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VAPO as catalyst for liquid phase oxidation reactions Part I: preparation, characterisation and catalytic performance

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Abstract

The preparation, characterisation and catalytic properties of vanadium containing alumino-phosphate molecular sieves (type AEL and AFI) are described in this paper. The molecular sieves were prepared by post-synthesis treatment and hydrothermal procedures. Several parameters were varied: nature of the template, crystallisation procedure and vanadium content. Tri-propylamine appeared to be the best template for the preparation of VAPO-5: highly crystalline, homogeneous batches (crystallite size: $2 \times 1 \times 1$ µm) with a maximum of about 2 wt% vanadium could be obtained in high yield (75–80%). Crystallographically pure VAPO-11 with a maximum of only 0.5 wt% of vanadium could be prepared. In VAPO the incorporation mode of vanadium gradually changes from tetra- to penta-coordinated when the amount of vanadium is increased. However the formation of vanadium pentoxide could not be detected. The vanadium containing molecular sieves were used as catalyst for the oxidation of allylic and secondary alcohols by tert-butyl hydroperoxide in the liquid phase. Compared with a homogeneous catalyst, bis(2,4-pentandionato)-oxovanadium(IV) (VO(a-cac)$_2$), the activity of vanadium containing molecular sieves is a factor 3–100 times lower. The activity of VAPO becomes higher when the vanadium content is increased. The decomposition rate of the peroxide is influenced by the pore structure, whereas no other effects on the selectivity are found.

Keywords: VAPO-5; VAPO-11; Synthesis; Molecular sieve; Oxidation catalysis

1. Introduction

Titanium silicalite 1 (TS-1) has shown to be a fascinating catalyst for the selective oxidation of small molecules like phenol and octene with hydrogen

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peroxide in the liquid phase [1]. The high selectivity observed, on the oxidant as well as on the substrate, can be attributed to the presence of isolated titanium sites in a shape selective, inorganic environment. However, due to the small pore diameter (approximately 0.52×0.55 nm) only small substrates can be oxidised and only hydrogen peroxide can be used as oxidant. Encouraged by the successful application of TS-1 and the hope that TS-1 should be the tip of the iceberg many chemists have been inspired to modify different types of molecular sieves in order to oxidise large sized substrates. Several approaches have been used. One approach is directed to the preparation of large pore titanosilicate based sieves like Ti-β [2] and Ti-MCM-41 [3]. Another approach comprises the preparation of compositional variants like metal substituted alumino-phosphates (MeAPO) with additional new framework topologies. Whereas other metal ions excluding titanium can be hardly incorporated into silica based sieves, the alumino-phosphate molecular sieves are more tolerant to metal ions like manganese, vanadium, cobalt and chromium [4], which may considerably expand the range of catalytic applications.

From literature various catalytically interesting wide-pore vanadium containing alumino-phosphates are known, prepared by hydrothermal or post-synthetic methods. The vanadium containing sieves possessing the AFI-structure (uni-dimensional 12-membered pores: 0.73×0.73 nm (Fig. 1)) are the most well studied, for example VAPO-5, VAPSO-5 (contains vanadium together with silicon) and V-AlPO$_4$-5 (alumino-phosphate supported vanadium oxide) [5–19]. Some attention has been paid to the preparation of VAPO-11, VAPSO-11 (AEL-structure; uni-dimensional pores: 0.63×0.39 nm (Fig. 1)) [5,20] and VAPO-31 (ATO-structure; distorted uni-dimensional pores: 0.54×0.54 nm) [21]. The VAPOs were characterised by using various methods. VAPO has been used as catalyst for liquid phase oxidation reactions: reported are the epoxidation of alkenes and allylic alcohols [12], alkylaromatics [12,13], phenol [12,13] and aniline [18] employing tert-butylhydroperoxide (TBHP) or hydrogen peroxide as oxidant.

In order to obtain a potential good molecular sieve catalyst for reactions in the liquid phase some requirements have to be met as demonstrated by the catalytic differences observed for various TS-1 samples [22]. An important property from a catalytic point of view is the development of a reproducible preparation method which gives the desired material in high yield. To minimise pore diffusion
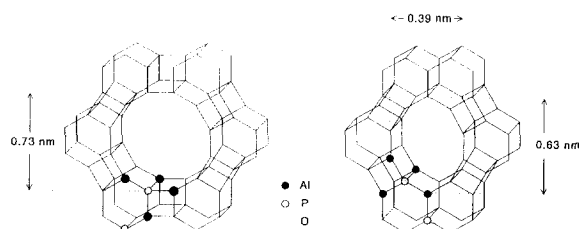

Fig. 1. Framework topology of AlPO$_4$-5(left) and AlPO$_4$-11(right).

limitations the material should be well defined, possessing a fully accessible microporous structure and consisting of small crystallites (preferably about 1 µm). Moreover, free vanadium pentoxide formation is not acceptable because it may disturb the desired catalytic reaction and there is a risk of leaching. Literature methods were adapted to prepare VAPO-5 and VAPO-11.

Vanadium containing alumino-phosphates (as well as framework substituted and framework attached vanadium ions) are subject of study in this and the next paper. While this part of the work deals mainly with the preparation, physical properties and comparison of the catalytic activity of various systems, the other deals with the stability of the material. The VAPOs were characterised by several techniques: X-ray diffraction (XRD), scanning electron microscopy (SEM), elemental analysis (AAS (V, Al); colorimetric (P)), sorption methods (*n*-butane) and diffuse reflectance UV-Visible spectroscopy (DRUVVIS). The VAPOs were used as catalyst for the oxidation of allylic alcohols and secondary alcohols with TBHP. The catalytic performance of the vanadium containing molecular sieve was compared to that of a homogeneous catalyst, bis(2,4-pentandionato)-vanadium(IV) ($VO(acac)_2$).

2. Experimental

2.1. Preparation of VAPO-5 (an example: S-E4)

In 40 ml (2.2 mol) of water 1.80 g (0.00711 mol V) of hydrated oxovanadium(IV) sulphate (obtained from Merck, Darmstadt, Germany, 99%) was dissolved. This solution was added to a solution of 27.0 g (0.234 mol P) of ortho-phosphoric acid (Riedel-de Haen, Hannover, Germany, 85%) in 40 ml (2.2 mol) of water. Then, under stirring 15.5 g (0.228 mol Al) of pseudo-boehmite (Condea, Hamburg, Germany, 75%) was added within 10 min. The suspension was vigorously mixed for 60 min at room temperature. To the viscous gel slowly and under stirring 15.0 g (0.148 mol) of triethylamine (Janssen, Geel, Belgium, 98%) was added. The resulting mixture was again vigorously stirred for 30 min. Then the gel was transferred into a teflon lined stainless steel static autoclave. The pH of the gel was determined before (pH ≈4–5) and after the crystallisation (pH ≈7). The gel was crystallised for 48 h at 170°C. The resulting product was recovered by centrifugation and washed with water. After drying at 80°C the sample was calcined in flowing air using the temperature program: 120°C, 1 h; heat up with 3°C min to 550°C; this plateau value was held for 4 h before the sample was slowly cooled down to room temperature. The sample was stored in a desiccator.

2.2. Preparation of VAPO-5 (an example: R-P10)

The preparation of this VAPO was comparable to that described for S-E4, except that tri-propylamine (Janssen, 98%) was used as template and the

crystallisation was performed in a Teflon lined stirred autoclave at 130°C and 30 rpm for 17 h.

2.3. Preparation of VAPO-11 (an example: S-D1)

In 40 ml (2.2 mol) of water 0.65 g (0.00257 mol) of hydrated oxovanadium(IV) sulphate (Merck, Darmstadt, Germany,99%) was dissolved and mixed up with a solution of 26.3 g (0.239 mol P) of ortho-phosphoric acid (Merck, Darmstadt, Germany,89%) in 40 ml of water (2.2 mol). Then 15.5 g (0.228 mol Al) of pseudo-boehmite (Condea, 75%) was added slowly under stirring. The suspension was stirred for 60 min at room temperature. After this ageing period 12.5 g (0.124 mol) of di-isopropylamine was added in 10 min. After stirring for another hour the gel was transferred to a static autoclave and crystallised at 200°C for 48 h. A similar work up procedure was used as described for the VAPO-5 synthesis.

2.4. Preparation of V-AlPO$_4$-5 (I-E0)

Vanadium oxide on AlPO$_4$-5 was prepared by reacting tri-methoxy-vanadium-oxide (VO(OMe)$_3$) with AlPO$_4$-5. Tri-methoxy-vanadiumoxide was prepared according to method followed by Funk [24]. Under argon atmosphere about 0.12 g of VO(OMe)$_3$ was dissolved in 25 ml of dry toluene. To the bright yellow solution 1.0 g of dry AlPO$_4$-5 was added. The solution turned orange. After 1 h the solid was removed from the reaction mixture by filtration. The crystallites were dried and calcined according to the standard procedure. The resulting product was bright yellow.

2.5. Characterisation of VAPO

2.5.1. XRD
Patterns were collected on a Philips PW 7200 X-ray powder diffractometer using a Cu-Kα source, with a scan speed of 1°/min. The diffractograms were corrected for baseline, background and K$_2\alpha$-elimination

2.5.2. Absorption
Pore volume measurements were carried out on a CAHN 2000 electro-balance using n-butane as sorbant. Approximately 15 mg of the sample was heated to 350°C in a stream of purified helium. After cooling down to room temperature the sample was exposed to n-butane.

2.5.3. SEM
Micrographs were taken using a Jeol JSM-840A Scanning Microscope. Operating conditions: 20–35 kV, $3.0 \cdot 10^{-11} - 1.0 \cdot 10^{-10}$ A, working distance 8 or 15 mm.

The samples were glued on a graphite block with a colloidal carbon paste and sputtered with gold.

2.5.4. Elemental analysis

Vanadium and aluminium were analyzed using a Perkin-Elmer PE 3030 Atomic Absorption Spectrophotometer. VAPO was dried for at least 1 h at 120°C before dissolving under heating in 10 ml of diluted sulphuric acid. Phosphorus was analyzed photometrically as molybdeneblue complex.

2.5.5. DRUVVIS

A Hitachi 150–20 spectrophotometer equipped with a diffuse reflectance unit was used. A well dried sample, often diluted with optical white $AlPO_4$-11, was ground in a ball mill for 45 min. Before being quickly transferred to the cell the sample was dried at 200°C and cooled down in a desiccator. After recording the spectrum and baseline correction the spectrum was converted to Kubelka–Munk units (f(R∞)). A dilution series of VAPO-5, prepared as described above, showed a linear relation between the dilution factor and the absorption intensity (f (R∞) <0.7).

2.5.6. ESR

The spectra were recorded on a Bruker ER 200D SRC spectrometer, operating with an X-band standard cavity and interfaced to a Bruker Aspect 3000 data system. The temperature was controlled by a Bruker ER 4111 variable temperature unit between 100–120 K.

2.6. Catalytic reactions

2.6.1. General procedure

A water-free stock solution of the substrate (0.45 M) and standard (0.05 M) in acetonitrile (Janssen, 99%) was prepared and stored on molsieves 3A. Substrates tested were 3-phenyl-2-propen-1-ol (Aldrich, Steinheim, Germany, 98%), 2-cyclohexen-1-ol (Aldrich, Steinheim, Germany, 95+%), 2-octanol (Janssen, 99%), 3-octanol (Janssen, 99+%) and cyclo-octanol (Janssen, 99%). Standards used were aceto-phenone (Janssen, 99%) and 3-hexanone (Janssen, 98%). A TBHP solution (1.4 M) was prepared by dissolving 15 ml of TBHP (Aldrich, Steinheim, Germany, 70% in water) in 70 ml of acetonitrile. The solution was made water-free by drying on calcium sulphate. After filtration the solution was stored on molsieves 3A. In a similar way a 0.9 M solution was prepared. Reactions were carried out under stirring in a thermostated glass reactor equipped with condenser and sampling port. Typically, 10 ml of a stock solution of substrate and 5 ml of the TBHP solution were combined before heating to the appropriate reaction temperature. Finally a well dried VAPO (at 150°C, overnight) was added to the reaction mixture. During the course of the reaction samples were taken and filtered

using 0.45 μm brown-rim filters (Schleicher and Schuell, Dassel, Germany). Part of the sample was used to analyze the peroxide content by iodometric titration, while another part was used for GC–analysis (Carlo Erba GC 6000 Vega series 2 equipped with autosampler and DB-1 column (J and W Scientific, Folsom, CA, USA)). Peroxides were destroyed before analysis by adding a tri-phenylphosphine solution to the samples. Reaction products of the substrates were identified by GC–MS. The concentration was determined by constructing calibration curves of the compounds. These compounds were purchased from commercial suppliers or prepared according to literature methods.

3. Results and discussion

3.1. The preparation of VAPO

The general gel composition used for the preparation of VAPO-5 is 1-x Al_2O_3 : 1.01 P_2O_5 : x V_2O_5 : 1.3 Template : y H_2O (x =0– 0.07; y =42 (static synthesis); y =35 (stirred synthesis); Template: triethylamine or tri-propylamine). For the preparation of VAPO-11 the following gel composition is used 1-x Al_2O_3 : 1.01 P_2O_5 : 1-x V_2O_5 : 1.0 iPr_2NH : 42 H_2O (x =0–0.07). Pseudo-boehmite and ortho-phosphoric acid are applied as aluminium- and phosphorous source, respectively. The use of oxovanadium(IV) sulphate [10,12,16] as vanadium source is preferred above vanadium pentoxide [5–11,13–15] to minimise the presence of vanadium clusters in the gel. Tri-ethylamine [10,15–17] and tri-propylamine [6,7,9,10,13] are commonly used as template for the preparation of VAPO-5, while di-isopropylamine is used for the preparation of VAPO-11 [5]. The gels are crystallised in static and stirred autoclaves. After work-up the products are calcined in air.

The main results of the preparations are described in Table 1. Clearly the type of template has an influence on the properties of the final product. Not only parameters like the final vanadium content and the structure type but also the yield and reproducibility of the preparation are determined by the template. Concerning the latter aspects the synthesis of VAPO-5 employing tri-propylamine as template is better. Yields are between 75–80% (based on the product without template). The preparation method is reproducible (S-P3 and S-P4). The product yield is only 30–35% when tri-ethylamine is used as template. Yields of VAPO-5 are much higher than values reported by Blasco et al. [16]. The VAPO-11 synthesis, employing di-isopropylamine, is efficient (better than 80% yield).

XRD gives the first indications of the quality of the sample. All prepared samples show essentially the same XRD pattern, independent of the preparation method of the VAPO-5 (Fig. 2). Additional phases other than AFI can be observed, with gels containing more than 3.5 at% vanadium (x >0.07). Also a ratio Al / P >1 in the gel does not yield a pure AFI product. The preparation of VAPO-11 is much more

influenced by the vanadium content of the gel. When high amounts of vanadium (x >0.02) are present in the gel no pure AEL can be obtained but additional crystalline phase(s) is (are) formed (Fig. 3). Variation of the crystallisation conditions (temperature (150–200°C), amount of template (0.5 T–1.5 T in gel formula) and aluminium source (aluminium-tri-isopropoxide instead of pseudo-boehmite) did not give a pure AEL phase.

Pore volume measurements show that all samples have a well developed micropore structure. The theoretical amount of n-butane that can be sorbed into a well defined $AlPO_4$-5 is about 0.130 ml g and for $AlPO_4$-11 0.10 ml g [23]. Practically, the pore volumes of all prepared samples fall within 70% of this value. Samples with a high amount of vanadium (>1.5 wt%) possess a lower micropore volume. This possibly indicates that these samples have more structural defects.

Fig. 4 shows some typical morphologies observed for the different preparation methods of VAPO-5. The main difference of morphology is found between the use of a static and a stirred autoclave. No clear influence of the template is found. The morphologies are reproducible. The batches obtained from a stirred autoclave are rather homogeneous with a crystallite size of about 1 μm. However, studying the samples at larger magnifications indicate that some crystallites are aggregated. The products obtained from a static autoclave may be best described as spherical particles of about 10–30 μm, sometimes stuck together. A closer observation reveals that the particles also consist of agglomerated crystallites. The size of these crystallites is comparable to those obtained from a stirred synthesis. Hysteresis of the di-nitrogen absorption isotherms show that the agglomerates are not massive. VAPO-11 shows a different morphology. The crystallites are generally small (less than 1 μm) but the batches are rather inhomogeneous. Moreover, also an amorphous phase can be observed.

In Table 1 the product composition (at%) is also mentioned. The composition was recalculated from the individual elemental analysis of the elements phosphorus, aluminium and vanadium obtained as wt%. The oxygen content is not included in this calculation. The sum of the elemental analyzes was never 100% but typically 95%. This systematic error can be due to the rapid sorption of water during the sample preparation. All products show a slight enrichment of the aluminium content.

The elemental analysis often has been used to obtain information about the incorporation mode [9,10,12]. However, by using the best available techniques, the maximum accuracy for a single element analysis is about 1%. This means that it is difficult to draw a conclusion from elemental analysis, when the guest ion is present at levels of about 1 wt%. The data from Table 1 suggest the presence of a small amount of aluminium-oxide impurity or incorporation of vanadium on a phosphorous position, which is in contrast to the results obtained by Montes et al. and Rigutto et al. [9,12].

While using the recipe employing tri-proylamine as template vanadium is efficiently retained in the final product up to high vanadium contents (1.5 wt%

Table 1

Charecterisation of various vanadium containing aluminophosphates

Code	Vgel[a] (at%)	Product Composition (at%)			V prod (%wt)	PV(ml g) n-butane	SEM morphology
		Al	P	V			
S-E1	0.42	50.60	49.20	0.18	0.15	0.090	dense agglomerates;20 μm
S-E4	1.52	49.50	49.40	1.16	0.91	0.109	dense agglomerates;15 μm
S-E6	2.55	50.20	48.60	1.18	0.93	0.116	dense agglomerates;15×10×8 μm
R-E8	2.03	49.90	49.10	1.00	0.99	0.113	hexagonal plates; 3×2×0.04 μm
S-PO	0.44	50.80	48.70	0.43	0.35	0.096	dense agglomerates;20–50 μm
S-P2	1.67	51.00	47.60	1.42	1.15	0.090	dense agglomerates;10–30 μm
S-P3	2.00	50.70	47.50	1.79	1.49	0.103	dense agglomerates;25 μm
S-P4	2.00	50.60	47.60	1.78	1.48	0.098	dense agglomerates; 30 μm
S-P8	3.45	49.40	48.20	2.45	2.10	0.081	dense agglomerates;15 μm
R-P10	2.03	51.30	47.00	1.75	1.43	0.100	bundle of fine rods;2×1×1 μm
S-D1	0.55	50.80	48.80	0.38	0.32	0.076	undefined and blocks
S-D2	1.17	50.70	48.60	0.76	0.63	0.066	blocks 1.0×0.04×0.4 μ m
I-EO	0	48.50	47.50	4.00	3.20	0.058 (0.096)[b]	agglomerates (10 μ m)loose crystallites

[a] Oxygen not included in the calculation.

[b] Pore volume of I-EO determined before reaction with VO(OMe)$_3$.

Codes: crystallisation: S=static autoclave, R=stirred autoclave.

Template: VAPO-5: E=triethylamine, P=tripropylamine; VAPO-11: D=diisopropylamine; I=post-synthesis treated AlPO$_4$.

vanadium). The efficiency $V_{product}$ / V_{gel} is almost 100%. At higher vanadium contents in the gel the efficiency decreases. Efficiencies reported for vanadium pentoxide as vanadium source are generally less than 50% [7,16]. Triethylamine influences the vanadium incorporation negatively. When tri-propylamine is employed VAPOs with more than 2.0 wt% vanadium can be prepared, while only 1.0 wt% of vanadium can be incorporated using triethylamine. Chemically, triethylamine and tri-propylamine molecules differ only in size, other properties like pK and polarity are at least comparable. It has been proposed that vanadium is incorporated on lattice defect positions [16,19]. A possible explanation for the difference between the use of different templates could be the formation of more defect sites in the alumino-phosphate lattice when tri-propylamine is used as template. From the work reported earlier it appeared that the presence of oxo-vanadium(IV) ions is not favorable for the crystallisation of alumino-phosphates [17]. The formation of the AFI structure is relatively little disturbed by the presence of the oxo-vanadium(IV) ions. The preparation of VAPO-11 is much more influenced: crystallographically pure VAPO-11 can only be obtained with low vanadium contents. A strong influence of the oxo-vanadium(IV) ions has also been found in the preparation of VAPO-44, which did not succeed [19]. On the contrary, employing the same recipe without oxo-vanadium(IV) ions present, AlPO$_4$-44 can be prepared.
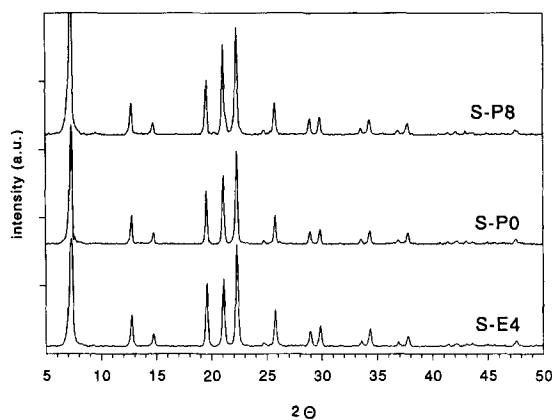
Fig. 2. X-ray diffractograms of VAPO-5:S-E4(0.91 wt% V); S-PO(0.35 wt% V) and S-P8(2.1 wt% V).
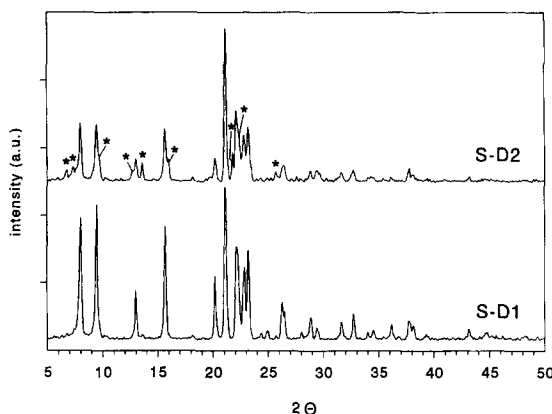

Fig. 3. X-ray diffractograms of VAPO-11:S-D1(0.32 wt% V) and S-D2(0.63 wt% V). Asteriks indicate the presence of impurities.

3.2. The vanadium site

The electronic absorption spectrum provides information about the V(V)-ion in a calcined VAPO. By employing this technique regions of four, five and six coordinated vanadium ions can be identified [25]. Often, the occurrence of five and six coordinated species is related to the formation of oligomeric or polymeric species. Calcined VAPO samples with a low vanadium content are white. These VAPOs show an absorption maximum at 36000 cm^{-1} (280 nm)independent of the template employed (Fig. 5). This shows that the coordination geometry of the vanadium sites in VAPO-5 and VAPO-11 is tetrahedral [7,16]. When the vanadium content of the VAPO is increased the material becomes yellow. The colour change
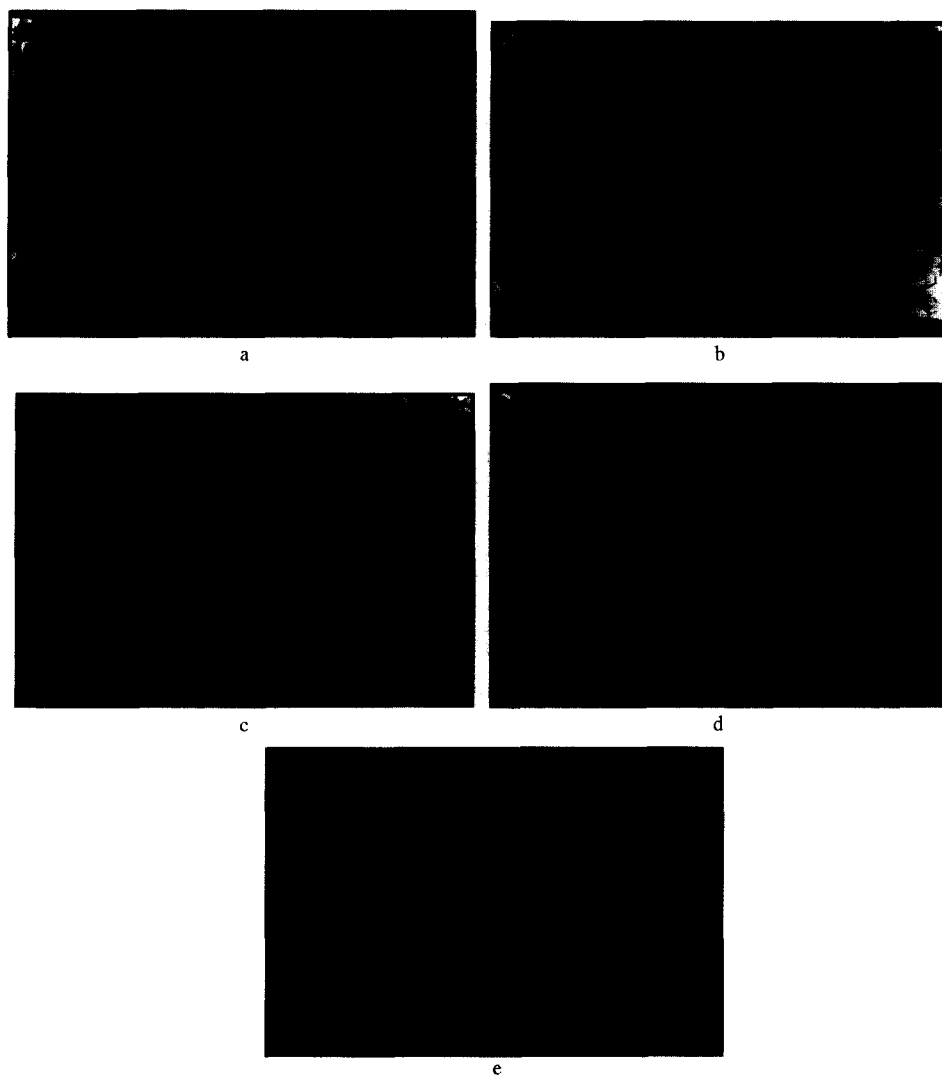
Fig. 4. SEM micrographs of various samples:VAPO-5: (a) S-P3:130; bar:100 μm; (b) S-P3:5000x; bar:1 μm; (c) R-P10:1400x; bar:1 μm and (d) R-P10:5000x; bar:1 μm; VAPO-11: (e) S-D1:8000x; bar:1 μm.

is reflected in the DRUVVIS spectra as an increasing absorption at 26000 cm^{-1} (Fig. 5). When the intensity of the spectra are normalised it can be seen that the shape of the spectra alters upon increasing the vanadium content of the VAPO, an indication for the formation of a different vanadium species which is most likely five coordinated (Fig. 6). When the amount of vanadium ions deposited on silica is increased similar changes are detected [25]. This change is even more pronounced in the spectrum of an $AlPO_4$-5 with a high vanadium content (3.20 wt%), prepared by sorption of tri-methoxy-vanadium(V) oxide followed by calcination. Vana-

dium(V) oxide physically mixed with $AlPO_4$-5 shows absorptions at 20500 cm^{-1} (shoulder), 24500 cm^{-1} and 36000 cm^{-1}, originating from a six, five and four co-ordinated species, respectively. Because a VAPO with the same vanadium content does not show the presence of five and six-coordinated species this proves that no vanadium pentoxide phase is present in VAPO (Fig. 6). Also spectra of VAPOs with a high vanadium content (2 wt%) bear no resemblance to the spectra of vanadium pentoxide mixed with $AlPO_4$-5. If all vanadium would be incorporated in a similar manner no change in the shape of the absorption curve would be expected upon increasing the vanadium content. Moreover, an abrupt change in the increase of the intensity would be expected when the maximum incorporation level of the vanadium ions is reached. Note that this situation is fundamentally different from a cobalt substituted alumino-phosphate (CoAPO) where the shape of the absorption curve between 14000–25000 cm^{-1} (400–700 nm) does not change upon increasing the cobalt content. The intensity of the absorption spectrum does increase linearly till about 3 wt% cobalt [25]. At higher amounts the intensity remains constant because no more cobalt can be tetrahedrally incorporated.

The detailed XRD spectra of S-P8 (2.1 wt% V) and I-E0 (3.20 wt% V) also show that no vanadium pentoxide phase is present in these materials (Fig. 7). Main peaks of vanadium pentoxide at 2θ =15.5°; 20.3°; 21.9° and 31.0° that can be clearly distinguished from the $AlPO_4$-5 peaks are not present in the diffractogram of VAPO-5. On the contrary, in the diffractograms of vanadium pentoxide physically mixed with $AlPO_4$-5 (2.1 and 7.5 wt% vanadium) the peaks of vanadium pentoxide can be easily identified. At least 1.0 wt% of vanadium pentoxide can be detected.

We suggest the following model for the vanadium site in a calcined VAPO. As deduced from DRUVVIS measurements all structural changes occur gradually. At low vanadium content (less than 1 wt% vanadium) mainly monomeric, (pseudo) octahedral vanadium(IV) species are formed (S1 and S2) [12,17], giving an ESR spectrum (not shown). During the calcination these species are oxidised to vanadium(V) and dehydrated, giving a tetrahedral species. Such species, when incorporated into the lattice, can only be present on a phosphorous(V) position and not on an aluminium(III) position because of the large charge deficiency. Charge excess or deficiency does not apply for species attached to the lattice and therefore the simultaneous presence of a tetrahedral oxovanadium(V) species (V=O), attached to a maximum of three hydroxyl functions cannot be excluded. DRUVVIS is not sensitive enough to discriminate between vanadium(V) and oxo-vanadium(V) species. When the vanadium content is increased five co-ordinated species also emerge, which may point to the additional presence of an oxovanadium(V) species on a aluminium position, which has been found by [51]V-NMR [12]. Five co-ordinated species might be also formed by coupling to another vanadium species (cluster). At high amounts of vanadium in the gel it is not unlikely that neighbouring aluminium(III) and phosphorous(V) are replaced by an ESR-silent, dimeric vanadium(IV) species. This is supported by the relatively low intensity of the ESR spectrum of a non-calcined VAPO-5 with a high vanadium content,
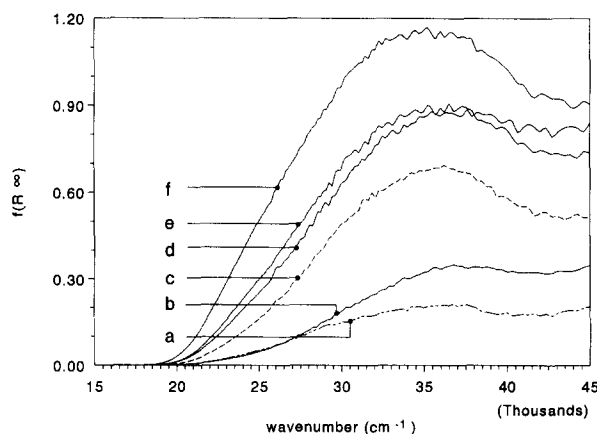
Fig. 5. Diffuse reflectance UV/Vis spectra of various VAPO samples prepared:VAPO-11 (a) S-D1(0.32 wt% V); VAPO-5: (b) S-PO(0.35 wt% V); (c) S-E4(0.91 wt% V); (d) R-P10(1.43 wt% V); (e) S-P3(1.49 wt% V) and (f) S-P8(2.10 wt% V). Samples with a f(R$_\alpha$)>0.7 were diluted. The absorption intensity is corrected by the dilution factor.
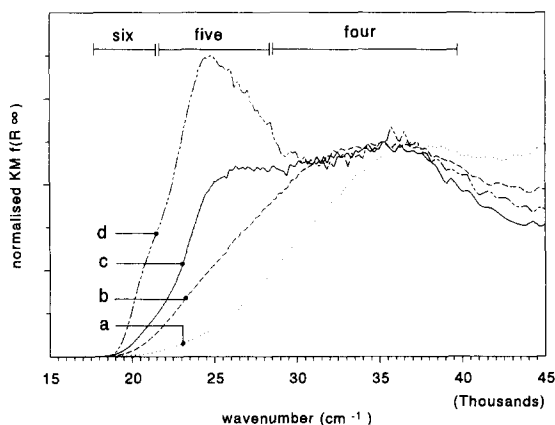

Fig. 6. Diffuse reflectance UV–Vis spectra of various vanadium containing aluminophosphates: a)S-PO(0.35 wt% V); b)S-P8(2.10 wt% V); c)I-EO(3.20 wt% V) and d)AlPO$_4$-5 physically mixed with V$_2$O$_5$ (0.36 wt% V). The spectra are normalised at 36000 cm^{-1}. Regions of six, five and four co-ordinated vanadium species are indicated.

compared with the intensity of the spectrum of a VAPO with low vanadium content (not shown). No pure VAPO can be obtained by hydrothermal synthesis, above 3.5 wt%, but impregnated VAPOs show that the formation of five co-ordinated species carries through. Possibly more interconnections between vanadium species are formed. However, at a level of 3.2 wt% vanadium, well defined vanadium pentoxide phase is still not formed. It is likely that the formation of different vanadium species has its origin in the preparation mixture. It is well known vanadium(IV) (the valency of the species present during preparation), as well as

vanadium(V), have a complicated chemistry in aqueous solution [26,27]. During the preparation the starting species, oxovanadium(IV), may be converted into a multinuclear species in a series of oxolation and olation reactions [27], and broke down again resulting in a (hydrated) vanadium(IV) species. These inter-conversions do occur mainly in a range pH 4–9, where the crystallisation takes places. This aggregation behavior is more pronounced at higher vanadium(IV) concentrations in solution. Some of these species are more likely to couple with framework species than others, for electrostatic reasons [26].

A note should be made about the possible location of the vanadium clusters. Given the pore size of AFI only small clusters can be accommodated. However, when these clusters are present inside the pores this should influence the pore volume dramatically but all VAPOs and even impregnated VAPO-5 (I-EO) have only a slightly lower absorption capacity. Thus, clusters are very small or located on the outer surface. By using Electron Dispersive X-ray analysis (EDX) no enrichment or irregularities in the distribution of vanadium on the crystallite could be detected. However, the nature of the sample (an irregular surface, inhomoge-
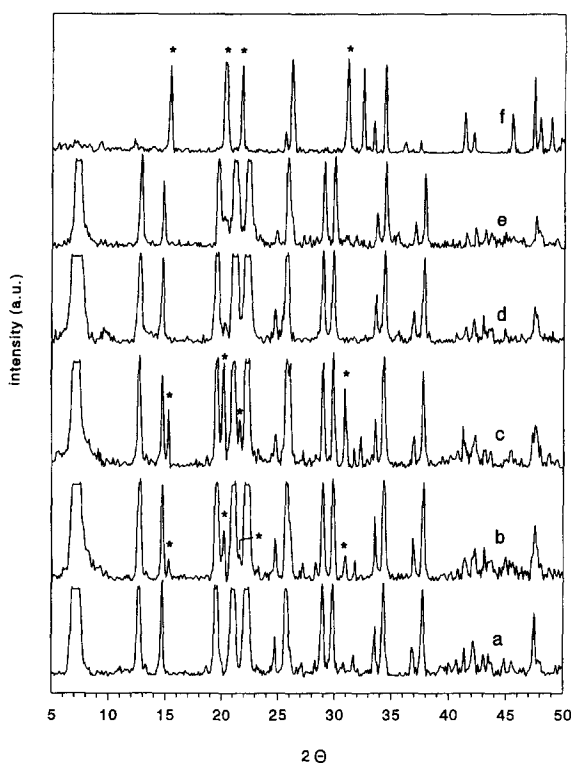

Fig. 7. Detailed X-ray diffractograms of various vanadium containing aluminophosphates: a) $AlPO_4$-5; b) $AlPO_4$-5 physically mixed with V_2O_5(2.1 wt% V); c) $AlPO_4$-5 physically mixed with V_2O_5 (7.5 wt% V); d)S-P_8(2.1 wt% V); e)I-EO(3.20 wt% V) and f)V_2O_5(56.0 wt% V). Stars indicate the peak positions of vanadium pentoxide.

neous (pore structure) and the low conductivity) seriously limits the reliability of the results obtained by this technique.

3.3. Reactions catalysed by VAPO

3.3.1. Oxidation of allylic alcohols

VAPO was used for the epoxidation of 3-phenyl-2-propen-1-ol and 2-cyclo-hexen-1-ol (Tables 2 and 3, see also Schemes 1 and 2). The first compound can be considered as a model for larger molecules with more than one reactive group, the latter molecule possesses a more reactive secondary alcohol function. Single component absorption experiments carried out analogue to those reported [28] showed that both allylic alcohols are easily absorbed into the pores of $AlPO_4$-5 and $AlPO_4$-11. This confirms that these molecules in principle have no steric restrictions to enter the micropores of VAPO-5 and VAPO-11. On reaction with TBHP two main products are observed: the alcohol epoxide and the allylic aldehyde/ketone. Surely VAPO shows a catalytic effect, but VAPO catalysed reactions are much slower than those catalysed by a homogeneous catalyst, bis(2,4-pentandio-nato)-oxovanadium(IV) compared on the same amount of vanadium present in the reactor. No significant differences were found between the VAPOs with a different pore geometry and a similar vanadium content. VAPO-5s prepared with triethylamine as template seem to be more active than VAPO-5s prepared with tripropylamine. Also reactions carried out in benzene are faster than in acetonitrile. I-P0 (a VAPO-5 prepared by post-synthesis treatment) shows comparable activity to the VAPO-5 although a fair comparison on similar vanadium content could not be made. Also, the higher the vanadium content of the VAPO-5 is, the more active and selective it will be. Contrary the reactions performed with the homogeneous catalyst the VAPO catalysed reactions are selective (90–100%) on the peroxide, indicating that non-productive peroxide decomposition does not take place. A note should be made about the colour of the reaction mixture. When a fresh VAPO-5 is contacted with a warm reaction mixture the colour of the VAPO-5 immediately changes to reddish-brown. During the reaction the colour fades slowly to yellow or white. When no more TBHP is present in solution the VAPO becomes green. A change of colour, however is not observed in case of VAPO-11. These observations are an indication that the vanadium sites present in VAPO-11 are different from those present in VAPO-5 which is not supported by characterisation studies. The red colour is also observed when a reaction is performed with $VO(acac)_2$. It was argued that the red colour is caused by a vanadium peroxide complex V(IV)-OOR [29]. An explanation that the colour change is not observed in case of VAPO-11 might be that the vanadium sites inside the pores of VAPO-11 are not accessible for reaction with TBHP. Nevertheless, VAPO-11 shows catalytic activity. Therefore there should be other active species present. Moreover, VAPO-5 still shows activity when the red colour has faded. In case of VAPO-5 the vanadium(V)-sites should be first reduced, which can be easily done with organic molecules at low temperatures.

3.3.2. Oxidation of alcohols

VAPO was used as catalyst for the oxidation of simple alcohols. Substrates studied were 2-, 3-octanol and cyclo-octanol (Scheme 1). Among the series of linear alcohols C6–C9 possessing a hydroxyl group on the 2-position, 2-octanol appeared to be the most active using TS-1 / H_2O_2 / acetone at 70°C [30]. All reactants are sorbed fast into $AlPO_4$-5 and $AlPO_4$-11. Although the dimensions of cyclo-octanol are comparable with the pore size of $AlPO_4$-11 single component sorption studies show that the maximum pore occupation at equilibrium is about 40%. Cyclo-octanol is sorbed almost quantitatively into the large pore $AlPO_4$-5. Tables 4–6 show the major results of the VAPO catalysed oxidation of the alcohols. The differences in activity between VAPO and $VO(acac)_2$ are much smaller than in the case of allylic alcohols. VAPO-11 is less active than a VAPO-5 with similar vanadium content. The selectivity towards the ketone is always high. Interestingly, the selectivity on TBHP is much higher in the case of VAPO-5 than VAPO-11. While S-D1 stays yellow during the reaction, S-P0 turns dark red. VAPO-5s with a higher vanadium content are more active.

From a preparative point of view a high yield of the desired product is important. However, the highest product yields obtained for the VAPO-5 catalysed reactions are 40–50%. Basically, the non-productive decomposition of the peroxide is the cause of the low absolute conversion of 3-octanol. Increasing the temperature resulted only in a lower selectivity based on the peroxide, without increasing the yield of 3-octanone. Therefore an experiment was performed where the total amount of peroxide was supplied in two portions. This two-step addition resulted in a lower reaction rate but not a higher overall yield. While in the second step the yield raised only a little, the peroxide was still decomposed at the same rate. Since

Table 2

The vanadium catalysed oxidation of 3-phenyl-2-propen-1-ol by TBHP

|	Catalyst (wt%V)	V_{total} (mmol)	TOF (mol/mol h)	t=100 min		
				Conv. sub (%)	Sel. prod. sub (%)	Sel. epox(%)
1	–	–	–	1	–	0
2	Vo(acac)$_2$ (19.2)	0.085	770	92	87	99
3	S-D$_1$(0.32)	0.076	7.80	26	82	85
4	S-PO(0.35)	0.090	7.20	25	74	81
5	S-PO(0.35)	0.087	38[a]	58	95	97
6	S-P3(1.48)	0.088	10	31	80	90
7	S-P8(2.05)	0.096	27	52	95	91
8	S-E4(0.91)	0.054	37	40	72	93
9	I-EO(3.20)	0.188	21	60	95	85

Conditions and experimental errors:

solvent: acetonitrile. [a] solvent: benzene.

t=50±1°C; [sub]/[TBHP]=1.05±0.08; [TBHP]/[V]≈38; conv: ±2%; sel: ±5%. TOFs are calculated at 30% conversion of the substrate.

Table 3
The vanadium catalysed oxidation of 2-cyclohexen-1-ol by TBHP

	Catalyst (wt%)	V_{total} (mmol)	TOF (mol/mol h)	$t=300$		
				Conv. sub (%)	Sel. Prod. sub (%)	Sel. epox(%)
10	–	–	–	14	55	0
11	VO(acac)$_2$(19.2)	0.085	132	80	87	65
12	S-D1(0.32)	0.079	2.7	22	75	55
13	S-P0(0.35)	0.086	3.7	21	65	48
14	S-P4(1.48)	0.080	6.3	43	84	68
15	S-P8(2.10)	0.083	9.6	49	93	76
16	S-E4(0.90)	0.053	9.8	32	70	59

Conditions and experimental errors: acetonitrile; $t=51\pm1°C$; [sub]=$0.29\pm0.01M$; [sub]/[TBHP]=1.16 ± 0.08; [TBHP]/[V]$\approx$38; conv:$\pm2\%$; sel:$\pm5\%$. TOFs are calculated at 20% conversion of the substrate. The TOFs are roughly corrected for the blank reaction.

Scheme 1. VAPO catalysed reactions described in this paper.
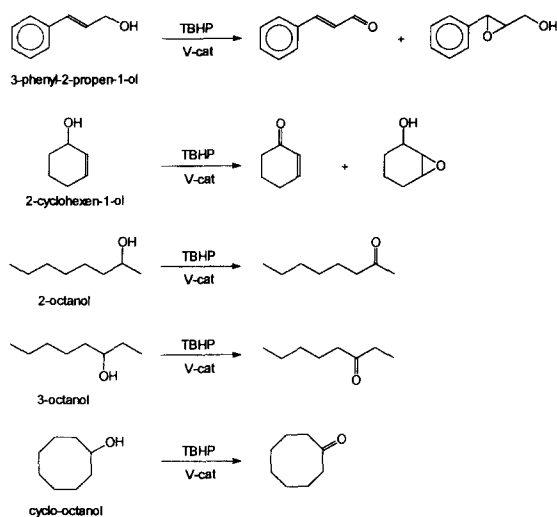
only a little octanol is converted in the second step it could mean that deactivation of the VAPO occurred.

A note should be made about the activity of VAPO compared to TS-1. On one hand, by using TS-1 and hydrogen peroxide as oxidant, 3-octanol was almost not reactive contrary to 2-octanol. On the other hand, VAPO catalysed oxidations with TBHP show no differences between these substrates. The low activity of TS-1 as catalyst for the oxidation of 3-octanol was explained in terms of sterical hindrance induced by the pore system. Apparently, the same argument cannot be used to explain the results obtained with VAPO.

$$\frac{S_0 - S_t}{S_0} \times 100\%$$: Conversion of the substrate (conv. sub.).

$$\frac{\sum_{i=1}^{n} P_{i,t}}{S_0 - S_t} \times 100\%$$: Selectivity of all indentified products on the total amount of products formed (sel. on sub.).

$$\frac{P_{i,t}}{\sum_{i=1}^{n} P_{i,t}} \times 100\%$$: Selectivity of one specific product on all identified products (for example: sel. epox.).

$$\frac{S_0 - S_t}{Ox_0 - Ox_t} \times 100\%$$: Selectivity on oxidant (sel. on ox.). The efficiency to convert a certain amount of substrate.

S_0 = amount of substrate on t=0 min.
S_t = amount of substrate on t=t min.
$P_{i,t}$ = amount of product formed on t=t min.
Ox_0 = amount of oxidant on t=o min.
Ox_t = amount of oxidant on t=t min.

Scheme 2. Definitions of various parameters.

Table 4
Vanadium catalysed oxidation of 3-octanol by TBHP

	Catalyst (wt%)	V_{total} (mmol)	TOF (mol/mol h)	t=400 min		
				Conv. sub (%)	Sel. prod. sub (%)	Sel. TBBHP(%)
17	–	–	–	5	100	–
18	VO(acac)$_2$(19.2)	0.088	18	46	85	35
19	S-D1(0.32)	0.106	0.8	12	100	100
20	S-D2(0.63)	0.105	1.4	17	100	100
21	S-P0(0.35)	0.125	2.4	31	90	35
22	S-P4(1.48)	0.117	2.8	40	90	40
23[a]	S-P4(1.48)	1)0.118	1.8	27	86	55
		2)0.118	≈1	48	95	45
24	S-P8(2.10)	0.128	6.5	43	85	45
25	R-P10(1.43)	0.114	2.7	30	100	45

Conditions and experimental errors: acetonitrile; t=71±1°C; [sub]=0.30±0.01 M(4.5 mmol): [sub]/ [TBHP]=1.40±0.05; [V]≈40; conv:±1%; sel:±5%. TOFs are calculated at 10% conversion of the substrate. The TOFs are roughly corrected for the blank reaction. [a] Two step addition of TBHP; amount t=0 min:3.30 mmol; to determine the reaction parameters of the second step the first step was carried out without sampling. At t=890 min (37% conversion of the substrate) an additional portion of the TBHP solution was added (amount 3.30 mmol TBHP); TOF determined at (37+10)% conversion. Conversion and selectivity of the second step determined at t=890+400 min.

4. Conclusions

VAPO-5 and VAPO-11 with a variable vanadium content can be prepared by hydrothermal synthesis in high yield. The preparation is strongly influenced by the vanadium content of the gel and the template used. Using tri-propylamine a highly

Table 5

Vanadium catalysed oxidation of 2-octanol by TBHP

Catalyst (wt%V)	V_{total} (mmol)	TOF (mol/mol h)	t=400 min		
			Conv. sub (%)	Sel. Prod. sub (%)	Sel. TBHP(%)
26	–	–	–	10	100	–
27	VO(acac)$_2$(19.2)	0.091	10	50	95	40
28	S-P4(1.48)	0.117	2.7	48	95	36

Conditions and experimental errors: acetonitrile; t=71±1°C; [sub]=0.30±0.01 M [sub]/[TBHP]=1.4±0.05; [TBHP]/[V]≈40; conv:±1%; sel:±5%. TOFs are calculated at 10% conversion of the substrate. The TOFs are roughly corrected for the blank reaction.

Table 6

Vanadium catalysed oxidation of cyclo-octanol by TBHP

Catalyst (wt%V)	V_{total} (mmol)	TOF (mol/mol h)	t=400 min		
			Conv. sub (%)	Sel. Prod. sub (%)	Sel. TBHP(%)
29		–	–	24	95	100
30	VO(acac)$_2$(19.2)	0.104	11.8	72	90	55
31	S-D1(0.32)	0.113	1.2	45	100	100
32	S-P4(1.48)	0.115	2.5	56	98	90

Conditions and experimental errors: acetonitrile; t=71±1°C; [sub]=0.30±0.01 M; [sub]/[TBHP]=1.4±0.05; [TBHP]/[V]≈40; conv: ±1%; Sel: ±5%. TOFs are calculated at 10% conversion of the substrate. The TOFs are roughly corrected for the blank reaction.

crystalline VAPO-5 with an uniform particle size distribution and an high vanadium content can be prepared.

The incorporation mode of vanadium depends on the vanadium content of the gel, rather than the preparation method. A tetrahedral species is observed at low vanadium contents in VAPO-5 as well as VAPO-11. At higher vanadium contents five co-ordinate species are also present, which means that a VAPO material contains various vanadium species.

The activity of VAPO is low compared with a homogeneous vanadium catalyst. The only effect of the microporous structure is the observation of fast decomposition of the peroxide in case of VAPO-5. Only minor differences in activity and selectivity are found between different preparation methods. VAPOs with a higher vanadium content are more active.

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