary structure corresponds to the manner of assembly of these nanoparticles at the microscopic level. These three structures can influence the catalytic functions of the material [3].

The acidity of HPA is purely Brönsted-type acidity, stronger than that of conventional solid acids such as SiO_2–Al_2O_3, zeolites, and H_3PO_4/SiO_2. According to literature data, they exhibit super-acid properties in the solid state (in the order of PW > SiW > P-PMo > SiMo > PV) with estimated values of around −13 for the Hammett function H_0 [2–4]. HPA have been used as catalysts in petrochemical reactions requiring electrophilic catalysis: alkylations, acylations, isomerisations, and the methanol-to-gasoline process [3–6]. This strong acidity is attributed to the large size of the polyanion, which has a low and delocalisable surface charge density, thus to the weak interaction between the polyanion and the proton, as found in liquid superacids (typically $SbF_6{}^-$) [7]. In addition, HPA are more active than mineral acids in several types of homogeneous reactions in both organic and aqueous solvents [8]. Due to the presence of high valent metal species such as Mo^{6+}, W^{6+}, or V^{5+} cations, HPA are good multi-electron oxidants [9,10]. POM and especially those systems containing Mo and V, have been successfully examined for the liquid-phase partial oxidation of alkenes and several aromatic compounds [1,11–17].

In view of these reports, we believe it worthwhile to examine the activity/selectivity of V-containing POM in the partial

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oxidation with H_2O_2 of valuable aromatics: benzene, bromobenzene, tetralin, and naphthalene. Moreover, the selective oxidation of 2-methylnaphtalene into K3 vitamin was also performed, in order to develop a green synthesis and, hence replace nasty Cr^{VI} homogeneous catalyst. Finally, this study was also devoted to the investigation of the influence of the tertiary structure of POM on their catalytic performance.

2. Experimental

2.1. Preparation procedures of POM

12-Molybdophosphoric acid ($H_3PMo_{12}O_{40}$), furnished by Fluka was used without further purification. Despite their awe-inspiring formula, POM are quite easy to prepare, via simple acidification of an aqueous solution containing an alkali metal salt of the heteroelement (molybdate or vanadate), and subsequent isolation of the material via ether extraction. Heteropolyvanadates (HPV) have been synthesised following the initial procedure described by Tsigdinos and Hallada [18], by mixing aqueous solutions of sodium molybdate dihydrate ($Na_2MoO_4{\cdot}2H_2O$, Fluka, 99.5 wt.%), disodium hydrogen phosphate dihydrate ($Na_2HPO_4{\cdot}2H_2O$, Fluka, 99 wt.%), and sodium metavanadate ($NaVO_3$, Fluka, 98 wt.%). Under vigorous stirring, concentrated sulfuric acid was added dropwise to acidify the solution. The red-coloured solution was cooled to 273 K, and kept for 2 h at this temperature before being extracted by diethyl ether. The resulting HPV-etherate complex was either dried at 333 K overnight to remove the solvent, or placed in a dessicator under sulfuric acid vapours for several days to allow a slow recrystallisation.

The compound $PVMo_{11}$ has also been prepared via a hydrothermal process [19], where a stoechiometric mixture of 0.98 g (0.01 mol) of phosphoric acid, 0.91 g (0.005 mol) of vanadium pentoxide and 14.4 g (0.11 mol) of molybdenum trioxide was suspended in 150 ml of distilled water. The mixture was stirred for 3 h at 353 K, and then cooled to room temperature. After removal of insoluble molybdates and vanadates, the HPA solution was evaporated and dried at 338 K for 48 h yielding orange crystals of anhydrous $PVMo_{11}$. The PV_2Mo_{10} was synthesized following the same hydrothermal procedure.

2.2. Characterisations

X-ray diffraction (XRD) patterns were acquired on a D8 Advance Bruker AXS powder diffractometer ($\theta/2\theta$) using monochromatised Cu-K_α radiation in the range of 2θ from 5 to 60°. Solid state ^{31}P MAS NMR experiments were carried out on a Bruker AVANCE DSX-400 spectrometer operating at a frequency of 161.98 MHz for ^{31}P using a Bruker triple resonance 4 mm MAS probe. ^{31}P chemical shifts were referenced with respect to 85% phosphoric acid. FT-IR measurements were performed with a PerkinElmer spectrum BX apparatus, using KBr pellets. UV–vis spectroscopy was carried out on a Cary 5E UV-VIS-NIR spectrophotometer. The specific surface areas (SSA) were measured by N_2 adsorption–desorption at 77 K using a Micromeritics TriStar apparatus (BET method). Scanning electron microscopy (SEM) micrographs were recorded on a JEOL FEG 6700F microscope working at 9 kV accelerating voltage. Before observation, the sample was covered by a carbon layer to decrease the charge effect during the analysis.

2.3. Liquid phase reaction

The different POM materials were tested in liquid phase oxidations of benzene, naphthalene, bromobenzene and tetralin at 333 K for 2 h. The partial oxidation of 2-methyl naphthalene (2 MN) was also performed for 24 h at 333 K. The operating conditions were as follows: 10 mL acetonitrile, 0.01 mol aromatic substrate, 0.05 mol H_2O_2 (30 wt.%). A five-fold excess in peroxide was used to study the catalyst resistance toward leaching. The products were analysed by GC (HP 5890 Series II) with a capillary column (PONA, 50 m).

3. Results and discussion

3.1. Characterisations

The BET surface areas of HPA were between 5 and 17 m^2/g, in agreement with previous investigations [20]. Pore size analyses showed that the distributions were broad, ranging from below 10 to 20 Å. Moffat demonstrated that these micropores result from the translation and rotation of the Keggin anions [21].

For example, the FT-IR spectrum of $H_5PV_2Mo_{10}O_{40}$ (V_2 compound) material is presented in Fig. 1. The four IR bands characteristics of the Keggin unit, obtained for the V_1, V_2 and V_3 compounds, at about 1057, 958, 871 and 784 cm^{-1} can be, respectively, assigned to P–O, M–O (M=Mo, V), inter-octahedral M–O–M, and intra-octahedral M–O–M vibrations [3,15]. Among the effect of the presence of the vanadium atom, the Mo–O and P–O vibration of the V_0 compound, are shifted, respectively, from 1066 to 965 cm^{-1} [3,15]. The bands located at 3300–3400 cm^{-1} and 1610–1650 cm^{-1} correspond to the presence of water in the sphere of coordination. The chemical composition of V_1, V_2 and V_3 was already confirmed by elemental analysis and potentiometric titrations of acidic hydrogen in the POM in the initial paper from Tsigdinos and Hallada [18]. Fig. 2 shows the ^{31}P MAS-NMR spectra of V_1 POM, and further evidenced the formation of the Keggin structure. Indeed two characteristic signals were observed at -3.77 and -4.24 ppm, corresponding to α- and β-isomers of the Keggin unit [21b].

Fig. 3 shows the XRD patterns for the different heteropolyvanadates. The typical reflexion at $2\theta = 9°$ is a typical feature of the Keggin structure [21,22]. Despite an increase of the V peaks (JCPDS tables), the relative intensity hardly decreases from the V_1 to the V_3 compound. In fact, the stability of the structure is limited to three V atoms per Keggin unit [3]. The stabilities of the HPV follow the order: $H_4PVMo_{11}O_{40} \approx H_5PV_2Mo_{10}O_{40} \gg H_6PV_3Mo_9O_{40}$, indicating that an increase in V content leads to a decrease in the stability of the Keggin structure. The crystallinity of the POM prepared under hydrothermal conditions is lower compared to the original procedure from Tsigdinos and Hallada [18]. The POM, $H_5PV_2Mo_{10}O_{40}$, was recrystallised under sulfuric acid vapours during 1 week, leaving organised microscopically orange crystals of hundreds of microns size. Hence, the microstructure of two $H_5PV_2Mo_{10}O_{40}$ materials was investigated by SEM analysis (Fig. 4). Whereas the $H_5PV_2Mo_{10}O_{40}$ material prepared under hydrothermal conditions (Fig. 4b) exhibit no crystalline microstructure but rather particles with a random morphology, the V_2 material which was allowed to recrystallize is constituted by several large prismatic crystals, having between 200 and 400 μm in length (Fig. 4a). More surprisingly, these long crystals are the result of an aggregation of smaller crystals having between 5 and 8 μm in length. It is noteworthy that the tertiary structure of this material has been influenced during the recrystallisation process. The mechanism explaining such organisation and aggregation degree is not fully understood yet, but we have observed a similar phenomenon recently with zeolites [23]. Based on the semi-empirical calculations done by Moffat [24], it should be possible to predict why and which of such organised structures are formed. Hence, one can hope the development of extraordinary inorganic architectures based on these molecules including some of the

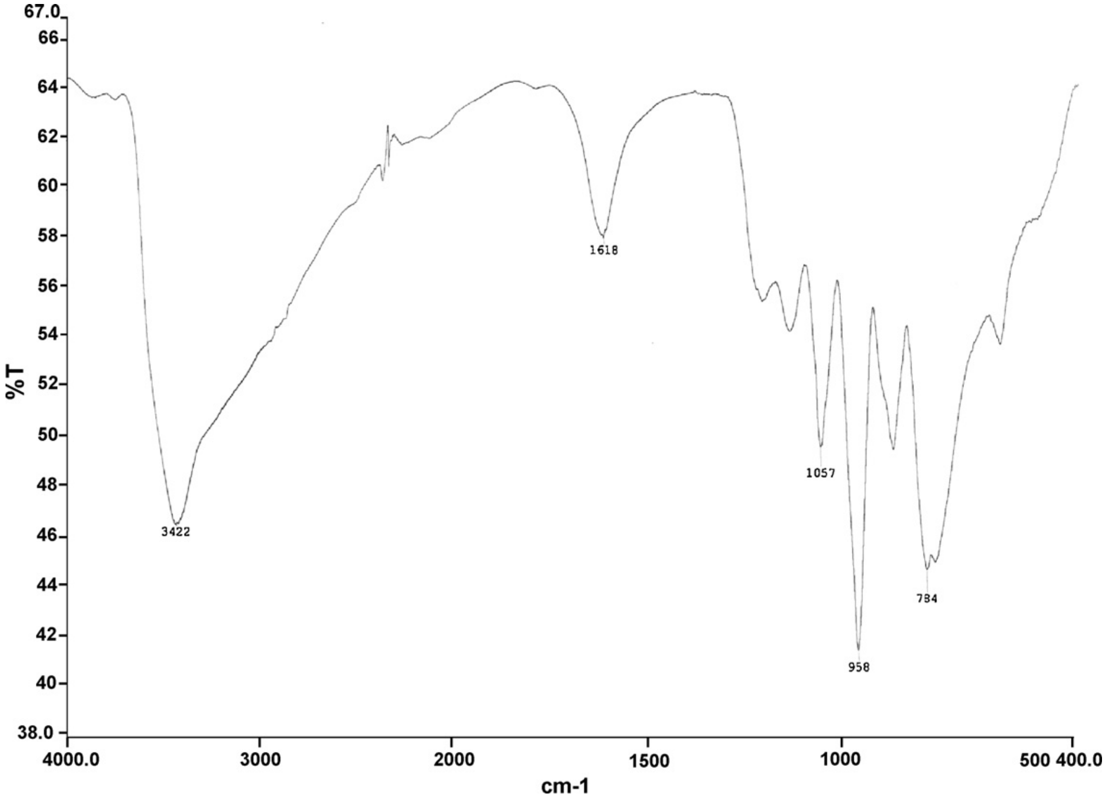


Fig. 1. FT-IR spectrum of $H_5PV_2Mo_{10}O_{40}$.

largest and beautiful polymetallic compounds, such as icosidodecahedron [25].

An UV–vis spectrum has been recorded for this $H_5PV_2Mo_{10}O_{40}$ material (Fig. 5). An absorption band can be observed at 305 nm, which corresponds to Mo^{6+} in octahedral position, and describes a ligand metal charge transfer (LMCT) state [26]. After adding hydrogen peroxide to this mixture, a new band is observed around 323 nm which corresponds to V peroxo species [26] indicative of the presence of V^{5+} species.

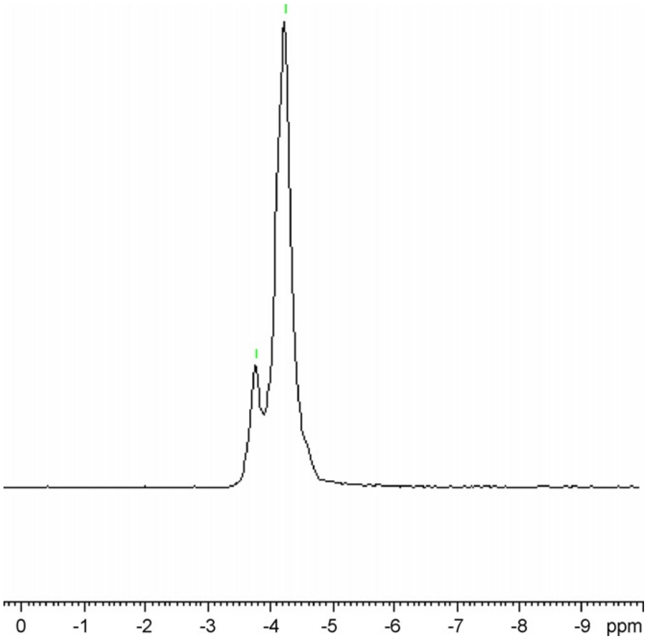


Fig. 2. ^{31}P MAS NMR spectrum of $H_4PVMo_{11}O_{40}$.

3.2. Catalytic activity

The hydroxylation of benzene has been used as a model reaction to test the activity/selectivity of our V-containing POM, depending on the number of V-atoms in the Keggin unit, the synthesis procedure ("classical" versus hydrothermal), and the tertiary structure in the case of organised POM crystals. Nomiya et al. reported that the $PW_{10}V_2$ and $PMo_{10}V_2$ system were more active in the reaction than the classical V_2O_5/H_2O_2 Milas reagent [27]. Fig. 6 presents the results for the different V-containing POM. It appears that only the V-containing phosphomolybdic systems

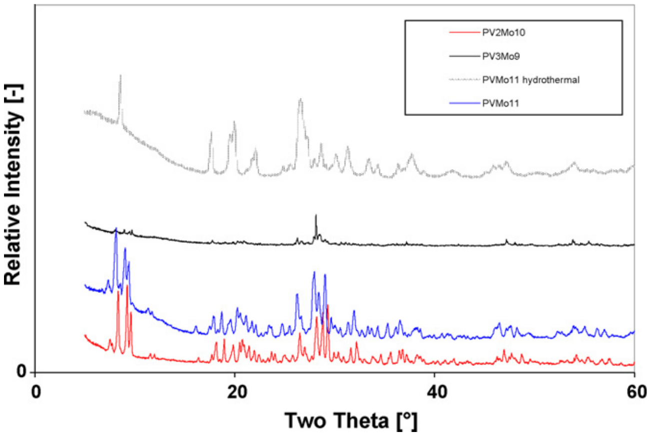


Fig. 3. Diffraction patterns for the different heteropolyvanadates.

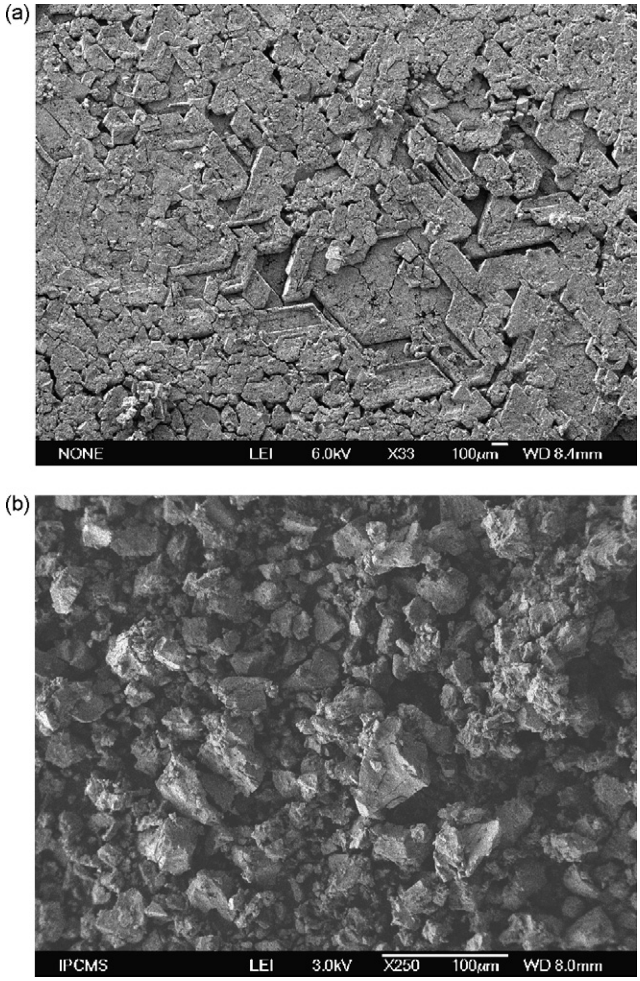


Fig. 4. SEM micrographs of (a) $PV_2Mo_{10}O_{40}$ crystals and (b) hydrothermal synthesized V_2 material.

are active in the hydroxylation of benzene. Furthermore, the benzene conversion into phenol was increased with the number of V-atoms present in the Keggin unit. The selectivity towards phenol formation was for all materials above 99%. The kinetics of the reaction, at initial times, shows a faster benzene consumption (determined by the slope of the curve) with an increase of the V-content, thus the PV_3Mo_9 remains the more active catalyst. However, the decomposition of hydrogen peroxide is a competing reaction that limits achievable phenol yields [28]. Nomiya et al. observed the same tendency [29], despite the low stability of V_2 and V_3 compounds. A combined influence of framework Mo and V was supposed to be responsible for the catalytic activity [27,29]. It is interesting to note that POM prepared via the hydrothermal route exhibited a higher phenol yield than its analog synthesised by the classical procedure [18].

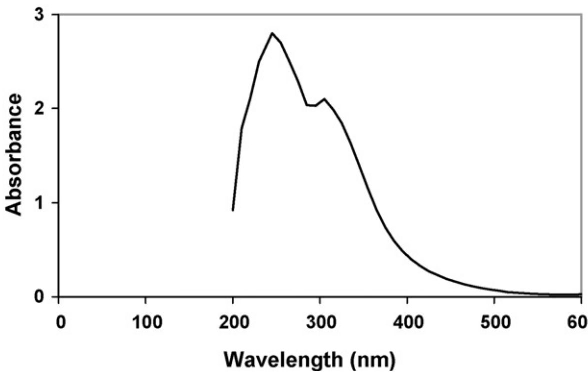


Fig. 5. UV–vis spectrum of $H_5PV_2Mo_{10}O_{40}$ in acetonitrile.

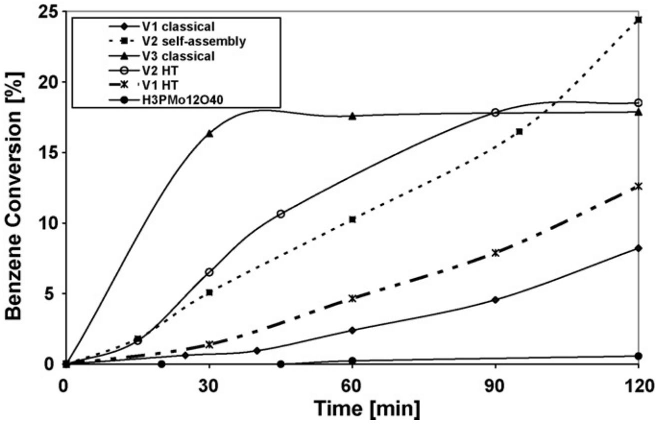


Fig. 6. Degrees of benzene conversion to phenol as functions of time.

Finally, the $H_5PV_2Mo_{10}O_{40}$ constituted by oriented crystals remains the more active and therefore promising catalyst. One can, therefore, argue that the tertiary structure of the POM plays a role in the catalytic oxidation of aromatics; thus the special and spatial organisation of these V-POM is of potential interest. It is possible that the mass transfer limitations of the reactants/products throughout these crystals have been improved.

The partial oxidations of naphtalene, bromobenzene, and tetralin were also performed with the different POM (Table 1). The well-organised V_2 POM was the more active (even more than the V_3) in the synthesis of α- and β-naphtols and bromophenol. Furthermore, a high yield toward tetralon was observed (34%) together with a 91% selectivity toward the desired β-tetralon could be obtained over this “smart material”. Hence, the activity of this crystalline V_2 POM remains higher than its V_2 analogous prepared under hydrothermal conditions (34% vs 21%).

Fig. 7 presents the conversion of 2 MN and the selectivity in vitamin K3 after 24 h. Whereas the 2 MN conversion was similar among all POM, the more efficient catalyst was again $H_5PV_2Mo_{10}O_{40}$ crystalline material. This further confirms the importance of having an appropriate tertiary structure of POM in catalysis. We have therefore tried to enhance the yield toward K3 vitamin while enhancing the ratio catalyst/2 MN reactant by a factor of 4. The last histogram presents the high 2 MN conversion together with a high selectivity, leading to a yield of 50% in K3 vitamin.

3.3. Catalyst stability: do POM behave has a Trojan horse?

One question frequently arises in systems containing H_2O_2: does any leaching of metal from the catalyst to the solution take place? Therefore, we have investigated the question following the

Table 1
Yields toward the different oxidized aromatic compounds

$H_{3+x}PV_xMo_{12-x}O_{40}$	Phenol	Naphtols	Bromophenol	Tetralon
$H_4PV_1Mo_{11}O_{40}$ classical synthesis	8.2	1.5	5.4	–
$H_4PV_1Mo_{11}O_{40}$ hydrothermal	12.6	3.7	–	–
$H_5PV_2Mo_{10}O_{40}$ hydrothermal	18.5	–	–	21.2
$H_5PV_2Mo_{10}O_{40}$ crystals	24.4	5.1	6.2	34.0
$H_6PV_3Mo_9O_{40}$ classical	17.9	3.6		42.8

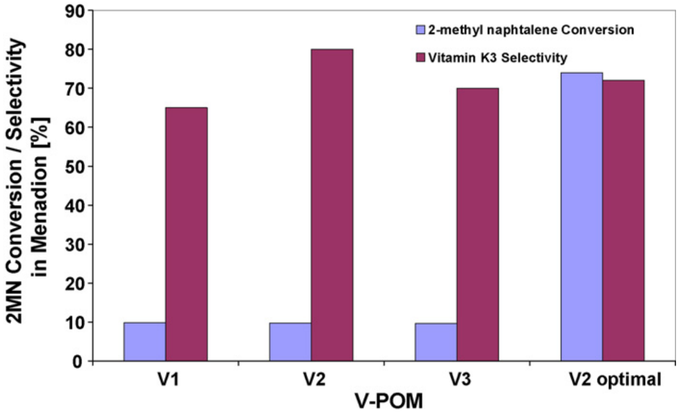


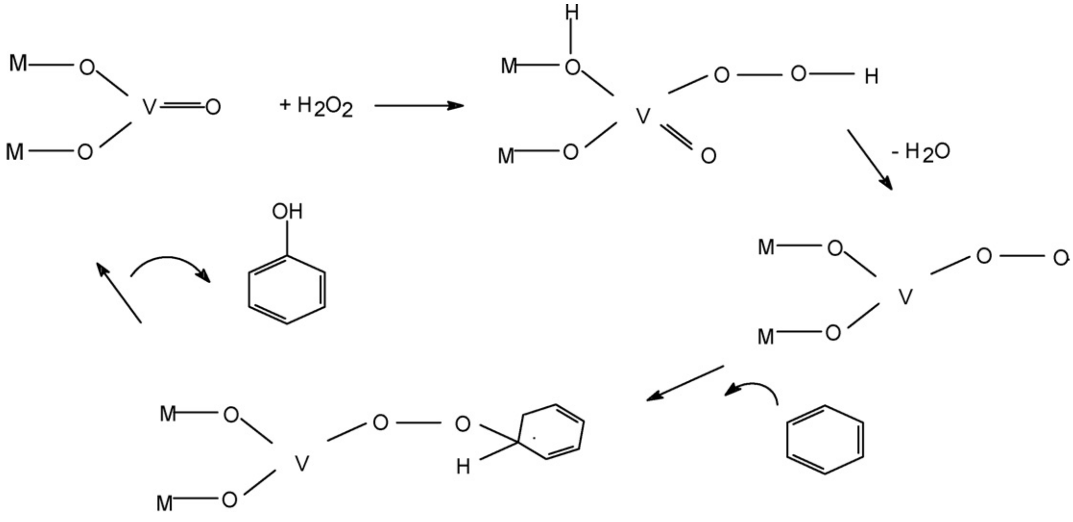
Fig. 7. Degrees of 2 MN conversion and selectivity in K3 vitamin as a function of the V-content in POM.

outstanding contributions from Sheldon [30,31]. He compared the continuous release of active species from a heterogeneous catalyst as a Trojan horse [31], thus raising the true heterogeneous behaviour of catalysts in liquid-phase oxidations. We have performed recycling experiments of tetralin oxidation into mainly β-tetralon with $H_4PVMo_{11}O_{40}$ and $H_5PV_2Mo_{10}O_{40}$ materials prepared by the classical procedure [18]. It appears that no significant loss of activity could be observed for the V_1 polyoxometalate, thus indicating its potential reusability. The tetralin conversion decreased from 21 to 14% during the second run with the V_2 material, thus raising the question of leaching. While a recycling experiment without a significant loss of activity is not a sufficient proof of heterogeneity ($H_4PVMo_{11}O_{40}$), a loss in activity does not necessary imply a leaching of active species (case of $H_5PV_2Mo_{10}O_{40}$). To answer this question, we have collected *at the reaction temperature* (to avoid an eventual soluble vanadium to be re-adsorbed upon cooling) the V_2 catalyst, after 150 min (15% tetralin conversion) and allowed the filtrate to react further. Hopefully, we found that after hot filtration the mother liquor did not react further. Therefore, we are able to conclude that even if part of the metal leaches, it does not produce an active homogeneous catalyst, and hence the reaction is truly heterogeneous. Whereas, V_1 and to some extent V_2 Keggin compounds behave similarly, a drastic decrease was observed with V_3 POM, probably due to Keggin structure decomposition as already observed by Nomiya et al. [27]. The relative stability toward leaching can also be explained by the large size of "organised" POM crystals as reported by Lempers for chromium species [31]. Indeed the amount of Cr leached was decreased from 34% to less than 0.5% while increasing the particle size from 5 to 75 μm [32].

3.4. Reaction mechanism

In these systems, the reaction may be promoted by the generation of peroxo species. A possible reaction mechanism similar to the one proposed by Mimoun et al. [33] for biomimetic V-peroxo complexes is proposed in Scheme 1. Oxygen transfer from the peroxo species to the aromatic ring may occur in a bimolecular fashion, and the hydroxylation of benzene will then take place by homolytic addition of the electrophilic radical species to the aromatic ring. As a test for the validation of this statement, the isotope effect k_H/k_D was determined from the competitive hydroxylation of benzene and benzene-d_6 (99.5%, Fluka) by $H_6PV_3Mo_9O_{40}$ in acetonitrile. The ratio of the yields of C_6H_5OH and C_6D_5OD was found to be 1 ± 0.1, indicating that C–H bond cleavage is not the rate-determining step of the reaction. Moreover, the only product detected by GC–MS was C_6D_5OD. This implies that an acid-catalysed mechanism via the $[^+OH_2OH]$ intermediate as reported by Olah and Onishi for liquid superacids [34], can be excluded for these catalysts. Indeed, C_6D_5OH could not be detected, indicating that H_2O_2 was not acting as an electrophile (which transfers OH^+ to the substrate) but rather as an oxidant (O-donor). Misono an Okahura had claimed that some heteropolyacids were solid superacids [2], however, the present results demonstrate that in our case these acidic functions were not used. Our experiments also support a mechanism involving a $[VOO]^*$ peroxo species generated by H_2O_2 decomposition. Vanadium peroxo complexes which are cleaved homolytically generating reactive electrophilic species behave differently from similar complexes of molybdenum known to be effective reactants for epoxidation of olefins. This could be the reason for the lower efficiency of the $H_3PMo_{12}O_{40}/H_2O_2$ system for this reaction. Kuznetsova et al. [28] reported that Fe^{3+}-substituted POM also effectively catalysed the oxidation of benzene to phenol with H_2O_2 in acetonitrile at 70 °C.

One striking feature of this study will be the immobilisation of Keggin structures either in mesoporous materials [35] or zeolites, or via coating on siliceous supports; our strong know in the preparation of such structured catalytic beds will help us to build perfectly tailored HPA/support couples at the reactor scale [20,36–38].



Scheme 1. Reaction mechanism involving V-peroxo species.

The finality of this work will be the smart combination of a multi-scale design of POM, ranging from tailored molecular composition [39,40], appropriate tertiary structure assembly and microscopic shape, together with a suitable reactor design.

Ship-in-a-bottle catalysis is a versatile way to increase the specific surface area of the HPA and to add shape-selective properties. Hence, such systems are able to mimic the behavior of natural enzymes [41].

4. Conclusion

One of the striking features of V-substituted heteropoly compounds in the partial oxidation of aromatics is their ability to transfer a single O-atom to the substrate under mild conditions. The catalytic performance of these POM, acting in a bulk-like manner [2,3], can be seriously improved while tailoring their primary (number of V-atoms in the Keggin unit), secondary, but also the tertiary structure. Hence, this study reports for the first time the microscopic arrangement of POM into organised and oriented 3D crystalline structure.

These V-containing materials appear to be versatile catalysts in liquid-phase oxidations of aromatic substrates, since their activity could be (at least partially) maintained after a second run. Moreover, the occurrence of homogeneous catalysis has been excluded; therefore, a true and active heterogeneous catalyst has been prepared.

The challenge will be a success in combining macroscopic, microscopic and molecular design for appropriate applications.

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References

[1] I.V. Kozhevnikov, Catal. Rev. Sci. Eng. 37 (1995) 311–352.
[2] M. Misono, T. Okahura, Solid superacid catalysts, Chem. Technol. (1993) 23–29.
[3] K.Y. Lee, M. Misono, “Heteropoly Compounds.”, in: Handbook Of Heterogeneous Catalysis 1 (1997) pp. 118–131.
[4] A. Corma, Chem. Rev. 95 (1995) 559–614.
[5] G.A. Olah, B. Török, T. Shamma, M. Török, G.K.S. Prakash, Catal. Lett. 42 (1996) 5–13.
[6] K. Na, T. Okuhara, M. Misono, Chem. Lett. (1993) 1141.
[7] G.A. Olah, G.K.S. Prakash, J. Sommer, Superacids, Wiley, New York, NY, 1985.
[8] Y. Izumi, K. Urabe, M. Onaka, Zeolite, Clay, and Heteropolyacid in Organic Reactions, VCH, Tokyo, Weinheim, 1992.
[9] R.A. Sheldon, Chem. Technol. (1991) 566–577.
[10] K. Nomiya, Y. Nemoto, T. Hasegawa, S. Matsuoka, J. Mol. Catal. A 152 (2000) 55–68.
[11] R. Neumann, M. de la Vega, J. Mol. Catal. 84 (1993) 93–108.
[12] K.I. Matveev, V.F. Odyakov, E.G. Zhizhina, J. Mol. Catal. A 114 (1996) 151–160.
[13] K. Nomiya, K. Hashino, Y. Nemoto, M. Watanabe, J. Mol. Catal. A 176 (2001) 79–86.
[14] C.L. Hill, C.M. Prosser-McCartha, Coord. Chem. Rev. 143 (1995) 407–455.
[15] R. Neumann, A.M. Khenkin, M. Dahan, Angew. Chem. Int. Ed. Engl. 34 (1995) 1587.
[16] R. Neumann, M. Lissel, J. Org. Chem. 54 (1989) 4607.
[17] R. Neumann, M. Levin, J. Am. Chem. Soc. 114 (1992) 7278.
[18] G.A. Tsigdinos, C.J. Hallada, Inorg. Chem. 7 (1968) 437–441.
[19] F. Kern, S. Ruf, G. Emig, Appl. Catal. A 150 (1997) 143–151.
[20] J.A. Dias, J.P. Osegovic, R.S. Drago, J. Catal. 183 (1999) 83–90.
[21] a) J.B. Moffat, J.B. McMonagle, D. Taylor, Solid State Ionics 26 (1988) 101–108; b) I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171–198.
[22] B. Louis, I. Yuranov, B. Viswanathan, A. Renken, Indian J. Chem. A 40 (2001) 837–840.
[23] S. Ivanova, B. Louis, M.J. Ledoux, C. Pham-Huu, J. Am. Chem. Soc. 129 (2007) 3383–3391.
[24] J.B. Moffat, J. Mol. Catal. 26 (1984) 385–396.
[25] M.T. Pope, Polyoxoanions: synthesis and structure, in: J. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, Pergamon Press, Oxford, 2004, pp. 635–678.
[26] N.A. Alekar, V. Indira, S.B. Halligudi, D. Srinivas, S. Gopinathan, C. Gopinathan, J. Mol. Catal. A 164 (2000) 181–189.
[27] K. Nomiya, H. Yanagibayashi, C. Nozaki, K. Kondoh, E. Hiramatsu, Y. Shimizu, J. Mol. Catal. A 114 (1996) 181–190.
[28] N.I. Kuznetsova, L.I. Kuznetsova, V.A. Likholobov, J. Mol. Catal. A 108 (1996) 135–143.
[29] K. Nomiya, K. Yagishita, Y. Nemoto, T. Kamataki, J. Mol. Catal. A 126 (1997) 43–53.
[30] I.W.C.E. Arends, R.A. Sheldon, Appl. Catal. A 212 (2001) 175–187.
[31] R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U. Schuchardt, Acc. Chem. Res. 31 (1998) 485–493.
[32] H.E.B. Lempers, R.A. Sheldon, J. Catal. 175 (1998) 62–69.
[33] H. Mimoun, L. Saussine, E. Daire, M. Postel, J. Fischer, R. Weiss, J. Am. Chem. Soc. 105 (1983) 3101–3110.
[34] G.A. Olah, R. Ohnishi, J. Org. Chem. 43 (1978) 865–867.
[35] L.C. Passoni, F.J. Luna, M. Wallau, R. Buffon, U. Schuchardt, J. Mol. Catal. A 134 (1998) 229–235.
[36] S. Ivanova, B. Louis, B. Madani, J.P. Tessonnier, M.J. Ledoux, C. Pham-Huu, J. Phys. Chem. C 111 (2007) 4368–4374.
[37] P.M. Esteves, B. Louis, J. Phys. Chem. B 110 (2006) 16793–16800.
[38] B. Louis, C. Subrahmanyam, L. Kiwi-Minsker, B. Viswanathan, P.A. Buffat, A. Renken, Catal. Commun. 3 (2002) 159–163.
[39] T.J. Barton, L.M. Bull, W.G. Klemperer, D.A. Loy, B. McEnaney, M. Misono, P.A. Monson, G. Pez, G.W. Scherer, J.C. Vartuli, O.M. Yogui, Chem. Mater. 11 (1999) 2633–2656.
[40] J.M. Thomas, R. Raja, Top. Catal. 40 (2006) 3–17.
[41] H. Márquez Alvarez, L.F. Brum Malta, M.H. Herbst, A. Horn, O.A.C. Antunes, Appl. Catal. A 326 (2007) 82–88.