Application of VAPO as catalyst for liquid phase oxidation reactions

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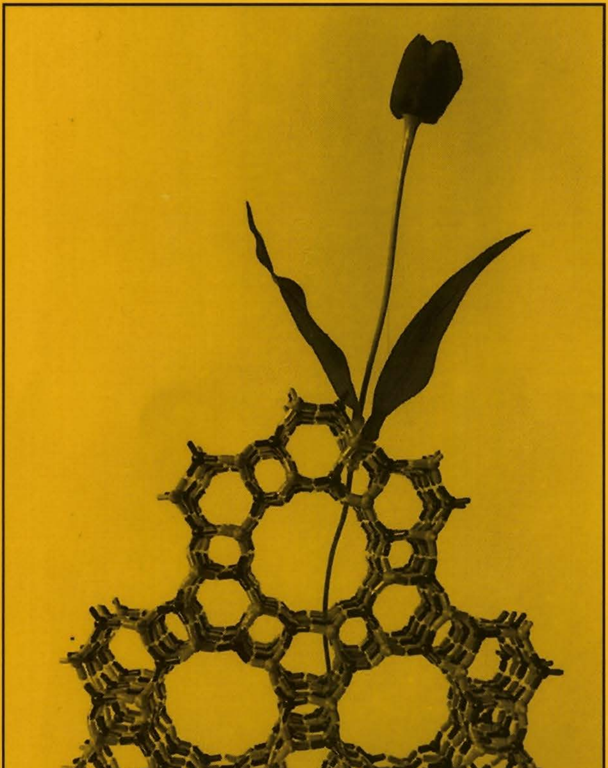

M.J. Haanepen

Application of VAPO as catalyst for liquid phase oxidation reactions

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof.dr. J.H. van Lint, voor een commissie aangewezen door het College van Dekanen in het openbaar te verdedigen op donderdag 28 maart 1996 om 16.00 uur.

door

Martinus Jacobus Haanepen

geboren te Haarlem

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Contents

VAPO-5
A black tulip
Both so fascinating
In their own way
But is it more than beauty ?

Abbreviations and Definitions

MeAPO	Metal Substituted Aluminophosphate
VAPO	Vanadium Substituted Aluminophosphate
VAPSO	Vanadium Substituted Siliconaluminophosphate
V-AlPO	Vanadiumoxide on Aluminophosphate
DRUVVIS	Diffuse Reflectance Electronic Spectroscopy
ESR	Electron Spin Resonance
XRD	X-ray Diffraction
EDX	Energy Dispersive X-ray Analysis
CVD	Chemical Vapour Deposition
SEM	Scanning Electron Microscopy
NMR	Nuclear Magnetic Resonance
AAS	Atomic Absorption Spectroscopy
GF-AAS	Graphite Furnace Atomic Absorption Spectroscopy
ICP-MS	Inductive Coupled Plasma Mass Spectrometry
PV	Pore Volume
TBHP	*t*-Butyl Hydroperoxide
TPMHP	Triphenylmethyl hydroperoxide

Conv Sub: Conversion of Substrate

Maximum amount of substrate that can be converted based on the amount of oxidant employed is 100%. (S_0 = amount of substrate t=0; S_t = amount of substrate t=t)

$$\text{Conv Sub} = \frac{S_0 - S_t}{S_t}$$

Sel prod on sub: Selectivity of all identified products on the amount of total product.

$S = P_1 + P_2 + \ldots + P_{\text{unidentified}}$ (P_1, P_2, ...: amount of identified products)

$$\text{Sel on Sub} = \frac{\sum P_{\text{identified}}}{S_0 - S_t}$$

Sel prod: Selectivity of one product on all identified products.

For example: Selectivity of the epoxide.

$$\text{Sel } P_i = \frac{P_i}{\sum P_{\text{identified}}}$$

General Objectives and Justification

1

Introduction

This thesis deals with the development of new catalytic systems for the selective oxidation of organic compounds in the liquid phase. Oxidation is one of the important methods to transform hydrocarbon feedstocks like alkanes, alkenes and aromatics into more sophisticated oxygenated products. Oxidation processes are also important in fine chemicals manifacture. Characteristic for fine chemistry is its wide variety of complex products and the relatively limited amount of manufactured product (less than 10000 ton / year). Fine chemicals are important starting materials for the synthesis of specialties like pharmaceuticals, flavor substances, dyestuffs and pesticides.

Despite their importance many oxidation technologies, nowadays used in fine chemistry, suffer from severe disadvantages which find their origin in the reaction itself [1]. Major problems are the use of environmentally unfriendly stoichiometric reagents and the lack of selectivity, as has been shown by many examples of these antique processes [1,2]. Both factors contribute to the massive production of waste. To give the reader an idea: for the production of 1 kg of desired product often more than 10 kg of waste is produced. This means that most of the atoms introduced at the start of the reaction are not part of the desired product and thus the atom-selectivity is very low.

An alternative clean process has to be much better than the existing process before it will be accepted, also for economical reasons. At the time the old processes were introduced, no other means of manufacturing the desired products existed. Nowadays, replacement by a fundamentally new process requires a replacement investment. In most cases this delays the introduction of new processes. In a few cases much better alternative processes already exist, like for example the Halcon process to produce propene oxide as alternative for the chlorohydrin process [5]. However, after 30 years, the old chlorohydrin process is still used, despite the production of much waste. In the future, however, it is to be expected that the costs of waste processing will exceed the profits made on the product in an increasing number of cases, thereby stimulating the replacement of old processes by new ones. However, in many cases alternative processes are not yet known and real progress can be made in the development of these alternatives.

As mentioned before part of the problem is the common use of environmentally unfriendly stoichiometric oxidants like for example potassium permanganate ($KMnO_4$) and potassium dichromate ($K_2Cr_2O_7$). Waste streams are mainly aqueous solutions containing metal ions, which are difficult to process further. In order to design a clean process oxidants like dioxygen, hydrogen peroxide and organic peroxides are a much better choice. The byproduct of these oxidants is only water or the corresponding alcohol. In the case of *t*-butylhydroperoxide (TBHP), the byproduct *t*-butanol can be dehydrated to isobutene, used in other processes, or converted to the peroxide again by reaction with hydrogen peroxide. However, in most cases these clean oxidants cannot be used directly because they are too unreactive or show too little selectivity to be useful [1-4]. The second part of the problem, a lack of selectivity, is often caused by the higher oxidation susceptiblity of the product compared to the substrate. Once a product has formed, it is more easier oxidised than the starting material. An example is de side-chain oxidation of methylaromatics towards the corresponding aldehyde. Without special precautions this aldehyde is easily oxidised to the unwanted acid [3].

In principle the solution to the problems of low reactivity and low selectivity is the use of a catalytic system to carry out oxidation reactions [3]. The catalyst used can be present in the same phase as the reactants (homogeneous catalyst) or in a seperate phase (heterogeneous catalyst). Generally, such a catalytic system contains a metal complex. The presence of (an) other, metal mediated, low energy reaction pathway(s) can make a selective reaction between the oxidant and the substrate more feasible. The use of a lower reaction temperature also retards the consecutive oxidation of more reactive reaction products. To control the selectivity this metal catalysed reaction should be the only tolerable reaction to take place. Nevertheless, it should be kept in mind that still a non-catalysed and non-selective direct reaction can take place between the substrate and the oxidant. To avoid this direct reaction the catalytic oxidation should be carried out at a relatively low concentration of the reactant and/or at low temperatures. In heterogeneously catalysed gas phase reactions the reaction temperature is fairly high, but the reactant concentration is relatively low. Combined with a short residence time of the components in the reactor, to suppress consecutive reactions, very good results can be obtained. A nice example is the oxidation of 3-methyl-3-buten-1-ol (isoprenol) to 3,7-dimethyl-2,6-octadienal (citral) [1]. However, catalytic gas phase oxidations are limited to relatively simple molecules. More complicated molecules cannot be brought easily into the gas phase and many of these molecules are unstable at elevated temperatures. Thus, the reaction has to be performed in the liquid phase, where the concentration of substrate molecules is usually much higher. Therefore, to suppress a direct reaction the catalytic oxidations should be preferably carried out at relatively low temperatures (0 - 200°C). Although catalytic gas phase oxidation processes are important [5], in this thesis emphasis is put on liquid phase oxidation processes.

During the last twenty years many catalytic systems were developed to improve activity and selectivity of oxidation reactions in the liquid phase. *A priori* it is possible to set up a list of desired properties of the potential oxidation catalyst. These properties are: at least a moderate activity, a high selectivity and good stability and regenerability.

- **Activity**

For a practical catalyst the turnover frequency (TOF) should be higher than 100 mol/mol.h (this means that 1 mol of substrate can be converted in 1 hour using 0.01 mol of catalyst).

- **Selectivity**

With respect to selectivity one can distinguish between chemo-, regio-, and stereoselectivity.
Chemo-selectivity is defined as the selectivity between reactions at different functional groups in a molecule like for example an allylic alcohol that possess an alkene function and an alcohol function. When two or more equivalent functional groups are present in the same molecule regio-selectivity can occur: the reaction takes

preferently place at one of the groups in the molecule. If during the reaction an asymmetric carbon is involved also stereo-selectivity may be introduced. Generally, a high chemo-selectivity is the least difficult to achieve. Regio- and stereo-selectivity, induced by the ligands, are more demanding on the catalyst design.

- **Stability and Regenerability**

For an applicable catalyst it should be possible to use it again several times without losing its original activity and selectivity. The catalyst itself should be oxidation resistant. Also, another preferable demand is that the catalyst can be easily recovered from the reaction mixture.

Up to now it proved to be complicated to combine all these demands in one catalytic system. Nature presents the examples that it is in principle possible: metallo-enzymes are highly active, selective and stable catalysts [1,2]. However, a limited stability outside the cell is the main reason why they can not be used directly in an industrial process. It is therefore not surprising that a lot of work has been done to mimic these systems. Such an idealised catalyst consists of a metal centre in a pre-formed cavity where a substrate can be bound in such a way that the preferred part is directed towards the active metal centre. It is possible to adjust the properties by altering the environment (ligands) around the metal centre. Many systems have been made, with sometimes spectacular results, regarding the activity and the chemo-, regio- and stereoselectivity. Examples are the beautiful porphyrin systems that can be used as epoxidation catalysts [6,7]. However, the often very complicated synthetic procedures, the recovery of these homogeneous catalysts and the limited long term stability are still major problems that hamper a large scale application of many interesting catalytic systems.

Recently metal substituted molecular sieves were introduced as oxidation catalysts. Metal substituted molecular sieves have an isolated metal ion in a uniform cage or channel, thereby showing some similarity towards biological catalysts. A potential advantage however is that these structures are built from inorganic materials like silica and alumina, which are much less susceptible to oxidative degradation. Moreover because they are solids they can be easily recovered from the reaction mixture, an important feature of systems to be used in the liquid phase. The success of this type of catalyst has been demonstrated by TS-1, a titanium substituted silicalite [8]. TS-1 can be used for the selective oxidation of many substrates that can be oxidized only with difficulty in other ways. However, the use of metallo-molecular sieves is not limited to the use of titanium alone. Examples of alternative systems are the metal substituted aluminophosphates (MeAPOs) [9]. A potential advantage compared to silicate and aluminosilicate systems is the large number of elements that can be introduced into the aluminophosphate framework. Both the succes of TS-1 and the wide variety of possibilities justify further research towards the use of metal substituted aluminophosphates or to quote professor Sheldon's words: '*TS-1 might be the tip of an iceberg: a representative of a whole family of excellent catalysts*' [10].

Scope of the Thesis

In this thesis emphasis is put on the application of metal substituted aluminophosphates as heterogeneous catalyst for liquid phase oxidation reactions. Only at the end of the thesis brief attention will be paid to the use of MeAPO as catalyst for gas phase reactions. In particular vanadium substituted aluminophosphates (VAPO) will be investigated. Vanadium has been chosen because it has a versatile oxidation chemistry in the liquid phase [11]. The research, as part of the IOP-Catalysis project (IOP = Innovatief Onderzoeks Programma = Innovative Research Programme), is approached from a catalyst development point of view. The reactions chosen are adapted from known reactions in the field of homogeneous oxidation chemistry. The main objectives of the project are the development of well-defined VAPO-systems and exploration of the possibilities and the limitations of VAPO as a heterogeneous liquid phase oxidation catalyst. However, it is not our aim to develop a new oxidation process in order to obtain a specified industrially desired product.

Chapter 2 describes the theory and applications of metal containing molecular sieves as oxidation catalyst. In chapter 3 and 4 the synthesis and characterisation of VAPO materials will be discussed. The characterisation will be mainly directed towards features which are essential for catalysis, like the structural definition of the VAPO molecular sieve. Chapter 5-8 deal with the application of VAPO in some liquid phase oxidation reactions. In chapter 5 attention is paid to the general performance (activity and selectivity) of the VAPO. An intriguing question here is the effect of the pore structure on the reaction. In chapter 6 the possible deactivation and regeneration will be discussed. Chapter 7 deals with the question whether or not VAPO acts as a heterogeneous catalyst. In chapter 8 possible improvements of the performance are discussed. Chapter 9 is a general discussion, where an answer will be given to the question if VAPO, and more generally MeAPO, can be a useful alternative catalysts for liquid phase oxidation reactions. Finally, attention will be paid to the application of MeAPOs in the gas phase isomerisation of *n*-butene towards isobutene.

This Project in the context of IOP-Catalysis

For the development of processes in the chemical industry a continuous innovation is necessary. Future demands are a more economical use of resources and energy, more attention to safety and less environmental pollution. More precision in chemical processes should be realised by the use of better (more active and selective) catalytic systems and the exploration of new synthetic routes. Because fine-chemistry deals with a wide variety of relative small scale processes it is not possible to develop a new catalyst for every process. Therefore possible catalysts should ideally be derived from known catalysts from bulk chemistry.

To stimulate this development IOP-katalyse was founded in 1989 by the Ministery of Economical Affairs to serve as a bridge between the industry and the university. Thereby it tries to bridge the gap between business oriented industrial research and the more fundamentally oriented university research [12]. As a consequence the results of fundamental research can be more easily implemented in commercial processes. IOP-katalyse has three main research themes:

- Innovation in fine-chemistry by application of hetereogeneous and homogeneous catalytic processes.
- Innovation in catalyst preparation and reactor technology to introduce new procedures.
- Innovation in fine-chemistry by the application of bio-catalytic processes.

The present project is directed towards the first main theme. The project, IOP 89005, is a combined research program of prof. dr. R.A. Sheldon / J.D. Chen M.Sc. (Delft University of Technology) together with prof. dr. ir. J.H.C. van Hooff / drs. M.J. Haanepen (Eindhoven University of Technology).

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Metal Containing Molecular Sieves and Oxidation Catalysis

2

Introduction

Many important catalysts consist of active material supported on a porous material. The porous structure provides a high surface area that can accomodate a high number of catalytically active metal sites. Various porous materials are known, like silica, alumina, active carbon, resins, clays and molecular sieves. The latter group is unique because molecular sieves are crystalline materials with a well defined pore structure. The size of the pores is comparable to that of many organic molecules, which offers the possibility to influence the reaction by a controlled interaction with the pores. Many different types of molecular sieves are known, among them the aluminophosphates or AlPOs. Molecular sieves as such are not active in oxidation reactions and should be modified by the introduction of metal ions. Various methods are known to functionalise a microporous material. The scope of these modification methods will be discussed. Thereby our main objective, use of metal containing aluminophosphates as catalyst for liquid phase oxidation reactions, will be kept in mind.

Oxidation reactions are generally fairly complex and should occur inside the micropores in order to maximise the number of catalytic sites that are used during a reaction. Due to the (strong) interaction of molecules with the pore walls, conventional theories about reactions have only limited applicability. The concept of 'reactions inside micropores' is still in its childhood and a firm theoretical base is lacking. Nevertheless, some insight in the encountered problems will be given. During the discussion examples of catalysis by metal containing molecular sieves will be given as illustration. As far as possible these examples are taken from liquid phase oxidation reactions.

After a short description of the properties of transition metal containing aluminophosphates (MeAPOs) the known applications as oxidation catalyst will be treated in depth. The overview will cover the literature up till August 1995. However, the last ten years, in literature only about twenty five papers about this subject appeared, although presumably many research programmes are dealing with this theme. Emphasis will be put on the advantages and problems concerning the use of MeAPOs as catalysts for liquid phase oxidation reactions in comparison with known catalysts.

Structure of Molecular Sieves

Molecular sieves can be built from various tetrahedral building blocks or T-atoms: silicon oxide $[SiO_4]^0$, aluminum oxide $[AlO_4]^{1-}$, phosphorus oxide $[PO_4]^{1+}$ and gallium oxide $[GaO_4]^{1-}$. Common combinations of building blocks are aluminosilicates or zeolites (Al, Si), silicalites (only Si), aluminophosphates (Al, P) and gallophosphates (Ga, P) [1,2]. Depending on the actual structure zeolites can be prepared with different silicon / aluminum ratio. The charge caused by the electron rich aluminum tetrahedra is balanced by positive ions. Silicalites are built from only silicon tetrahedra and are electroneutral. In aluminophosphates (AlPOs) and gallophosphates (GaPOs) the aluminum / gallium to phosphorous ratio is exactly one, and consequently the charges of the ions are perfectly balanced.

The pore structure of a molecular sieve can extend in one, two or three directions. Many structures have been identified that are abbreviated by a three letter code [3]. The pore size can vary between 0.3 nm (zeolite A, LTA) and 1.1 nm (cloverite, CLO) and is comparable with the size of many organic molecules [4]. For the use as catalysts only the sieves with the larger pores are of interest.

Recently new materials were invented by Mobil, that possess a pore diameter between 2 and 10 nm (MCM materials) [5]. However, although these materials have a well defined pore structure, they only show a long range ordening and therefore are not crystalline. They can best be regarded as intermediate between highly crystalline molecular sieves and amorphous silicas or aluminas.

Molecular sieves are prepared by hydrothermal synthesis [6]. The starting materials are mixed in the appropriate ratio. Often a structure directing molecule, the template, is added to obtain the desired sieve. Primary, secondary, tertiary amines and quartenary ammonium ions are commonly used templates. The mixture, often a gel, is generally crystallised at 100-200°C in an autoclave. After work-up the template is removed by thermal treatment in air or dioxygen (calcining).

Functionalisation of Molecular Sieves

The molecular sieves as described do not show catalytic activity in oxidation reactions and should be modified. Active sites can be introduced in various ways. The method of choice depends on the nature and properties of the metal ion and the molecular sieve. Basically these methods can be divided into four groups: ion exchange, impregnation, ship-in-the-bottle approach and substitution. Examples of the products obtained by these methods are shown in figure 1. Within each group variations may occur. The last method (substitution) is applied to prepare the aluminophosphate molecular sieves used in this work.

- **Ion exchange**

The molecular sieve is contacted with a solution containing the appropriate metal ion. This method is only applicable to molecular sieves that have cationic sites, therefore this method is almost solely used for zeolites. Common examples are Co-Y, Pd-Y and Cr-Y [7], but in principle every metal ion can be introduced in this way. However, the limited stability of the ion exchanged system is a severe problem when used in a liquid phase oxidation reaction [91,93].

- **Impregnation and chemical vapor phase deposition**

A metal complex or metal salt is dissolved and absorbed by the molecular sieve followed by a thermal treatment to decompose the complex [8]. A variant thereof is the absorption of a volatile metal complex (CVD). After calcining the resulting metal or metal oxide may be coupled chemically to the framework of the molecular sieve. Examples are the absorption of $TiCl_4$ on dealuminated mordenite, $Mo(CO)_6$ / $W(CO)_6$ on zeolite X/Y and $Ni(C_5H_5)_2$ on AlPO-5 [9]. A disadvantage is the formation of loosely bonded sites and multinuclear particles.

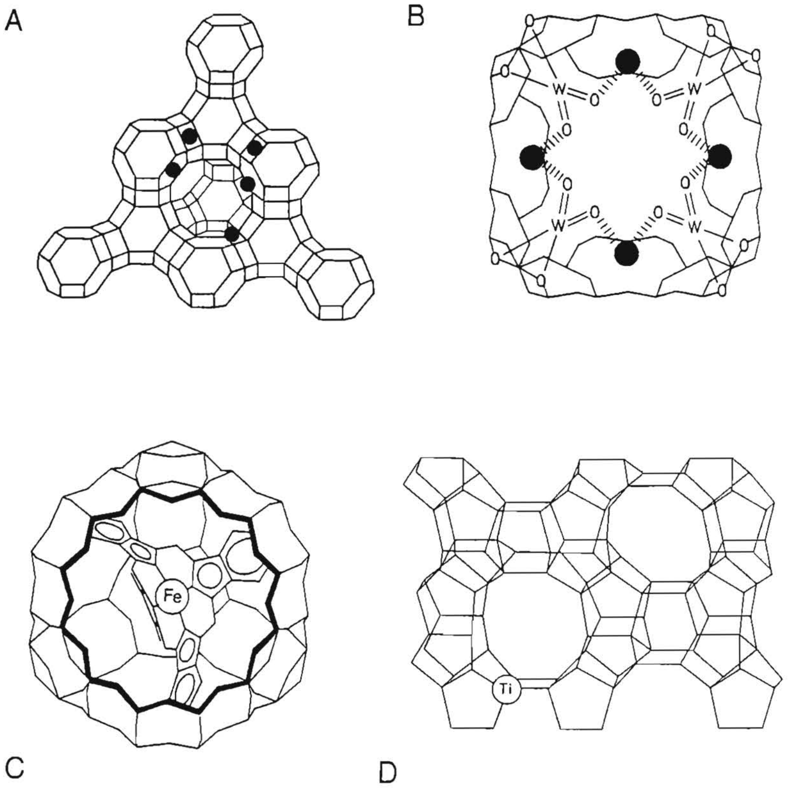


Figure 1: Examples of metal containing molecular sieves prepared by different methods.

A. Cationic sites in zeolite X/Y (adapted from: C.R.A. Catlow *et al.*, Solid state ionics, 70/71 (1994) 513).

B. WO_3 into the zeolite Y. After absorption of $W(CO)_6$ the material is calcined (adapted from: G.A. Ozin *et al.*, J. Am. Chem. Soc., 114 (1992) 8959).

C. Iron phtalocyanine encaged in the supercage of zeolite Y (modified after: D.E. De Vos *et al.*, Macromol. Symp., 80 (1994) 161).

D. Titanium(IV) incorporated into the framework of silicalite-1 (TS-1) (modified after: B. Kraushaar-Czarnetzki, Thesis, Eindhoven University of Technology (1989)).

Drawings by C.E. Haanepen.

- **Metal complexes into molecular sieves**

This procedure involves the attachment of organometal- or coordination complexes inside the molecular sieve [10]. This can for example be done by ion exchange methods. However, for the proposed application as oxidation catalyst in the liquid phase the 'ship in the bottle' approach is much more promising. The metal complex is assembled in the cavity of a molecular sieve like faujasite (zeolite X and Y) and cannot leave the cavity because of its dimensions. A variant of this method is the use of the metal complex as template molecule. The functionalisation of molecular sieves by introducing a metal complex in the sieve offers a wide flexibility in imposed geometry and donoratoms. Moreover, highly active and selective complexes known from homogeneous catalytic chemistry can be used. Examples of the ship in the bottle approach are iron phtalocyanine and manganese bipyridyl complexes in zeolite X, Y and EMT [11].

- **Substitution of the metal ion into the lattice**

The metal ion is introduced in the synthesis mixture and is substituted for building blocks of the framework [12]. In this way the metal ion becomes part of the molecular sieve lattice. In case of perfect substitution, or so called 'isomorphous substitution', the metal ion should be tetrahedrally coordinated. An advantage compared with impregnation or CVD methods is that it is in principle possible to obtain materials with highly dispersed metal centers. The resulting material is completely inorganic, which might be an advantage for the application as oxidation catalyst.

Because the flexibility of the molecular sieve lattice is limited, their is a maximum to the size of the metal ion that can be incorporated. In silicate, aluminosilicate and aluminophosphate molecular sieves first row transition metal ions are the largest ions that can be possibly incorporated. Moreover, also the charge of the metal ion is important. If this charge is different from the charge of the substituted T-atom, at the same time charge defects are created, that have to be compensated in order to obtain a stable structure.

In the hydrothermal synthesis of zeolites and silicalites the pH of the synthesis mixture is high (pH > 10) in order to dissolve the silicon and aluminum source. This puts a serious restriction to the applicability of this method because most metal ions form insoluble hydroxides under these conditions. Practically only titanium, vanadium and iron give good results [12]. TS-1, our source of inspiration, is succesfully prepared in this way. Characterisation studies point out that the metal ion is indeed present in a highly dispersed state, probably monomeric. Other metal ions like Zr^{4+} and Sn^{4+} have also been reported to be incorporated in silicalites, but characterisation methods used give no convincing answer. The effective pH of the gel can be decreased by the addition of fluoride-ions, which leads to some improvements of the method [13]. Another variant is a post synthetic method where boron is incorporated into the lattice and afterwards substituted for the metal ion [14]. The pH problem does not play a predominant role in the synthesis of MeAPOs [2,15]. MeAPOs can be prepared between pH 3 and 10. Most metal ions do not precipitate under these conditions. Therefore, there is a possibility to incorporate for example cobalt- and manganese ions.

It should be realised that due to the complexity of the condensation processes taking place during the molecular sieve synthesis, the formation of uniform sites will be hard to control. For example, the incorporation of silicon in the aluminophosphate lattice gives rise to the formation of silicon islands [2]. Also the reproducability of the synthetic procedure can be a problem. In order to design a better controllable and more rational preparation method knowledge about the processes taking place on a molecular and sub-molecular level is needed, however only a few studies are devoted to this subject [16]. Furthermore the donor atoms are restricted to lattice type oxygens. The development of phosphonitrido (P-N) molecular sieves opens the way to the use of nitrogen type donors [17].

The concept of 'Reactions in Micropores'

The way from substrate to product using a porous catalyst is a complex process involving many elementary steps. In the description of a reaction on a porous catalyst in many cases not only the reaction itself has to be taken into account but also the supply of reactants and the removal of the products from the pores [18]. Figure 2 gives insight in the processes taking place inside a porous catalyst on a molecular level. The reactant(s), present in the gas- or liquid phase, should enter the porous system. Thereby a liquid/solid or gas/solid barrier has to be past. Once absorbed into the pore the molecule has to diffuse to the active site, where it can react. Finally, the product(s) should diffuse away from the active site towards the bulk.

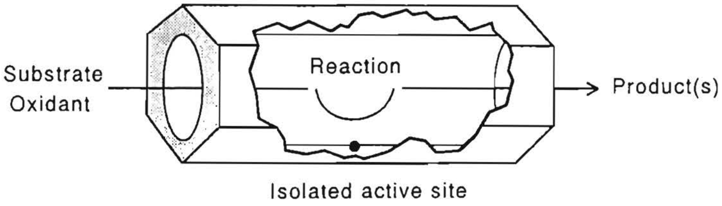


Figure 2: Transport and reaction in the molecular sieve.

Suppose a porous material where the pore diameter is much larger than the size of the reactant. When the surface barrier has been past the reactant is able to move freely inside the pores. The influence of the pore walls on the movement of the reactant is small. Bimolecular reactions can occur and the products are easily interchanged and can easily leave the pore system. Selectivity patterns are solely determined by steric and electronic properties of the active sites. The situation becomes different when the size of the pores is decreased and becomes comparable with the reactant size, a situation arising in molecular sieves. This implies that molecules inside the pore cannot pass each other. When the reaction is carried out in the liquid phase with a penetrable solvent the situation is even more complicated by the presence of solvent molecules. It is clear that application of molecular sieves as catalyst for liquid phase (oxidation) reactions lead to a complex situation involving multi-component diffusion combined with reaction.

The total performance of a molecular sieve catalyst is determined by the combination of transport and the reaction taking place on the metal site (activity and selectivity). To simplify the discussion these areas are discussed seperately.

Absorption and diffusion

The absorption and movement of molecules inside the pores is of importance when considering reactions in molecular sieves because a strong interaction with the pores is expected [19-21]. Most studies of absorption and transport of molecules deal with gas phase rather than liquid phase applications. Molecules with a size smaller than the pore size are readily and strongly absorbed into the pore because the heat of absorption exceeds the loss of entropy. Compared with gas phase conditions it can be expected that the occupation level of the pores under liquid phase conditions are high for several reasons: lower temperature, high concentration, use of more polar and larger molecules with stronger absorption coefficients.

The degree of pore filling is of importance for the transport of molecules. Assume a string of molecules in a straight pore. The molecule in the centre cannot move, neither left nor right, unless one of its neighbours moves. More translational freedom of motion is possible in a two-dimensional or three-dimensional pore system. The diffusion of the molecule depends on the movement of other molecules. The movement of the molecule can be regarded as jumps from one position in the pore to another and is different from normal free diffusion in a gas or liquid. The transport of molecules in a straight pore, single file diffusion, were simulated by Monte-Carlo calculations [22]. Some important conclusions emerged from similations where the diffusion was combined with the simplest chemical reaction (transformation from molecule A into B (isomerisation)). As can be expected the transport of the molecules appeared to be a strong function of the string length and occupation level. It follows that chemical reactions are dramatically retarded in a single-file system. The simulations show that the reaction is strongly transport-controlled and is most likely to occur in the vicinity of the orifices of the molecular sieve channel. The molecules close to the pore mouth have the highest chance to escape from the pore. Product B formed deep in the pore is not replaced by new reactant A. A strong influence of the reaction rate on the crystallite size can therefore be expected. From the simulations it can be concluded that bimolecular reactions like A + B → C, which are typical for oxidation reactions, might be even more unlikely to proceed within the pores of a mono-dimensional sieve. In this reaction the ordening of the absorption of molecules A and B is expected to play an important role in the process, because the reactants cannot interchange inside the strung. The optimal arrangement would be ABABABABAB, other arrangements like AAAABAAAAB (A absorbed in favor of B) lead to a lower reaction rate. Moreover, the simultaneous absorption of the solvent (S) reduces the chance that two molecules react even further: ASASASBSSA. Difficulties related to the preferential absorption of one reactant are for example observed in the Friedel-Crafts acylation of toluene by acetic acid catalysed by NaCe-Y [23].

Shape selectivity

There are three major effects on the selectivity of a reaction that find their origin in the sterical interaction of the molecule and the pore [19,20]. These are: molecular exclusion or substrate selectivity, product selectivity and transition state selectivity. Substrate selectivity is based on the fact that substrates with a size larger than the pore size are not able to enter the pores to take part in a reaction. The opposite effect, product selectivity, deals with product molecules that cannot leave the molecular sieve structure. The third important expression of shape selectivity is the restricted transition state selectivity. Certain products cannot be obtained because the reaction pathway involves bulky intermediates or transition states that cannot be accomodated in the available free space, while the size of both substrate and product permit movement in the pore. Therefore, this effect should be more dominant in bimolecular rather than monomolecular reactions. Because shape selectivity is an intrinsic property it is independent of the crystallite size of the molecular sieve.

Of course, the question is how principles of shape selectivity can be applied to liquid phase oxidation reactions. Substrate-, product- and restricted transition state selectivity are well known from many gasphase reactions [19,20]. Restricted transition state selectivity, for example, is demonstated in the isomerisation of xylenes on a modified ZSM-5 zeolite [23]. The catalyst showed a remarkable improvement of the p-xylene selectivity. Obviously, transition state selectivity is the most important means to gain additional selectivity in liquid phase oxidations. Oxidation reactions are irreversible and interconversions of isomeric products, as observed in many reactions are not very likely. Therefore product selectivity is not to be expected [12]. In contrast with the use of molecular sieves as cracking or isomerisation catalysts where complex feeds are used, in fine chemistry the starting materials are much more defined. Therefore, substrate selectivity is only interesting at higher conversions of the substrate. In the course of the reaction the substrate should enter the molecular sieve rather than the reaction products.

Clear examples of shape-selective oxidation, in the liquid as well in the gas phase, are not abundant. Some principles are demonstrated by the use of homogeneous oxidation catalysts [24]. For example, the least reactive alkene function present in 1-methyl-4-(1-methylethenyl)-cyclohexene (limonene) can be epoxidised rather selectively by a sterically hindered porphyrin catalyst, which is an example of transition state selectivity. Molecular sieves can also show shape selective oxidation properties. An interesting example is the α-hydroxylation of alkanes at room temperature with hydrogen/dioxygen mixtures using a small pore Pd(0) containing zeolite 5A as catalyst [25]. This reaction is of particular industrial importance because the β-position of the alkane is much more reactive. This problem can be circumvented when the β-positions of the alkane are masked by the pore wall and not accessible for a reaction anymore, while the α-positions at the crossings of the 3-dimensional pore system are accessible. Unfortunately, the pores of the zeolite become blocked during the reaction but analysis of the products present inside the pores show indeed an increased selectivity towards the hydroxylation of the α-position. Later on in this thesis some other examples of proposed shape selectivity effects will be met.

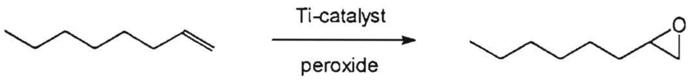
The remarkable performance of titanium substituted silicalites

The titanium substituted silicalite TS-1 is an unique catalyst in many aspects. Most importantly TS-1 is able to catalyse reactions not observed for other titanium compounds [26,27]. Despite the previously described problems, TS-1 is an example where the concept of 'reactions in micropores' seems to work.

The most striking feature of TS-1 is that hydrogen peroxide and polar solvents like water and methanol can be used. In table 1 a comparison has been made between TS-1 and other titanium containing catalysts for the epoxidation of 1-octene by peroxides [34]. Generally it is difficult to compare catalysts, because the experimental procedures are not standarised. However, although reaction conditions vary somewhat, useful information can be obtained from the table. Among all mentioned catalysts TS-1 is the best at a relatively low temperature. All other systems use the less reactive TBHP as oxidant.

It should be noted that all titanium complexes mentioned do only function in waterfree aprotic solvents. An additional example of a commonly used homogeneous catalytic system that needs strictly waterfree conditions is the Sharpless catalyst, titanium(IV) tetraisopropoxide / diethyltartrate that epoxidises allylic alcohols stereoselectively [35]. Water and other alcohols seriously retard the reaction. Moreover, not only deactivation of the catalyst but also hydrolysis or alcoholysis of the epoxide can be a problem, that occurs to a lesser extend when TS-1 is used. In the table also data is shown about titanium on silica. This catalyst is like TS-1 a heterogeneous catalyst that shows a relatively high selectivity towards epoxidation. The structure of the active site of titanium on silica is believed to be similar to TS-1.

Table 1: Epoxidation of 1-octene catalysed by titanium catalysts.



Catalytic system						Results			Ref
Catalyst	Oxidant	Solvent	[sub] [ox]	T(°C)	t(h)	Conv Sub (%)	Sel on Sub (%)	Sel on Ox (%)	
TiO_2	TBHP	-	6.4	110	21	<73	9	?	[28]
$MgTiO_3$	TBHP	-	6.4	110	12	<28	1	?	[28]
Ti/SiO_2	TBHP	-	6.4	110	1	<86	90	?	[28]
Ti/SiO_2	TBHP	B	1.0	90	24	<31	?	<56	[29]
$Ti(OBu)_4$	TBHP	B	1.0	90	24	<34	?	<10	[29]
Ti-Al-β	TBHP	AN	5.0	90	1.7	25	80	100	[30]
			4.0	50	5	16	100	98	[31]
Ti-Al-β	H_2O_2	M	4.0	50	2	36	6	79	[31]
			5.0	40	1.7	46	0	97	[30]
Ti-β-Li*	H_2O_2	M	5.0	40	1.7	27	87	89	[30]
Ti-Bβ*	H_2O_2	AN	2.0	70	1	21	80	>50	[14]
TS-1	H_2O_2	M	4.0	50	2	44	80	97	[31]
			5.0	40	1.7	93	76	98	[30]
TS-1*	H_2O_2	AC	3.0	80	2	66	>90	>70	[33]

*: Best catalyst selected from table.
Solvent: M = methanol, AN = acetonitrile, B = benzene, AC = acetone

Historically, titanium on silica can be seen as a non microporous predecessor of the microporous TS-1.

The performance of the titanium molecular sieves is strongly dependent on the synthetic procedure. Only a TS-1 with small crystallites (typically <0.5 μm) and tetrahedrally coordinated titanium gives good results [36]. Also other titanium zeolites show activity. Results, similar to TS-1 can be obtained with TS-2, titanium silicalite with the MEL structure [37]. The preparation of titanium containing zeolite β is more

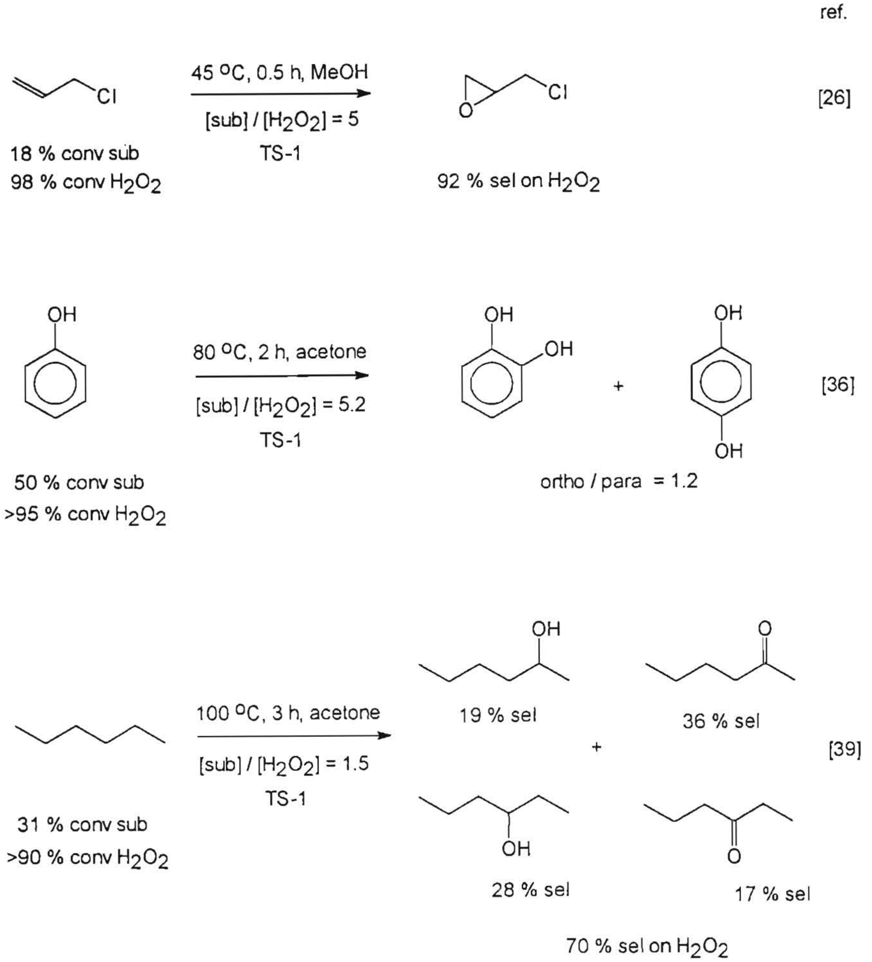


Figure 3: Examples of reactions catalysed by TS-1.

difficult. Ti-Al-*β* prepared by conventional methods always contains aluminium and consequently Brønsted acid sites that have a negative effect on the epoxide yield. Two succesful approaches have been used to reduce the number of Brønsted sites: neutralisation by alkalimetal ions (Ti-*β*-Li) [30] and preparation of an aluminum free boron-*β* followed by complete substitution by titanium (Ti-B*β*) [14]. Recently also the direct preparation of aluminium-free Ti-*β* was reported [38].

In some cases TS-1 is a superior catalyst compared with other systems, either in selectivity or activity (figure 3). TS-1 is able to epoxidise relatively inert substrates like allyl chloride [26], even more selectively than a good homogeneous catalyst molybdenum hexacarbonyl ($Mo(CO)_6$) [29]. TS-1 hydroxylates phenol in acetone selectively to the dihydroxylated products 1,2-dihydroxybenzene and 1,4-dihydroxybenzene [26,27,36]. When small crystallites are used the turnover frequency is about 110 mol/mol.h (32 mmol of phenol is converted in 1 hour using 0.29 mmol of titanium) [36]. The reaction is sensitive to TiO_2 impurities in the catalyst and therefore it can be used as model reaction [36]. Some improvement of the selectivity towards the 1,4-isomer is observed compared with conventional catalysts, which is explained in terms of shape selectivity [26]. Because extensive polymerisation of the phenol molecules to form tar species is retarded, the reaction can be carried out up to phenol conversion levels of more than 30%. When conventional catalysts are used (acids, iron salts) the maximum conversion of phenol is limited to 5-10%. A third example of a remarkable performance of TS-1 is the oxidation of alkanes under mild conditions to hydroxylated products (alcohols and ketones), a reaction not observed for other (homogeneous) titanium catalysts [39]. However, it was argued that this reaction is initiated by the presence of TiO_2 impurities in the catalyst [33].

Many more applications of TS-1 as an oxidation catalyst are known. Hydrogen peroxide is always applied as oxidant. A reasonable yield of product (with high selectivity based on substrate and peroxide) can be obtained when TS-1 is used in these reactions, particulary with linear molecules up to C_{12}. Some reactions (mainly described in patent literature) are [41-45]:

- Oxidation of alcohols towards aldehydes or ketones. In the case of primary alcohols also carboxylic acids are formed at higher conversion levels of the substrate.
- Epoxidation of dienes towards monoepoxides and epoxidation of allylic alcohols.
- Oxidation of thio-ethers towards sulfones and sulfoxides.
- Ring hydroxylation of activated alkylaromatics like toluene and methoxy toluene.
- Oxidation of vinylbenzenes to beta-phenylaldehydes (for example the oxidation of styrene to phenylacetaldehyde).
- Ammoxidation of cyclohexanone towards cyclohexanone oxime.

- Oxidation of primary, secondary and tertiary amines (including pyridines) towards oximes, hydroxylamines and N-oxides, respectively.
- Oxidation of anilines.

However, despite its tremendous scope, TS-1 is not able to oxidise a relatively reactive substrate like cyclohexene. Moreover, TBHP cannot be applied as oxidant. These observations are attributed to steric hinderance provided by the pore structure of TS-1. Other unusual and subtle phenomena like the observed low activity of 3-octanol compared with 2-octanol [26,44] are interesting for further discussion, because they also suggest that some kind of controll of the activity of the molecular sieve is possible by adjusting the pore structure.

In contrast with the numerous applications of titanium containing molecular sieves, other metal ion substituted molecular sieves have hardly been used as catalysts for liquid phase oxidation reactions. Among the other sieves vanadium containing systems are the best known [12]. For example VS-1, VS-2, V-NCL-1 and V-Mor were prepared [46]. VS-2 was tested as a catalyst for the hydroxylation of alkanes and aromatics [47,48]. Generally a deeper oxidation is observed with vanadium catalysts compared with titanium systems under the same conditions [47]. It was found that VS-2 is able to hydroxylate the side-chain of aromatics and the primary carbon in alkanes. A lower activity and selectivity is observed when VS-2 instead of TS-2 is used as catalyst for the oxidation of phenol [47]. Recently, VS-1 and VS-2 were tested as catalyst for the oxidation of p-chlorotoluene to p-chlorobenzaldehyde with hydrogen peroxide [49]. Unfortunately, an important parameter, the selectivity based on peroxide, is not reported but is probably low, which indicates that these systems do not work as desired.

Proof for validity of the concept

There is convincing evidence that reactions proceed within the pore system of TS-1 and not on the outer surface of the catalyst or in solution. The most important arguments in favor of an intraporous catalysed reaction are:

- No reaction is observed when TS-1 is used with included template. Therefore, the pore system has to be accessible for the reactants before a reaction can occur. However, the titanium species on the outer surface may also be blocked by template molecules. Therefore, if the reaction would only occur on the outer surface of the catalyst, this argument alone gives no decisive answer.

- Although no stability data of TS-1 have been published, the contribution of dissolved titanium to the activity is expected to be minor. Fast deactivation by strong complexation of the polar solvent and hydrogen peroxide is expected. For titanium on silica it has been shown that, although there is some titanium loss during the reaction, this leached titanium does not contribute significantly to the reaction [28].

- Reactive substrates with a size larger than the pore size of TS-1 do not react [26,27], examples are cyclohexene and t-butylbenzene.

- No reaction of substrates with TBHP has been observed, although TBHP is able to enter the pores of TS-1. For geometric reasons reactions seem to be not possible (shape selectivity). A titanium molecular sieve with larger pores, Ti-β does catalyse reactions with TBHP (see also table 1).

- Turnover frequencies are unreasonably high for the catalytic reaction only takes place on the outer surface of TS-1. It is well proven that titanium is homogeneously distributed throughout the crystallites. Calculation reveals that a cubic crystallite with dimensions of 0.1 x 0.1 x 0.1 μm has an outer to inner surface ratio of 1%. The outer surface contributes only 0.1% to the total surface area when crystallites of 1x1x1 μm are used. Consequently, if only outer surface titanium catalyses the reaction the real TOFs would be more than 100 times higher, which would be unrealistic. The calculated TOFs, assuming all titanium taking part in the reaction, are already relatively high (> 100 mol/mol.h).

- The oxidation rate of phenol is dependent on the crystallite size [36], which suggest intracrystalline mass transfer limitations. However, this argument may be blurred by the fact that the selectivity of the reaction also changes. Large TS-1 crystallites show a much lower selectivity based on hydrogen peroxide, indicating that side reactions, like the non-productive decomposition of the peroxide take place, which causes tar formation. This probably disturbs the hydroxylation of the phenol. A similar dependence of the reaction rate on the crystallite size was also found in the oxidation of alcohols by TS-1 [44]. This reaction differs from the oxidation of phenol that only a ketone is formed as product. Therefore the argument of intracrystalline mass transfer limitations probably still holds.

Structures and Properties of Metal Substituted Aluminophosphates

Several aluminophosphate structures have been reported in the literature. Some of these structures are similar to those found for zeolites and silicalites, but many are new. The properties of the framework topologies with large pores, which are interesting for catalysis, are collected in table 2. Note that some structures cannot or have not been synthesised as pure aluminophosphate. The most commonly used, and the most stable structures, are the frameworks with AFI and AEL topology. For the sake of clarity the structures of these materials are shown in the accompanying figure. Most of the $AlPO_4$ structures possess an one-dimensional pore structure, which might be a disadvantage with respect to the supply and removal of the molecules from the poresystem (see page 16). Frameworks possessing pores in more directions are AFR, AFS and AFY.

Unfortunately, many of the interesting microporous aluminophosphate molecular sieves are less stable than their aluminosilicates analogues [50, 51]. Dissolution of the aluminophosphate framework occurs in acidic and basic media [51]. On the other hand the thermal stability of AlPO-5 is excellent (up till 1000°C) [50]. VPI-5, which was the record holder in pore size for some time [52], appeared not to be stable and is transformed to the AlPO-8 structure upon calcination [53]. Recently, silicon containing VPI-5 with improved stability was prepared [54]. JDF-20 transforms into AlPO-5 upon heating [64]. The AFY structure, that can only be prepared containing cobalt or magnesium (CoAPO-50 or MgAPO-50), collapses upon removal of the template by calcining.

Many metal ions can be introduced in the AlPO framework *exempli gratia* Be, B, Mg, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge and As [2,14,65]. Properties of the

Table 2: Framework topologies of some selected AlPOs and MeAPOs.

Type		Pore structure	ref
AFI	AlPO-5	Straigth 10-ring pore (0.73 x 0.73 nm)	[50]
AEL	AlPO-11	Straigth 10-ring pore (0.63 x 0.39 nm)	[55]
ATO	AlPO-31	Distorted 12-ring pore (0.54 x 0.54 nm)	[56]
ATS*	MAPO-36 CoAPO-36	12-ring pore (0.75 x 0.65 nm)	[57]
FAU*	CoAPO-37	12-ring pore (0.74 x 0.74 nm) + supercage 1.3 nm.	[58]
AFR*	SAPO-40	12-ring pore (0.67 x 0.69 nm) + 8-ring pore (0.37 x 0.37 nm)	[58]
AFO	AlPO-41	Straigth 10-ring pore (0.43 x 0.70 nm)	[59]
AFS	AlPO-46	12-ring pore (0.63 x 0.63 nm) + 8-ring pore (0.40 x 0.40 nm)	[60]
AFY*	CoAPO-50, MgAPO-50	12-ring pore (0.61 x 0.61 nm) + 8-ring pore (0.40 x 0.43 nm)	[61]
AET	AlPO-8	14-ring pore (0.79 x 0.87 nm)	[62]
VFI	VPI-5	18-ring pore (1.3 x 1.3 nm)	[63]
	JDF-20	20-ring pore (≈ 1.3 x 1.3 nm) + supercage (2.9 nm)	[64]

*: AlPO-analogue does not exist.

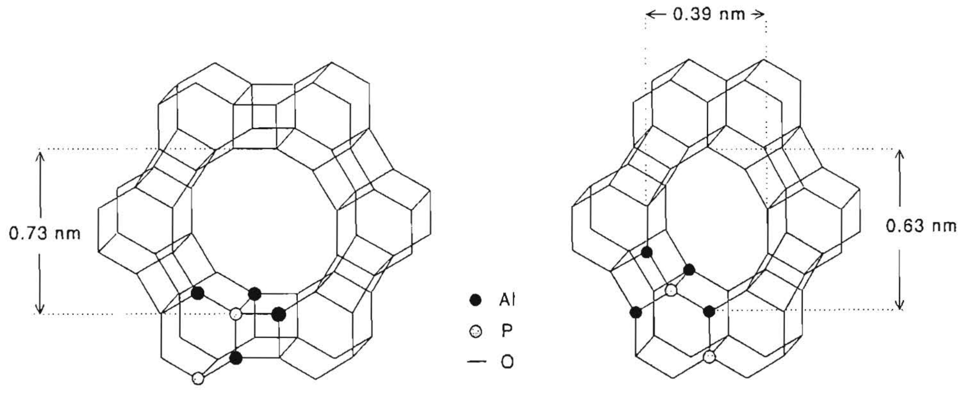


Figure 4: Structure of AlPO-5 (left) and AlPO-11 (right).

catalytically most interesting MeAPOs are briefly decribed in table 3. Some information is available about the characterisation of other potentially interesting MeAPOs not mentioned in the table, like CuAPO [66] and FeAPO [67]. Only during the last few years has detailed information become available regarding the structures of MeAPOs. The structure of the metal site is a matter of much debate in literature [12]. The most important question concerning the characterisation of MeAPOs is whether the metal is really framework substituted or not and if the metal ion has unique properties. The main reason for often conflicting results is due to the lack of a technique that can distinguish between framework and extra-framework species. From the table it is clear that the results are strongly dependent on the nature of the guest ion. Only in the case of cobalt framework substitution has been established. Other metal ions are only incorporated partially (anchored to the lattice) and/or are present as metaloxides.

Table 3: Properties of some selected MeAPOs.

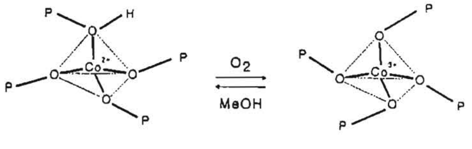
MeAPO	Properties
CoAPO-5	• Replacement of cobalt(II) for aluminum(III) [68-70]. • Before calcining Co(II) (blue), after calcining Co(III) formation (green) [68-70]. The presence of this oxidation state is matter of debate, the color change is also attributed to changes in the coordination sphere of the cobalt(II) [71]. A change from green to blue is observed upon interaction with dihydrogen at elevated temperatures and with MeOH at room temperature, attributed to reduction from Co(III) to Co(II) [68]. However, a redox cycle Co(II) → Co(III) seems to be essential for catalytic activity. • Framework cobalt: tetrahedral, extraframework cobalt: octahedral [69]. • Co-content: 0 - 2.5 %wt; more gives extra framework cobalt [68]. • After reduction of CoAPO strong Lewis acidity resides [72,73]. An additional weak P-OH is necessary to compensate the negative charge excess. A model for the site is proposed and confirmed by others [74,75]. • Possible clustering of cobalt (Co-O-P-O-Co) even at low cobalt content [76].  **Above: Proposed structure of cobalt in CoAPO (calcined / reduced) [72-75].**

Table 3 (continued)

MeAPO	Properties
CoAPO-11	• Co-content: 0 - 1.5 %wt; more gives extra framework cobalt [68]. • Reduction of the cobalt is more difficult than with CoAPO-5 which can possibly be explained in terms of less clustering of the cobalt [76].
MnAPO-5	• Only 0.1 %wt Mn can be incorporated in the framework as deduced from EPR measurements [77,78]. Additional species are present in manganese enriched Mn(II) regions. In a non-calcined MnAPO Mn(II) has a distorted octahedral symmetry. Spectra of calcined MnAPO and impregnated Mn-$AlPO_4$-5 showed great similarity. • During calcining the color of the MnAPO changes from white to purple, which is indicative for the formation of Mn(III) [79]. A reversible $Mn^{2+} \rightarrow Mn^{3+}$ redox cycle is proposed. The formation of Mn(III) is denied by others [80]. • MnAPO has Lewis and Brønsted-acid properties [73].
MnAPO-11	• X-Ray structure determination on a single crystal of as-synthesized MnAPO-11 with a high Mn-content (4.4 %wt Mn) showed incorporation of the Mn(II) into the lattice on an aluminium position) [81]. • In a calcined MnAPO-11 only a small amount of Mn(II) is incorporated as deduced from EPR measurements [82].
CrAPO-5	• Chromium contents up to 2.5 %wt were reported [83,84]. • Before calcining Cr(III) (light green), after calcining various species are present Cr(III), Cr(V) and Cr(VI). The color of the calcined product is yellowish-green. • In the as-synthesized material Cr(III) has an octahedral coordination, and is not incorporated in the lattice. No tetrahedral Cr(III) can be observed. Most of this non-incorporated Cr(III) is present as small Cr_2O_3-clusters. These oxides have different properties than bulk Cr_2O_3. Calcined AlPO-5 impregnated with Cr(III) salts show much spectroscopic resemblance to CrAPO-5 [83]. The formation of a chromium(VI)dioxo species onto a defect site is proposed by others [84]. • Chromium in a calcined CrAPO has a strong Lewis acid character, combined with a weak Brønsted acid site [84]. • Cr(VI) is reduced by CO to Cr(III) and Cr(II). Cr(VI) is formed back by treatment in dioxygen atmosphere or air at elevated temperatures. The oxidation-reduction properties of CrAPO are similar to that of chromium oxide (CrO_3) on silica [83].
VAPO-5	• Up to 2.5 %wt vanadium can be introduced in VAPO-5. The AFI structure is partially destroyed when more than 2.5 % is incorporated [85-88]. • Non-calcined VAPO is grey-blue, due to the presence of V(IV), while calcined VAPO is bright yellow (V(V)). Calcined VAPO is reduced by aromatics at low temperatures (< 373 K). • Both substitution of vanadium for aluminum and phosphorus has been suggested [85-87], and also the presence of extra-framework species cannot be excluded [88]. V(IV) is highly dispersed as revealed by EPR. Calcined VAPO contains tetrahedral or five coordinated V(V).

Reactions catalysed by MeAPOs

Several microporous metal containing aluminophosphates are reported to catalyse oxidation reactions. The majority of these applications concern liquid phase oxidation reactions, while only a few applications are dealing with gas phase oxidation reactions.

Liquid phase oxidation reactions

· Cobalt containing aluminophosphate

The first reported application of a metal containing aluminophosphate was the use of CoAPO as a heterogeneous catalyst for the selective oxidation of *p*-hydroxytoluene to *p*-hydroxybenzaldehyde by dioxygen [89,90] (figure 5). The potential advantages of this system compared with the commonly applied homogeneous catalyst cobalt acetate are the easy regenerability and the improved selectivity towards the desired product *p*-hydroxybenzaldehyde. The reaction is carried out at T = 50-80°C in strongly alkaline methanol. Like in the homogeneous process, the basic solution is necessary to activate the *p*-hydroxytoluene. Preferably a three-fold excess of sodium hydroxide over *p*-hydroxytoluene is used. Reported selectivities to *p*-hydroxybenzaldehyde are larger than 90%. At higher temperature somewhat lower selectivities towards the aldehyde are reported [90]. Both CoAPO-5 and CoAPO-11 show a similar behaviour [90]. The observed selectivity on dioxygen is low (< 50%) due to oxidation of the solvent methanol towards formic acid, which reacts with the excess sodium hydroxide to form sodium formate and water.

It has been reported that CoAPO-5 [89] and CoAPO-11 [90] could be re-used for at least ten times keeping the conversion and selectivity of a fresh CoAPO as measured after prolonged reaction times. Regeneration by calcining appeared not to be necessary. However, more recent results [90] show a decrease in initial reaction rate after a few reaction cycles.

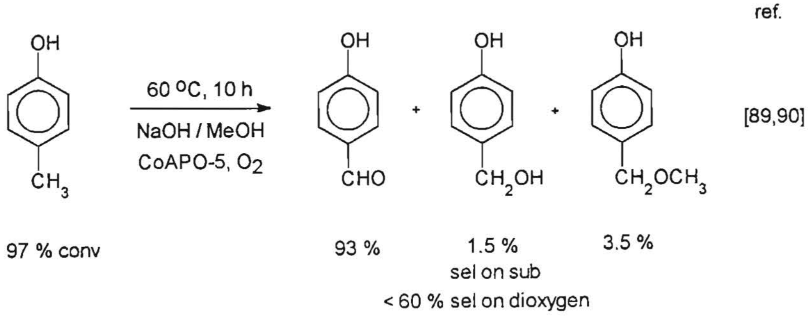


Figure 5: Oxidation of *p*-hydroxytoluene catalysed by CoAPO-5.

This was ascribed to partially dissolution of the CoAPO lattice thereby releasing cobalt ions in solution. Due to analytical difficulties cobalt could not be detected in the reaction mixtures directly. Therefore some experiments under dinitrogen atmosphere were performed to avoid the formation of sodium formate and reaction products. After removal of the CoAPO from the reaction mixture by filtration, small amounts of cobalt (max 10%) could be detected in the filtrate. Experiments using a homogeneous cobalt chloride catalyst at comparable (low) concentration level showed that similar activity and selectivity patterns could be obtained. Also, an experiment where the catalyst was filtered off after a short reaction time showed no changes in rate of the reaction of the filtrate. Therefore it was concluded that in this reaction CoAPO acts as a precursor for a homogeneous catalyst, rather than a true heterogeneous catalyst.

Another reported application of CoAPO is its use as a catalyst for the cyclohexane oxidation with dioxygen. Depending on the reaction conditions different products are obtained. Of interest are the CoAPO catalysed cyclohexane oxidation towards cyclohexanol / cyclohexanone mixtures [91-93] and the deep oxidation towards hexanedioic acid (adipic acid) [94-96].

The oxidation of cyclohexane towards cyclohexanol/cyclohexanone mixtures has been carried out in glacial acetic acid at T = 80-140°C using air as oxidant (figure 6) [91,92]. Under these conditions the product cyclohexanol is converted to its acetate ester which protects the alcohol against further oxidation. It was found that a substrate / acetic acid ratio > 4 is necessary to prevent leaching of the cobalt from the CoAPO lattice [91]. When a lower ratio was used more than 20% of the cobalt dissolved in the reaction mixture. It is interesting to note that Co-SAPO-5 (containing ion exchanged cobalt) was very unstable with respect to the cobalt loss under conditions were CoAPO-5 was found to be stable. CoAPO-16 (a structure possessing small pores) was nearly inactive. Under dinitrogen atmosphere, cyclohexane could be directly oxidised using CoAPO-5, whereas 2,2-dimethylbutane was not reactive.

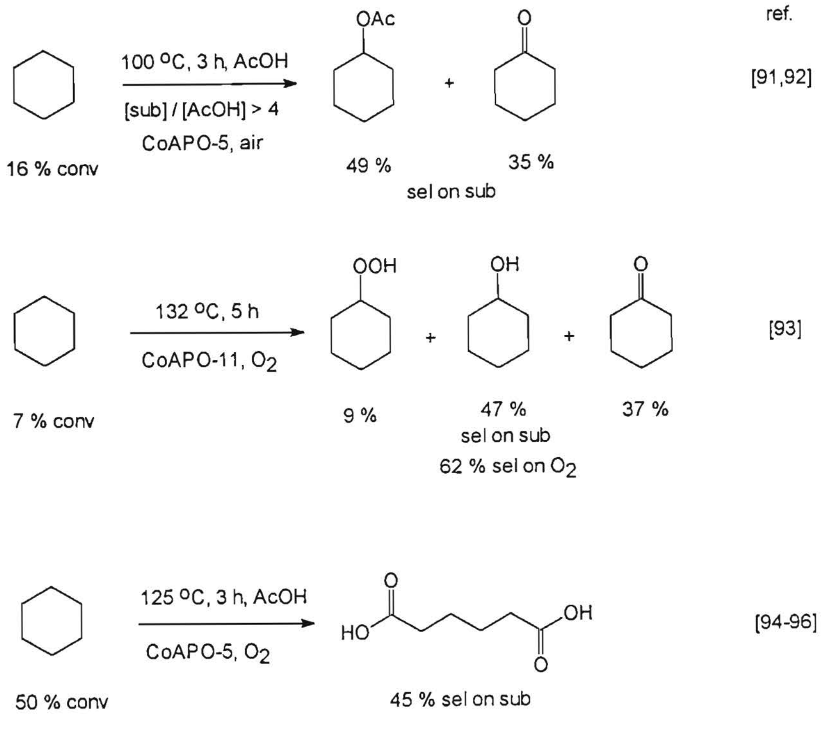


Figure 6: Oxidation of cyclohexane catalysed by CoAPO under various reaction conditions.

The reaction has also been carried out without any solvent using pure dioxygen at T = 130°C [93]. The performance of CoAPO-5 and CoAPO-11 was compared with the commonly applied homogeneous cobalt naphtenate catalyst and cobalt exchanged zeolite Y. Because the products are more sensitive to further oxidation than the substrate the reaction was carried out at low conversion levels of the substrate (about 5%). It was concluded that CoAPO is an active catalyst for this reaction. After removal of the catalyst from the reaction mixture the CoAPO could be used again after calcination without loss of activity. The CoAPO appeared to be stable: only 12 ± 3 ppb of Co could be found in solution. It was argued that this tiny amount of dissolved cobalt could not be responsible for the observed activity. For 100 ppb of dissolved cobalt naphtenate under the same reaction conditions only a six times lower conversion was found. Under the same conditions CoY, prepared by ion exchange methods, lost much of the cobalt during the reaction, indicating that CoAPO is in principle a different kind of catalyst. Next to the desired products an important reaction product appeared to be cyclohexyl hydroperoxide. The next step, decomposition of the peroxide towards cyclohexanol and cyclohexanone over CoAPO-5 appeared to be rather difficult as was found in an experiment were cyclohexyl hydroperoxide was used a substrate [100]. Because of more pronounced diffusion limitations in the small pore CoAPO-11 than in CoAPO-5 a lower activity of the CoAPO-11 was expected [93]. Surprisingly, CoAPO-11 was found to be more active than CoAPO-5. However, an inexplicably high substrate conversion of 2% was observed when AlPO-11 (without cobalt) was used, whereas AlPO-5 showed no activity at all. The use of acetic acid as promoter for the reaction caused leaching of the cobalt, although a substrate to acid ratio > 4 was used [92]. Furthermore, acetic acid seemed to act as inhibitor rather than a promoter.

The oxidation of cyclohexane to hexanedioic acid using CoAPO-5 as catalyst has been studied in much detail [94-96]. The applied reaction conditions were T = 115-135°C for 8 h using dioxygen as oxidant and acetic acid as solvent. Variation of the cobalt content of CoAPO, the amount of CoAPO, solvent effects (C_1 - C_6 acid), temperature, dioxygen pressure and the addition of promoters were studied. Yields of 45% hexanedioic acid at 50% conversion could be reached within 3 h. The cobalt content of CoAPO-5 (0.77-6.5 %wt Co), amount of CoAPO (0.01-2.5 g) and dioxygen pressure did not affect the reaction rate. The actual used substrate to acid ratio was about 1.3. Not surprisingly leaching of cobalt was observed (18% for a CoAPO containing 0.77 wt% of cobalt) [92]. Experiments with a homogeneous catalyst at relatively high cobalt concentration (more than 10 times higher compared with the loss of cobalt) show only a minor conversion of the substrate. From this experiment it was concluded that CoAPO acts as a true heterogeneous catalyst. Some remarks can be made about the cobalt content of the CoAPOs used. It was shown that a maximum level of 2.5 wt% of cobalt could be retained in the CoAPO-5 lattice [68], while in the discussed experiment CoAPOs containing up to 6.5 wt% cobalt were used.

- **Chromium containing aluminophosphate**

A number of articles about the application of chromium containing aluminophosphates [89,97-102] have appeared. CrAPO-5 has been found to be active in several reactions: decomposition of organic peroxides, oxidation of primary and secondary alcohols and the oxidation of alkanes and alkylaromatics. Several examples with some typical reaction conditions are shown in figure 7 and 8.

CrAPO-5 appeared to be a rather good catalyst for the oxidation of secondary alcohols [99,101,102]. Both dioxygen and TBHP could be used. The observed selectivities were relatively high, based on both substrate and peroxide. Double bonds such as those present in 2-methyl-5-(1-methylethenyl)-2-cyclohexen-1-ol (carveol) (figure 7) did not react. CrAPO-5 was recycled 4 times without significant decrease of conversion and selectivity based on data after 16 hour reaction time [101]. However, no initial reaction rates, which should be more valuable, were reported. Calcination of the CrAPO-5 between the successive steps appeared to be neccessary to restore activity. Primary alcohols could also be oxidised as shown by figure 7.

The oxidation of cyclohexane has been studied too [102]. Related to this reaction is the decomposition of alkyl hydroperoxides, from which especially the decomposition of cyclohexyl hydroperoxide and cyclohexenyl hydroperoxide by CrAPO-5 has been studied in detail [100,101]. Compared with the CoAPO-5 catalysed cyclohexane oxidation the CrAPO-5 is more selective towards the ketone. Decomposition of other peroxides also showed a higher selectivity towards the ketone, compared with the performance of homogeneous catalysts.

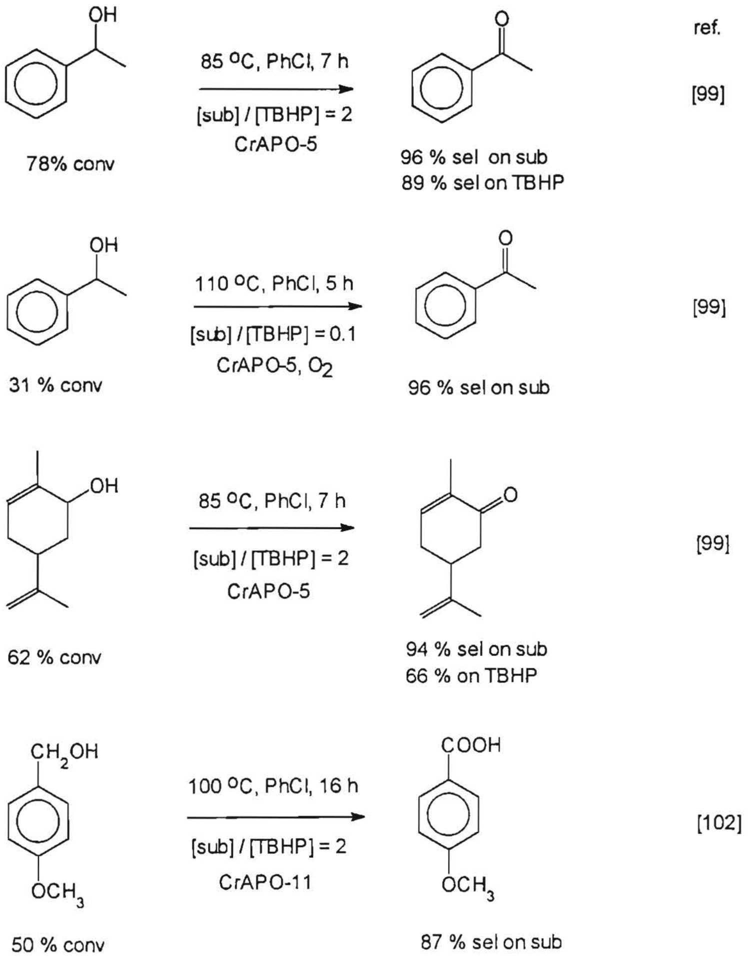


Figure 7: Some typical examples of the oxidation of alcohols catalysed by CrAPO.

Bulky organic peroxides like triphenylmethyl hydroperoxide could not be decomposed using CrAPO-5, while a homogeneous catalyst like chromium acetylacetonate ($Cr(acac)_3$) decomposes this peroxide easily. These observations were taken as an indication that the reaction takes place inside the pores of the CrAPO-5 [102]. Calcination of the CrAPO appeared to be neccessary to restore activity. After reaction no chromium ions could be found in the solution.

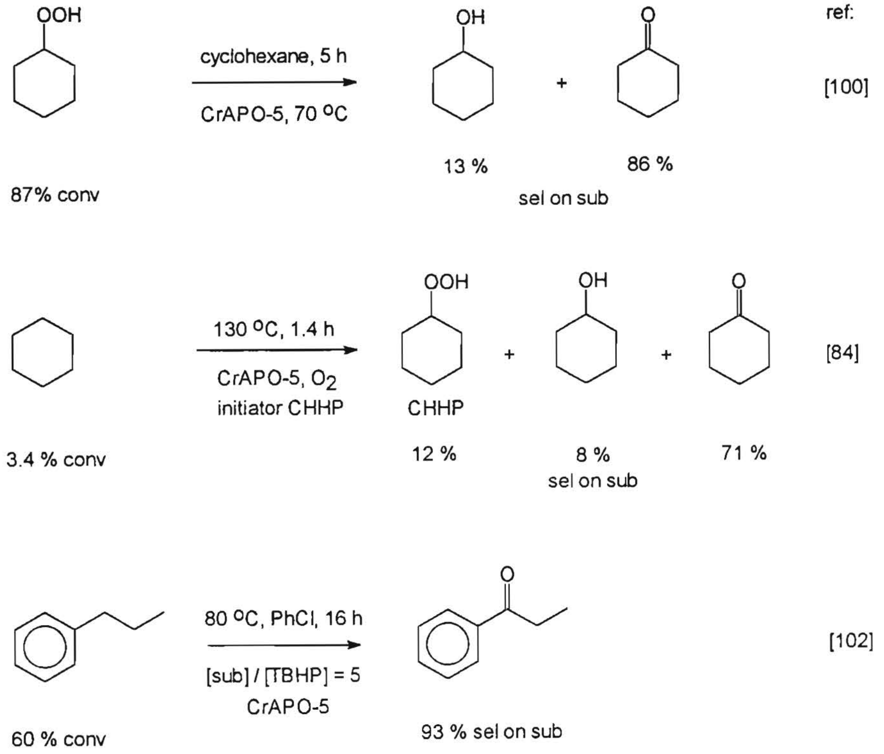


Figure 8: Miscellaneous reactions catalysed by CrAPO.

CrAPO-5 has been found to catalyse the oxidation of alkylaromatics to the corresponding alfa-ketones by applying TBHP as oxidant, an alternative process for Friedel-Crafts acylations [101]. A strong solvent effect was found in these reactions. Chlorobenzene gave the best results. Compared with homogeneous chromium catalysts CrAPO-5 was found to be more effective based on TBHP. CrAPO also showed activity as a catalyst for the oxidation of alkanes. It is interesting to note that no calcination step was necessary between successive reactions to restore activity of the CrAPO-5 when used as catalyst for the 1,2,3,4-tetrahydronaphthalene (tetralin) oxidation.

· Vanadium containing aluminophosphates

Vanadium containing aluminophosphate (VAPO-5) has been reported to be an active and stable catalysts in the epoxidation of alkenes and allylic alcohols by TBHP in chlorobenzene [87]. Some examples are shown in figure 8. Observed conversions and selectivities are relatively high. Cis-trans isomerisation hardly takes place as demonstrated by the epoxidation of cis-2-heptene. ^{51}V-NMR data showed that most of the available vanadium sites were accessible for a reaction with TBHP. Triethylamine was found to be preferably oxidised above 2,3-dimethyl-2-butene. The epoxidation of the latter compound started only after consumption of the triethylamine. Triphenylamine, that can not enter the pores of VAPO-5, did not influence the rate of the epoxidation reaction. Therefore it was concluded that the reaction takes place solely inside the pores of VAPO-5.

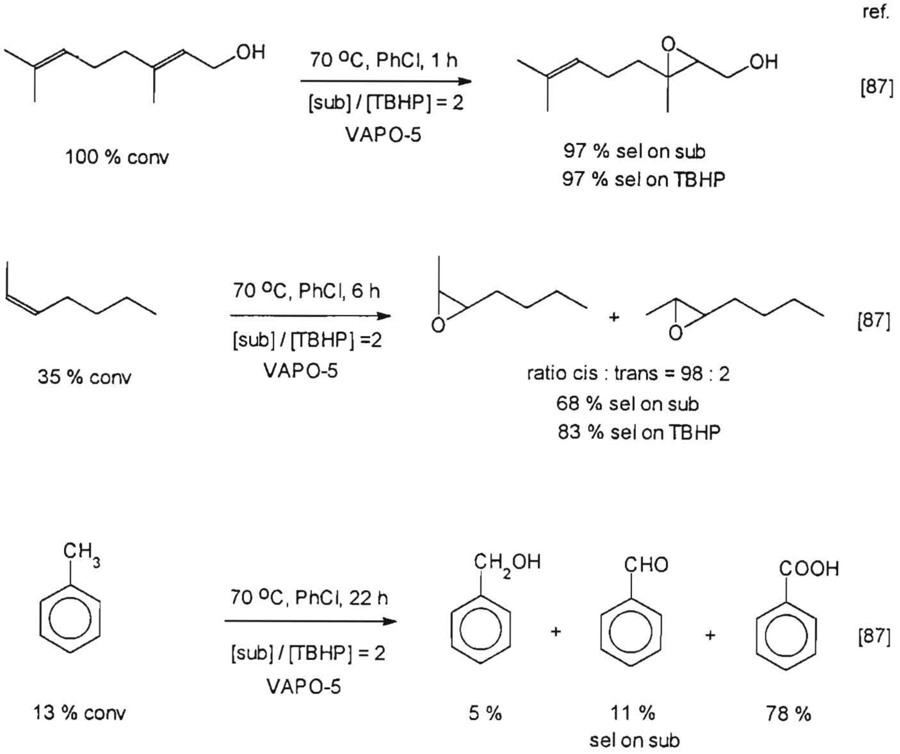


Figure 9: Reactions catalysed by VAPO.

VAPO-5 has also been tested as a catalyst for the oxidation of alkylaromatics using TBHP [103] or hydrogen peroxide [87,103]. The reactions using TBHP proceed rather slowly and the observed final conversions were low. Only side-chain oxidation has been observed. VAPO appeared not to be a suitable catalyst for the oxidation of toluene by hydrogen peroxide [103]. Extensive leaching of vanadium occured and no oxidation products were observed. Phenols were converted relatively rapidly but unselectively to quinones, whereas methoxybenzene was inert [87,103]. VAPO has also been tested as a catalyst in the oxidation of aniline with hydrogen peroxide and TBHP [104]

Some data have been published regarding the oxidation of cyclohexene and toluene catalysed by VAPO-31 [106]. The conversion of the substrate is probably very low, because of the rather low reaction temperature that was used (30°C).

- **Titanium containing aluminophosphates**

TAPSO-5 has been tested as catalyst for the epoxidation of cyclohexene by TBHP (figure 9) [107,108]. While TS-1 is not active in the epoxidation of cyclohexene by TBHP, the wide-pore TAPSO-5 is able to catalyse this reaction. In fact, the TAPSO can be regarded as the active site of TS-1 (presumably $(OSi)_4Ti$) incorporated in an aluminophosphate lattice. Both hydrogen peroxide and TBHP can be used as oxidant but different reaction products are formed. In case of hydrogen peroxide the predominant product is 1,2-cyclohexanediol, the presumed hydrolysis product of 7-oxabicyclo [4.1.0] heptane (cyclohexene oxide). The remarkably high selectivity based on the peroxide, until this moment only observed for titanium silicalite, makes this catalyst interesting for the oxidation of larger substrates. TAPSO is the first application of a MeAPO where hydrogen peroxide can be applied as oxidant. The incorporated silicon lowers the hydrophilicity of the MeAPO, which offers the possibility of fine-tuning the absorption properties of the catalyst.

Anatase free TAPO-5 and TAPO-11 have been tested as catalysts for the hydroxylation of phenol with hydrogen peroxide [109]. However, the selectivity of products based on the peroxide was not reported. The three fold excess of hydrogen peroxide over substrate that was used and the relatively low substrate conversion of 30% suggests that predominately peroxide decomposition takes place.

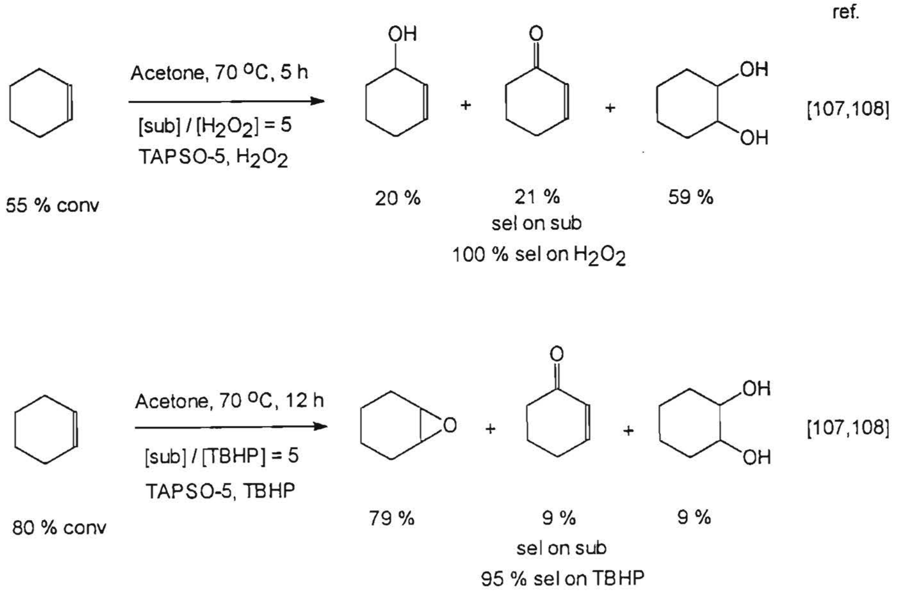


Figure 10: TAPSO catalysed oxidation of cyclohexene.

Gas phase oxidation reactions

Coupling of methane to C_6-C_{10} hydrocarbons has been reported to occur on MeAPO-5 and MeAPO-34 (Me = Co, Mn, Fe) [110]. The MeAPOs can be regenerated in situ either electrochemically or by passing dioxygen pulses through the reactor. VAPO-5 showed activity as a catalyst for the ammoxidation of propane to acrylonitrile [111]. When toluene and dioxygen were passed over VAPO-5 at 348°C total combustion of the toluene occured [105]. MnAPO-5, MnAPSO-5, Mn-APO-5, VAPO-5 and MgVAPO-5 have been tested as catalysts for the selective oxidation of ethane and propane to the corresponding alkene using dioxygen as oxidant [112-116].

Concluding Remarks

During the last few years it has become clear that the application of molecular sieves as oxidation catalyst in the liquid phase is not straightforward, but suffers from many problems. The validity of the concept 'reaction in micropores' is controversial. In many cases it is not sure whether the observed performance stems from a pure intraporous reaction. Theory predicts strong diffusion limitations, while it can be shown that TS-1 works in the way it is desired. Generally most attention is focused on the performance of the catalyst rather than on the behaviour of the catalyst. A critical evaluation of the known examples of catalysis by MeAPO does not show a dramatic shift in selectivity or increased activity. The facts that most activity in the oxidation of p-hydroxytoluene catalysed by CoAPO stems from dissolved cobalt rather than framework cobalt and that CrAPO needs to be calcined before re-use probably indicates that the concept does not hold in these cases. However, the wide variety of substrates and reaction conditions do not justify general rules. Nevertheless it seems clear that much attention has to be focused on the catalyst itself (stability and regenerability). Because there are doubts about the validity of the concept in relation to MeAPOs it is necessary to determine the contribution of the reactions that take place in the micropores.

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Synthesis and Characterisation of VAPO-5 and VAPO-11

3

Introduction

In this chapter the preparation and general characterisation of vanadium containing aluminophosphates will be discussed. The obtained materials have been used for the reactions described in the following chapters. As mentioned before in chapter 2, the preparation method is often decisive for the performance in catalytic reactions. From this chapter also a list of important requirements for obtaining potentially successful catalyst can be derived. Important properties are:

- Reproducible preparation from easily available sources.
- A well defined and accessible microporous structure.
- A small crystallite size (< 1 μm) to minimise pore diffusion limitations.
- Reasonable amount of isolated substituted metal ions.
- No free metal oxide formation.
- Tightly bonded metal ions.

This list of properties is used as a guideline for the synthesis of the vanadium containing molecular sieves. There are two commonly used preparation techniques: direct hydrothermal synthesis and post synthesis modification. In principle the hydrothermal synthesis offers a better way to obtain a material with highly dispersed vanadium ions than post synthesis treatment. From the list of interesting $AlPO_4$ structures (see page 25), the synthesis of vanadium analogues of the AFI structure (VAPO-5, VAPSO-5 and V-AlPO-5) is the most well studied [1-15]. These materials possess a relatively high stability, a large pore size and are easily prepared. VAPO-11 (AEL) [1] and VAPO-31 (ATO) [16] are also interesting.

The recipies for the preparation of VAPOs by hydrothermal synthesis are derived from standard methods used to prepare non-metal containing molecular sieves. As phosphorus source *ortho*-phosphoric acid has always been used. Pseudoboehmite [4,6,12,13] and less commonly aluminium triisopropoxide [9] were applied as aluminium sources. Vanadium pentoxide [1-8,10-12] and oxovanadium(IV) sulfate [7,9,13] can be used as vanadium sources, while ammonium vanadate gives only poorly defined products [7]. Triethylamine [7,14], tripropylamine [4,6-8] and tetrapropylammoniumhydroxide [9] were common template molecules to prepare VAPO-5. The addition of fluoride ions to the synthesis mixture of VAPO-5 resulted in the formation of better defined crystallites [9]. A somewhat different synthesis of VAPO-5 was decribed recently employing hydrazine and/or oxalic acid as additives for the reduction of the applied vanadium source vanadium pentoxide *in situ* [12,13]. Addition of fluoride ions to this gel did not lead to better products [12,13]. After crystallisation (between 150-200°C) and work-up, the template is removed by calcining in air. It is not clear if the reported variations in preparation methods yield different products with respect to the incorporation of vanadium ions. On first sight the differences seem to be small. VAPO-11 has been prepared using dipropylamine or diisopropylamine as template [1]. Diisopropylamine has been used as template for the synthesis of VAPO-31 [7].

Post modified vanadium oxide on AlPO-5 has been prepared by physical mixing of the AlPO-5 with vanadium pentoxide [10]. Alternatively, V-AlPO-5 was prepared by impregnation of ammonium vanadate from aqueous solution [5] or absorption of oxovanadium(V) trichloride from the gasphase into the sieve [11]. All preparation methods were followed by calcining [5,10,11].

In this chapter emphasis is placed on the direct synthesis of VAPO-5 and VAPO-11 by hydrothermal methods. The most important objective is the preparation of well defined VAPOs with variable vanadium content and crystallite size. Only the general properties of the samples will be discussed like the vanadium content, purity, yield, pore volume and morphology. Questions concerning the structure and location of the vanadium site(s) will be mainly discussed in the following chapter. For the characterisation of the products common techniques are used [17]: XRD; SEM; elemental analysis (P, Al and V), and determination of the pore volume (PV) by sorption methods (*n*-butane and dinitrogen). For the description of the VAPO synthesis the general recommendations of the IZA Synthesis Commission are followed [18]. The experimental procedures are mentioned at the end of the chapter.

Results and discussion

Synthesis of VAPO-5

VAPO-5 has been synthesized according to a slightly modified literature method [4]. The used aluminium-, phophorus- and vanadium source are pseudoboehmiet (AlOOH), ortho-phosphoric acid (H_3PO_4) and hydrated oxovanadium(IV) sulfate ($VOSO_4.5\ H_2O$), respectively. Triethylamine and tripropylamine were used as template. In this thesis these systems will be referred to as the 'triethylamine synthesis' (products 'E') and the 'tripropylamine synthesis' (products 'P'). The components were mixed in a molar ratio as given by the gel formula. In this formula the sources of the elements are expressed in their oxidic form. The actual used gel composition for the synthesis of VAPO-5 is:

$1\text{-}x\ Al_2O_3 : 1.01\ P_2O_5 : x\ V_2O_5 : 1.3\ T : y\ H_2O.$

$x = 0 - 0.07$;
$y = 42$ (static synthesis) or $y = 35$ (stirred synthesis);
$T = Et_3N$ or Pr_3N

The vanadium content of the gel is the main variable. During the preparation all mixing orders and ageing times were kept constant. The final gels were viscous and had a slightly acidic pH between 4-5. The mixture was crystallised at 160°C-170°C for 48 hours using a static autoclave. A stirred autoclave operated at 130°C for 18 hour was used to stimulate the formation of small crystallites. The combination of a more concentrated gel, lower crystallisation temperature and shorter crystallisation time are well known factors to induce the formation of many crystallisation nuclei resulting in small crystallites. After work-up the products were calcined in air at 550 °C.

Table 1: Synthesis of VAPO-5 using triethylamine as template.

Code	V_{gel}[a] (at%)	Prod. Comp. (at%)[a] Al	P	V	$V_{prod.}$ (%wt)	PV (ml/g) *n*-butane	SEM morphology
Static synthesis							
E0	0	50.4	49.6	0.0	0.0	0.096	-[b]
E1	0.42	50.6	49.2	0.18	0.15	0.090	dense agglomerates diameter 20 μm
E2	0.97	-[b]	-	0.31	0.26	0.093	particles ≈ 1 μm; some agglomerates
E3	1.28	-[b]	-	0.64	0.53	0.101	-[b]
E4	1.52	49.5	49.4	1.16	0.91	0.109	dense agglomerates 15 μm
E5	1.93	51.9	47.0	1.13	0.92	0.115	dense agglomerates 12 x 8 x 8 μm
E6	2.55	50.2	48.6	1.18	0.93	0.116	dense agglomerates 15 x 10 x 8 μm
Stirred synthesis							
E7	1.01	54.6	44.9	0.52	0.488	0.097	stacked hexagonal plates (2 x 2 x 0.3 μm)
E8	2.03	49.9	49.1	1.00	0.992	0.113	-[b]

---

[a]: Oxygen not included in the calculation.

[b]: Not determined.

Table 2: Synthesis of VAPO-5 using tripropylamine as template.

Code	V_{gel}[a]	Prod. Comp. (at%)[a]			$V_{prod.}$	PV (ml/g)	SEM morphology
	(at%)	Al	P	V	(%wt)	*n*-butane	
Static synthesis							
P0	0.44	50.8	48.7	0.43	0.35	0.096	dense agglomerates 20-50 μm
P1	0.81	-[b]	-	0.70	0.59	0.094	dense agglomerates 15-25 μm
P2	1.67	51.0	47.6	1.42	1.15	0.090	dense agglomerates 10-30 μm
P3	2.00	50.7	47.5	1.79	1.49	0.103	dense agglomerates 25 μm
P4	2.00	50.6	47.6	1.78	1.48	0.098	-[b]
P5	2.00	-[b]	-	1.70	1.40	0.086	-[b]
P6	2.50	50.7	47.2	2.02	1.68	0.102	dense agglomerates 10-20 μm
P7	2.91	49.6	47.9	2.29	1.90	0.093	dense agglomerates 30 μm
P8	3.45	-	-	2.45	2.03	0.081	dense agglomerates 15 μm
Stirred synthesis							
P9	1.20	51.6	47.3	1.11	0.912	0.102	bundle of fine rods 2 x 0.5 x 0.5 μm
P10	2.03	51.3	47.0	1.75	1.43	0.100	bundle of fine rods 2 x 1 x 1 μm

[a]: Oxygen not included in the calculation.
[b]: Not determined.

The results of the 'triethylamine synthesis' and the 'tripropylamine synthesis' are described in table 1 and 2, respectively. As can be seen the tables show striking differences between the use of different templates, especially with respect to the vanadium content in the final product.

An important parameter is the yield. Yields are not commonly mentioned in the field of molecular sieve synthesis. Nevertheless, for a presumed application on an industrial scale high yields are important. Although not mentioned in table 1 and 2, the product yields were superior in the case of the synthesis with tripropylamine. The product yield of VAPO-5 obtained from a synthesis with tripropylamine is between 75-80 % (product without template), while it is only 30-35 % in the case of triethylamine. The yield is independent of the vanadium content in the gel.

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. Diffraction patterns of calcined products obtained from a triethylamine synthesis (E4) and static tripropylamine syntheses (P0 and P7) are shown in figure 1. These patterns are similar to those reported in the literature [19].

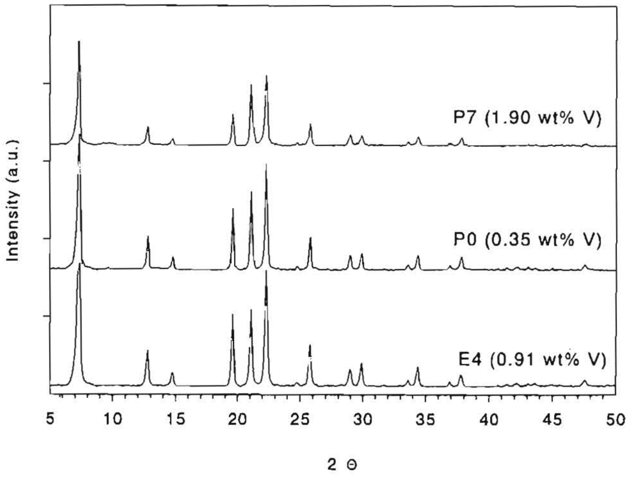

Figure 1: Some typical diffractograms of VAPO-5

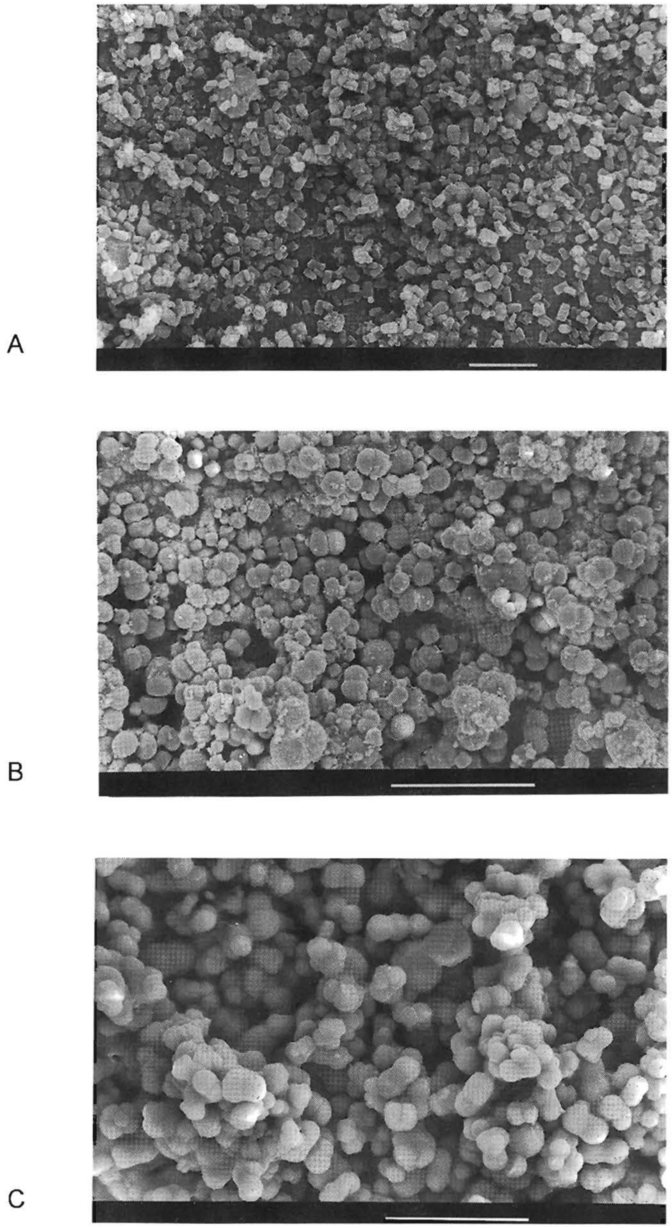

Figure 2: Different morphologies observed for VAPO-5.
A. E10 (1400x; bar: 10 μm);B. E4 (300x; bar: 100 μm); C. P6 (300x; bar: 100 μm).

No additional phases than AFI are present. The intensity of the peaks in the product with a high vanadium content seemed to be somewhat lower, indicating some loss of crystallinity. It should be noted that the preparation of the gel has to be performed very carefully: poor mixing resulted in the formation of crystalline impurities with a non-porous tridymite structure, which has main peaks at 2Θ = 20.2°; 21.8° and 35.5° (Cu-Kα).

Pore volume measurements showed that all samples have a well developed micropore structure. The maximum loading of *n*-butane in AlPO-5 is about 0.130 ml/g [20]. Practically, the pore volumes of all prepared samples fall within 70% of this value. A trend seems to be a slight decrease of the pore volume when the vanadium content becomes higher. This possibly indicates that the samples with the higher vanadium content have more structural defects. A too low pore volume may manifest itself in a diminished reaction rate because the active sites become less accessible for the reactant. It should be noted that a few distortions or structural defects may block a one-dimensional pore structure completely.

Figure 2 shows some typical examples of morphologies obtained from the different preparation methods. The main difference in morphology was found between the use of a static and a stirred autoclave. The crystallisations carried out in a stirred autoclave yield, as expected, much smaller particles than the products from a static crystallisation. In figure 2A a typical product from a stirred crystallisation can be seen. The batches are rather homogeneous with a crystallite size of about 1 μm. A closer look reveals that some crystallites are aggregated. On the other hand, products obtained from a static autoclave may be described as spheres of about 10-20 μm, sometimes stuck together. However, a more closer look reveals that the spherical particles also consist of much smaller crystallites, comparable with those obtained from a stirred synthesis. Thus, stirring prevents the agglomeration of the crystallites. The spherical particles can therefore be regarded as more or less dense agglomerates of small crystallites. The size of such crystallites is typically smaller than 1 x 0.3 x 0.3 μm. Sometimes hexagonal crystallites can be recognised. Note that the direction of the pores is probably perpendicular to the hexagonal plane of the crystallite [22]. The statement that the particles are not massive is supported by the observation of hysteresis in the nitrogen absorption isotherms. Therefore in addition to micropores the particles also possess a mesoporous structure. Despite a mesoporous structure the outer surface contributes only little to the total surface area. The total surface area of a VAPO-5 calculated from dinitrogen absorption isotherms (BET method) was about 280 m^2/g. The (outer) surface area of a dense phase VAPO is only 5 m^2/g, and contributes less than 2%. On a molecular or nanometer level it is not to be expected that the reactants 'feel' a difference between products prepared by a stirred synthesis or a static synthesis. The only difference between the 'stirred' and the 'static' method is the formation of more or less dense aggregated crystallites. From an industrial point of view the large aggregates are preferable because they are more easier to remove from the reaction mixture by filtration.

In table 1 and table 2 the product composition has been mentioned. This 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 analysis was never 100%, but typically 95%. This systematic error can be due to the rapid absorption of water during the sample preparation. The product composition, given in at%, is normalised at 100%. Products from the triethylamine synthesis and the tripropylamine synthesis always show a slight enrichment of the aluminium content. The elemental analysis refers to the question, asked for all MeAPOs, whether the guest ion is substituted for the aluminium or phosphorus. For ions like cobalt(II) or manganese(II) this question seems trivial, the most likely position seems is the aluminium ion. For vanadium(IV) the situation is less clear [6,9,14].

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 about the substitution pattern, when the guest ion is present at levels of about 1 %wt. The data from table 1 and 2 suggest the presence of a small amount of aluminiumoxide (Al_2O_3) or substitution of vanadium for phosphorus (Al = P + V), contrary to results mentioned in literature [9].

The preparation of the VAPO with tripropylamine seemed to be well reproducible with respect to the purity and the vanadium content (table 2: compare P3, P4 and P5). The triethylamine synthesis appeared to be more sensitive to small variations in the recipe as can also be seen in the scattering of the data points in figure 3. In these figures the amount of vanadium in the gel is directly compared with the amount of vanadium found in the final product. In the tripropylamine synthesis vanadium is efficiently incorporated into the lattice ($V_{product}$ / V_{gel} ≡ 90-100 %; for products containing less than 1.50 %wt V). Compared with reported results, vanadyl sulfate as vanadium source is much more effective than vanadium pentoxide, where the efficiency is generally less than 50 % [4]. Triethylamine influences the efficiency of the vanadium incorporation negatively. *Via* the tripropylamine synthesis more than 2.0 wt% of vanadium can be incorporated, while via the triethylamine synthesis 1.0 wt% of vanadium is a maximum. Comparable maximum amounts have been mentioned in the literature [7,9]. The reason for this observed behaviour is not clear. Chemically, triethylamine and tripropylamine differ only in their size, other properties like pK and polarity are at least comparable. It has been proposed that vanadium is incorporated on lattice defect positions [9,13]. A possible explanation for the differences between the triethylamine synthesis and the tripropylamine synthesis could be the formation of more defect sites in the aluminophosphate lattice when tripropylamine is used as template. Another possible explanation can be the strong interaction of vanadium with the template under reaction conditions [13].

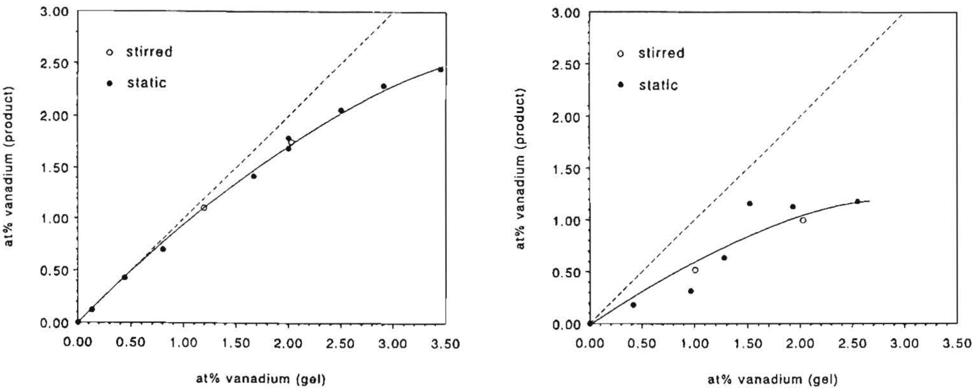

Figure 3: The effect of the template on the efficiency of the incorporation of vanadium: tripropylamine (left) and triethylamine (right). The dashed line represents the case were there is a one-to-one relation between the amount of vanadium in the gel and the amount of vanadium found back in the product. The figures includes data from additional VAPO-5 products not mentioned in table 2 and 3.

B. Synthesis of VAPO-11

The VAPO-11 synthesis is much less documented than the VAPO-5 synthesis [1]. In order to prepare a well defined VAPO-11 the following gel composition has been used.

1-x Al_2O_3 : 1.01 P_2O_5 : 1-x V_2O_5 : 1.0 T : 42 H_2O

x = 0 - 0.07;
T = Pr_2NH or iPr_2NH

Comparable gel compositions were used to prepare CoAPO-11 [23].
Pseudoboehmite, phosphoric acid and oxovanadium sulfate were used as starting materials. After mixing the gel had a pH between 2-3. The gel was crystallised at 200°C for 48 h. After work-up the template was removed by calcining in air at 550°C. Products with the highest vanadium content are yellow coloured.
Properties of some typical products (products 'D') are described in table 3.

The yields of the VAPO-11 synthesis are high (about 80%, calculated for product without template). XRD spectra show that samples with a low vanadium content (< 0.5 %) are sufficiently pure. However, crystalline impurities are formed when the vanadium content increases (figure 4). At the same time, the intensity of the X-ray diffractogram, which is a measure for the crystallinity of the sample, decreased. The main peaks of the impurities are found at 2Θ = 5.9°; 6.3°; 9.8°; 12.8°; 13.7°; 15.9° (Cu-Kα). The amount of the impurities were estimated to be more than 10%. Because these impurities have reflections at very low 2Θ it probably originates from a microporous aluminophosphate with a pore size larger than that of VAPO-11.

The pore volumes of the pure samples, measured by n-butane absorption, are about 20% lower compared with reported values [22]. Note that the poor quality of sample D3 as determined by XRD is directly reflected in a lower pore volume. The VAPO-11 batches consist of fine blocks with dimensions less than 1 μm (figure 5), sometimes together with a not well crystallised gel-like phase. Several parameters were varied to obtain a pure VAPO-11 with a high vanadium content (> 0.5 %wt)

Table 3: Synthesis of VAPO-11 using diisopropylamine as template.

Code	V_{gel} [a] (at%)	Prod. Comp. (at%) [a] Al	P	V	$V_{prod.}$ (%wt)	PV (ml/g) n-butane	SEM morphology
Static synthesis							
D0	0	50.4	49.3	0.0	0.0	0.068	- [b]
D1	0.55	50.8	48.8	0.38	0.32	0.076	undefined + blocks (≈ 0.8 x 0.6 x 0.4 μm)
D2	1.17	50.7	48.6	0.76	0.63	0.066	blocks (≈ 1.0 x 0.4 x 0.4 μm)
D3	2.00	- [b]	-	1.11	0.93	0.052	- [b]

[a]: Oxygen not included in the calculation.
[b]: Not determined.

and a high crystallinity: the crystallisation temperature and -time, the amount of template, the template itself and the aluminium source. Variation of the crystallisation temperature (150°-200°C) en time (24-84 h) did not lead to any improvements of the quality of the obtained VAPO-11. At lower crystallisation temperature even more peaks are found at low 2Θ. The amount of template strongly influences the pH of the gel. Upon increasing the template / Al_2O_3 ratio from 1.0 to 2.0 the pH of the gel rises from 2.6 to 6.5. Under these conditions still VAPO-11 is still formed but never free from crystalline impurities. From the VAPO-5 synthesis it is known that the pH rises quickly to about 7 or 8 when the crystallisation starts [6]. The actual pH becomes probably comparable during all crystallisations, which explains the small influence of the initial pH on the composition of the final product. With aluminium triisopropoxide as aluminium source instead of pseudoboehmite no other crystalline phases were obtained but the samples had a relatively low crystallinity and low pore volume (less than 0.05 ml/g n-butane).

The poor quality of the products is probably caused by the high reactivity of aluminium triisoproxide. The use of another template, dipropylamine, in the

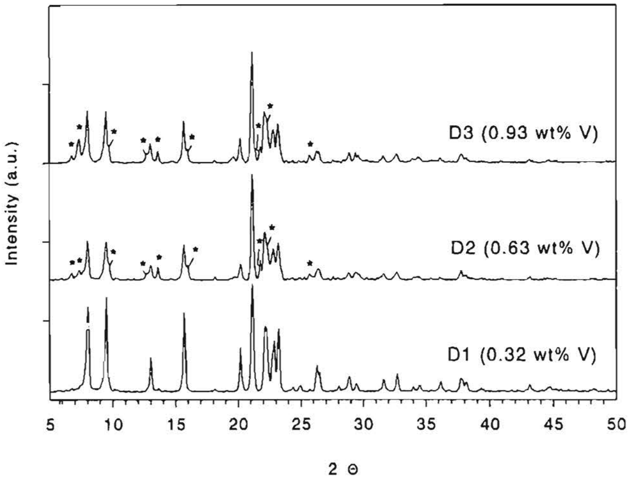

Figure 4: Typical XRD patterns of VAPO-11 products.
A: D1 (0.32 wt% V); B: D2 (0.63 wt% V); C: D3 (0.93 wt% V).
The stars indicate impurities.

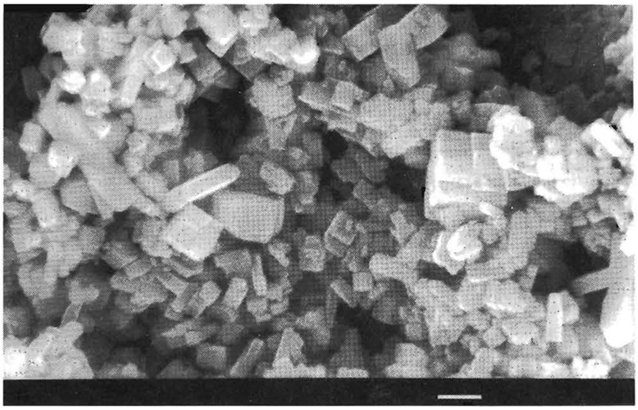

Figure 5: Typical morphology observed for VAPO-11.
D2 (8000x, bar: 1 μm)

standard synthetic method gives an as synthesised VAPO-11 without impurities. However, the structure collapses partially upon calcining, yielding a mixture of VAPO-11 and tridymite.

Obviously, the preparation of pure, highly crystalline VAPO-11 with a high vanadium content needs a different synthetic procedure. The presence of oxovanadium ions in the gel is therefore not favorable for the crystallisation of aluminophosphates. The formation of the AFI structure in the VAPO-5 synthesis is relatively less disturbed by the vanadium ions. On the other hand, the hydrothermal synthesis of a VAPO-31 appeared to be even more critical than the VAPO-11 synthesis. A crystallographically pure AlPO-31 (ATO) could be prepared using a modified procedure described in the literature [20,21]. The addition of a very small amount of oxovanadium sulfate (less than 0.1 wt% V) to this gel did not result in the formation of VAPO-31 but to an impure VAPO-11 in low yield. From the literature it is known that the vanadium containing analogue of the chabazite structure, VAPO-44, could also not be obtained while the synthesis of AlPO-44 was possible [15].

Concluding remarks

Regarding properties like the quality of the product, yield, efficiency and reproducibility tripropylamine is the template of choice for the preparation of VAPO-5. Pure VAPO-5 with a vanadium content of 2.0 %wt can be prepared using tripropylamine as template. Homogeneous batches with crystallites smaller than 1 μm can be prepared by stirred synthesis. In a static synthesis the crystallites tend to aggregate. Small amounts of vanadium have already a negative effect on the crystallisation of VAPO-11. Using the standard preparation method samples with less than 0.5 %wt vanadium could be prepared which were crystallographically pure.

Experimental Procedures

Sources

The following chemicals were used:

Hydrated oxovanadium(IV) sulfate, Merck, 99%;
Ortho-phosphoric acid, Riedel-de Haen, 85% or Merck, 89%;
Pseudo-boehmite, Condea, 75%;
Triethylamine, Janssen, 98%;
Tripropylamine, Janssen, 98%;
Aluminium triisopropoxide, Janssen, 98+%;
Diisopropylamine, Janssen, 99%;
Sulphuric acid, Merck, 98% P.A.

Synthesis of VAPO-5-E5 (Static, template = triethylamine)

In 40 ml (2.2 mol) of water 2.40 g ($9.1.10^{-3}$ mol V) of hydrated oxovanadium(IV)sulfate was dissolved. This solution was added to a solution of 27.0 g (0.234 mol P) of *ortho*-phosphoric acid in 40 ml (2.2 mol) of water. Then under stirring 15,5 g (0.228 mol Al) of *pseudo*-boehmite was added within 10 minutes. The suspension was vigirously mixed for 60 minutes at room temperature. To the viscous gel slowly and under stirring 15,0 g (0.148 mole) of triethylamine was added slowly. The resulting mixture was again vigirously stirred for 30 minutes. Then the gel was transfered into a teflon lined stainless steel static autoclave. The pH of the synthesis mixture was determined before and after the crystallisation. The mixture was crystallized for 48 h at 160-170°C. The resulting product was recovered by centrifugation and washed with water. After drying at 80°C this sample was calcined in flowing air using the temperature program: 120°C, 1 h; heat up with 3°C/min to 550°C that is kept at this level for 4 h; slowly cool down to room temperature. Samples were stored in an dessicator.

Synthesis of VAPO-5-P10 (Stirred, template = tripropylamine)

A solution consisting of 4.80 g ($1.90.10^{-2}$ mol V) of hydrated oxovanadium(IV) sulfate and 53.0 g (0.460 mole P) of *ortho*-phosphoric acid in 140 ml (8.6 mol) of water was prepared. To this solution 30.5 g (0.448 mol Al) of *pseudo*-boehmite was added in small portions. During this process the solution was stirred at room temperature. This stirring was continued for 60 minutes after the addition. After that 30 g (0.296 mol) of tripropylamine was slowly added and the mixture was stirred for another 30 minutes. The gel was crystallised in a 300 ml teflon lined stirred autoclave at 130°C and 30 rpm for 17 hours. The work-up procedure was similar to the procedure decribed earlier.

Synthesis of VAPO-11-D1 (Static, low vanadium content)

A oxovanadium(IV)sulfate solution was prepared by dissolving 0.65 g ($2.57.10^{-3}$ mol) of hydrated oxovanadium(IV) sulfate in 40 ml (2.2 mol) of water. This solution was mixed up with a solution of 26.3 g (0.239 mol) *ortho*-phosphoric acid in 40 ml of water (2.2 mol). Then 15.5 g (0.228 mol Al) of *pseudo*-boehmite was added slowly under stirring. The suspension was stirred for 60 minutes at room temperature. After this ageing period 12.5 g (0.124 mol) of diisopropylamine was added in 10 minutes. After stirring for another hour the gel was transfered to a static autoclave and crystallised at 200°C for 48 h. A similar work-up procedure was used as decribed for the VAPO-5 synthesis.

Synthesis of VAPO-11 (Static, high vanadium content, aluminium triisoproxide)
In 40 ml (2.2 mol) of water 47.0 g (0.226 mol Al) aluminium triisopropoxide was slowly added and under stirring in one hour at room temperature. After adding 5 g of the aluminiumtriisoproxide some drops of phosphoric acid were added to speed up the hydrolysis. To the resulting gel a combined solution of phosphoric acid and oxovanadium(IV) sulfate was added in 10 minutes (26.3 g (0.239 mol P) of *ortho*-phosphoric acid and 2.4 g (0.0948 mol V) of hydrated oxovanadium(IV) sulfate dissolved in 40 ml (2.2 mol) of water). The stirred grey blue solution was aged for additional 15 minutes before it was transferred to a static autoclave and crystallised at 180°C for 40 hours. After work up the product was sieved.

Instrumental
X-ray diffraction patterns were collected on a Philips PW 7200 X-ray powder diffractometer using Cu-Kα radiation. Data was obtained between $2\alpha = 5°C$ and $2\alpha = 50°C$ with a scan speed of 1° per minute. The patterns were corrected for baseline, background and K2α-elimination.

Pore volume measurements were carried out on a CAHN 2000 electrobalance using n-butane sorption. Approximately 15 mg of the sample was heated to 350°C in a stream of purified helium (225 ml/min). After cooling down to room temperature the sample was exposed to n-butane (flow n-butane = 18 ml/min). The pore volume was calculated from the absorbed amount. Nitrogen absorption isotherms were measured with a Sorptomatic 1900 (Carlo Erba). Each sample was degassed at 300°C for 4 hours.

SEM photographs were taken using a Jeol JSM-840A Scanning Microscope. The operating conditions were 20 - 35 kV, $3.0.10^{-11}$ - $1.0.10^{-10}$ A, working-distance 8 or 15 mm. The samples were glued on a graphite block with a colloidal carbon paste. Alternatively, a suspension of VAPO in isopropanol was prepared by mixing in an ultrasonic bath. A small droplet was brought on a graphite block and dried in air. Finally samples were sputtered with gold.

Vanadium and aluminium were analysed using a Perkin-Elmer PE 3030 Atomic Absorption Spectrophotometer. The standard addition method was used for the determination of vanadium, while a calibration curve was used for the analysis of aluminium. VAPO was dried for at least one hour at 120°C. About 0.10 - 0.25 g of VAPO was dissolved under heating in 10 ml of diluted sulfuric acid. Phosphorus was analysed photometrically as molybdeneblue complex according to NEN 3104 (1973). Aluminium and phosphorus were determined from the same solution.

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Structure of the vanadium site(s) in VAPO

4

Introduction:

The properties of the metal site of a catalyst (valency, coordination number, structure, bonding to donor atoms and redox behaviour) may influence the performance of the catalyst. An illustrative example is the difference in catalytic activity between monomeric titanium species in TS-1 and polymeric anatase (TiO_2).

The nature and properties of the vanadium site in (aluminophosphate) molecular sieves is a subject of debate in literature [1-8]. Up till now it has still not unambiguously been proven that the vanadium ions are incorporated in the framework. The incorporation mechanism is probably much more complex than in the case of cobalt(II) [9], not only because of the different charge but also because vanadium(IV) is prone to condensation reactions in solution which lead to a variety of oligomeric species [10]. Nevertheless, it seems clear that at least part of the vanadium ions are bound to the lattice, because they cannot simply be removed from it by ion exchange or washing [4,7].

Several techniques were applied to study the vanadium site in VAPO-5. The most important are: ESR [2-8], DRUVVIS [3,6,7], XPS [3], temperature programmed techniques [2,3,7] and ^{51}V-NMR [4,7]. The structure of the vanadium site present in both non-calcined (V(IV)) and calcined samples (V(V)) was studied. Models (figure 1A and 1B) show hypothetical structures after substitution of aluminium or phosphorus by vanadium. Substitution of phosphorus by V(IV) [2] is mainly favoured by arguments like the similarities between vanadium and phosphorus chemistry [11,12]. The other model, replacement of an aluminium ion for an oxovanadium one

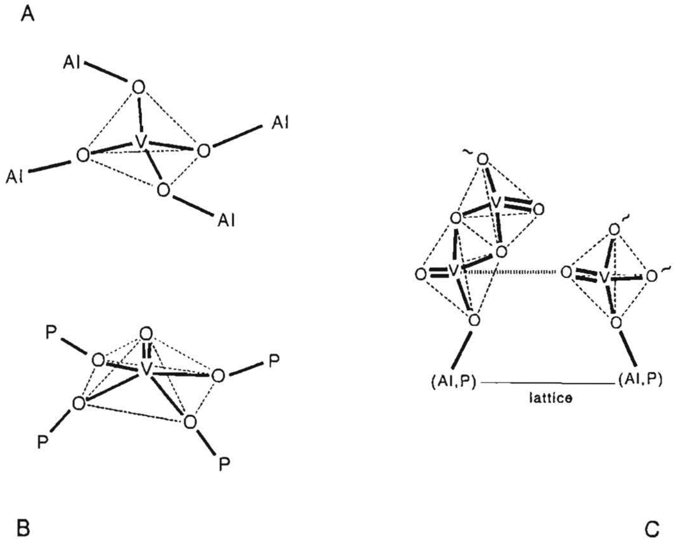


Figure 1: Suggested models for the vanadium site in calcined and dry VAPO-5.

A. Vanadium(V) on a phosphorus position [2], resulting in a four coordinated species.

B. Five coordinated oxovanadium(V) on an aluminium position [4].

C. Clustering on a defect site [6]. This example shows two four coordinated and a five coordinated species.

(V=O(II)) seems to be more convincing, since it is supported by spectroscopic evidence [4]. From ^{51}V-NMR and ESR data it was concluded that vanadium in a calcined VAPO-5 is present as a monomeric square pyrimidal oxo complex and thus imperfectly substituted (a perfectly substituted vanadium should be tetrahedral). As discussed earlier arguments based on elemental analysis cannot distinguish between replacement of aluminium or phosphorus in VAPO because the available analysis techniques are not accurate enough.

Both propositions have in common that the vanadium sites are monomeric. The key argument used for this conclusion is the highly resolved ESR spectrum observed for a non-calcined VAPO [2-8]. However, clustered vanadium(IV) ions may be invisible due to line broading caused by spin-spin coupling of strongly interacting ions. Earlier, it was attempted to determine the amount of vanadium(IV) in VAPO-5 quantitatively by ESR-spectroscopy as well as by manganometric titration [3]. If the vanadium ions tend to cluster the amount of vanadium(IV) found by ESR would be lower than those detected by titration which detects all vanadium(IV). Actually, this difference was negligible [3], indicating that the vanadium is monomeric. Recently it was found that the measured spin density corresponded to less than 10% of the vanadium(IV) present in VAPO [6]. From this combined DRUVVIS and ESR study it was concluded that the multinuclear vanadium(IV) species are attached to rather than incorporated into the framework (figure 1C). A similar conclusion was drawn from a study of the incorporation of vanadium in VAPSO-5 [8].

For our purpose, the application of VAPO as a catalyst for liquid phase oxidation reactions, we strive for a well defined VAPO-material. The major questions deal with the nature and number of different vanadium species. Futhermore, the calcination procedure may be important. Upon calcining vanadium(IV) is oxidised and dehydrated, which may also have an influence on its incorporation. For instance, due to thermally induced condensation reactions vanadium pentoxide (V_2O_5) may be formed. Since it is known that vanadium pentoxide shows catalytic activity in many oxidation reactions but in a rather non-selective way, it may disturb the reactions (see chapter 5).

In the present study several techniques (DRUVVIS and ESR) were applied to investigate the vanadium site in a series of VAPO-5 and VAPO-11 samples. The synthetic procedures for these samples were decribed in the previous chapter. In chapter 3 it was also shown that VAPOs prepared with triethylamine as template are different from those for which tripropylamine was used. It is not clear whether or not a different synthetic procedure can give rise to the formation of different vanadium sites. Attention will be paid towards this aspect.

Results and discussion

DRUVVIS

The electronic absorption spectrum provides information about various aspects of the V(V)-ion. Firstly, the coordination number of vanadium can be deduced from it. Regions for four-, five and six coordinated vanadium ions can be identified [13].

Secondly, the comparison of spectra of VAPOs with different vanadium contents makes it possible to detect changes such as the formation of different vanadium oxide phases (monomeric, oligomeric or polymeric). However, DRUVVIS is not sensitive enough to distinguish between incorporated and extra-lattice vanadium sites. For a fair comparison of the spectra they need to be recorded in a quantitative way. However, this is not possible without special precautions. To obtain a quantitative absorption spectrum various requirements must be fulfilled. Details about this technique are discussed in the appendix.

· Variation of the vanadium content in VAPO

VAPO-5 samples with a low vanadium content are white. When the vanadium content of the VAPO increases the material shows a yellow color. The color change is reflected in the DRUVVIS spectra as an increasing absorption below 25000 cm^{-1} (figure 2). The samples prepared with tripropylamine show an increasing absorption when the vanadium content becomes higher. A similar feature is observed for samples prepared with triethylamine. However, samples prepared from a gel containing more than 0.90 at% vanadium show a decreased absorption.

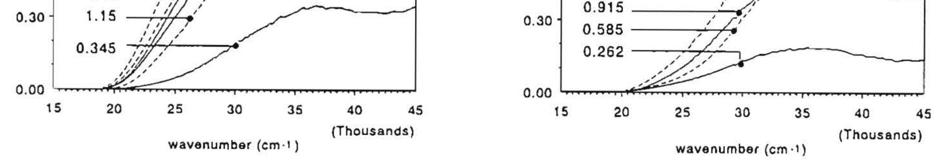


Figure 2: DRUVVIS spectra of dry VAPO-5 with a variable vanadium content: Tripropylamine synthesis (left); Triethylamine synthesis (right).

In chapter 3 it was demonstrated that triethylamine and tripropylamine give different results with respect to the formation of the AlPO-5 lattice. Comparing DRUVVIS spectra of VAPO-5s prepared with different templates and a similar final vanadium content does not show any influence on the final surrounding of the vanadium ions. The spectra of VAPO-11 are comparable to those found for VAPO-5 (not shown).

If the vanadium content of the samples is increased, the shape of the absorption curve alters. This is shown in figure 3. Samples with a low vanadium content show an absorption maximum at about 36000 cm^{-1} (280 nm). At higher vanadium contents the intensity around 26000 cm^{-1} (385 nm) increases relative to the intensity of the 36000 cm^{-1} band. This is an indication for the formation of an additional vanadium species, which is even more predominant in the spectrum of a aluminophosphate supported vanadium oxide with a high vanadium content.

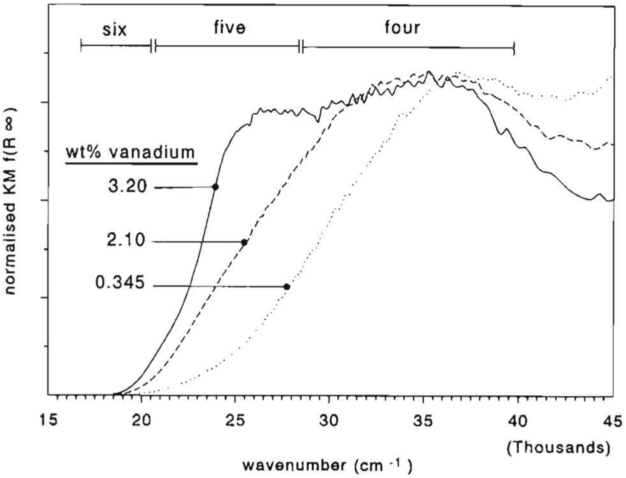


Figure 3: DRUVVIS spectra of dry VAPO-5 with a variable vanadium content showing the change of the shape of the absorption upon increasing vanadium content. Regions for four, five and six coordinated species are indicated.

The origin of the observed transitions is the charge transfer $O^{2-} \rightarrow V^{5+}$. The position of the absorption maximum is strongly influenced by the number of donor atoms [13]. Roughly, octahedral vanadium shows an absorption maximum between 17000 - 20000 cm^{-1} (500-600 nm), five-coordinated vanadium between 20000 - 28000 cm^{-1} (350-500 nm) and four-coordinated vanadium between 28000 - 40000 cm^{-1} (250-350 nm). From the spectra it can be deduced that VAPOs with a low vanadium content contain mostly tetrahedrally coordinated vanadium(V). At higher vanadium contents an additional five-coordinated species is formed. With respect to this property, VAPO resemblances vanadium oxide supported on silica or alumina [14,15]. In these materials vanadium is also tetrahedrally coordinated at lower vanadium contents. At higher amounts additional five- and six coordinated species appear.

If the intensity of the 36000 cm^{-1} band is plotted against the vanadium content of various VAPOs it is observed that the intensity does not increase linearly but flattens off (figure 4). The intensity of the 26000 cm^{-1} band increases more rapidly as the vanadium content increases. Strikingly, apart from some scattering, all samples (VAPO-5s, VAPO-11s and an impregnated VAPO) fall on this line. This shows that the structure of the vanadium site is relatively independent of the preparation method and structure of the lattice.

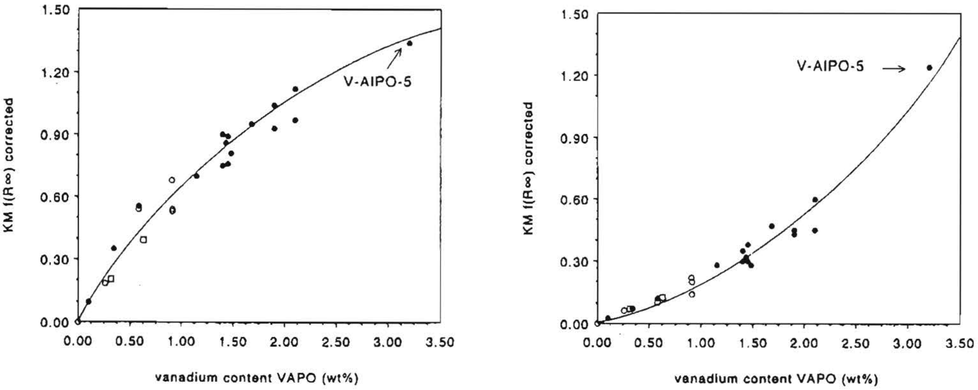


Figure 4: Intensity of the absorption at different wavenumbers *versus* the vanadium content of various VAPO samples at 36000 cm^{-1} (left) and 26000 cm^{-1} (right).

The DRUVVIS spectrum of VAPO is compared with that of the model compound vanadium pentoxide (figure 5). For a fair comparison polycrystalline vanadium pentoxide was physically mixed with $AlPO_4$-5. The vanadium contents of the VAPOs and the diluted V_2O_5 samples were comparable. Single crystals of vanadium pentoxide are built up from interconnected zigzag sheets [16]. Vanadium(V) is in a distorted octahedral coordination environment, which is responsible for the absorption at 20000 cm^{-1}. However, the actual spectrum of V_2O_5 shows five coordinated as well as four coordinated vanadium(V) species. This can be explained by disruption of the relatively weak bonding between the sheets [14] and the relatively small crystallites. Clearly, the DRUVVIS spectrum of VAPO-5 is different from that of bulk vanadium pentoxide.

• Variation of the calcination temperature of VAPO

In order to determine the influence of the calcination procedure on the structure of the vanadium site(s) the calcination temperature was varied between 450°C - 850°C (figure 6). A VAPO-5 with a relatively high vanadium content was used (1.90 wt%). The spectra of samples calcined at 450 and 550°C are essentially the same.

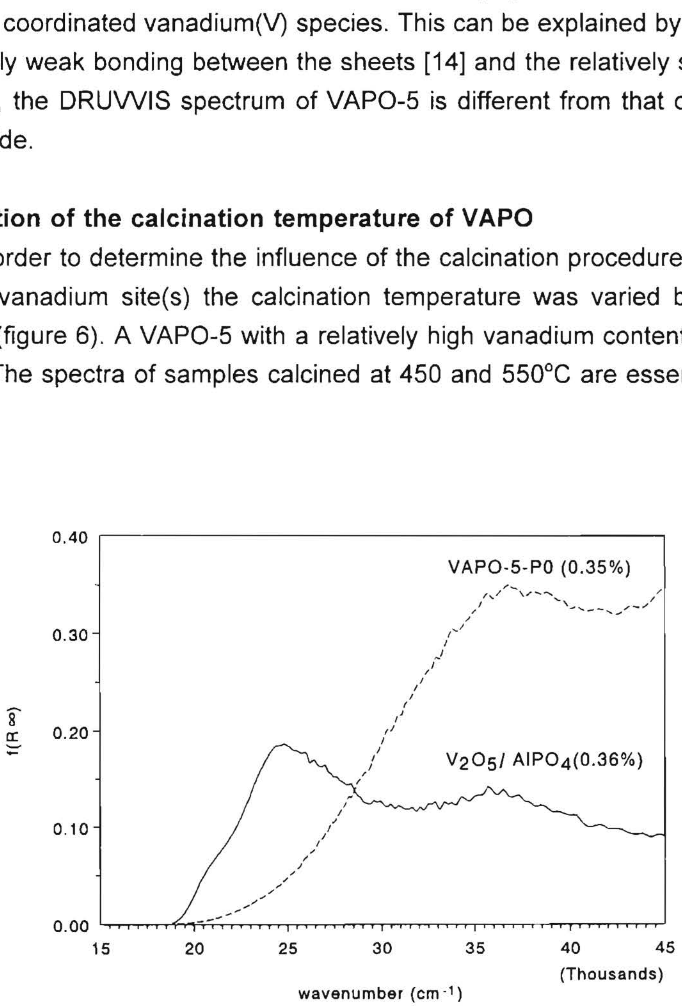


Figure 5: Comparison between the DRUVVIS spectrum of VAPO-5 and V_2O_5.

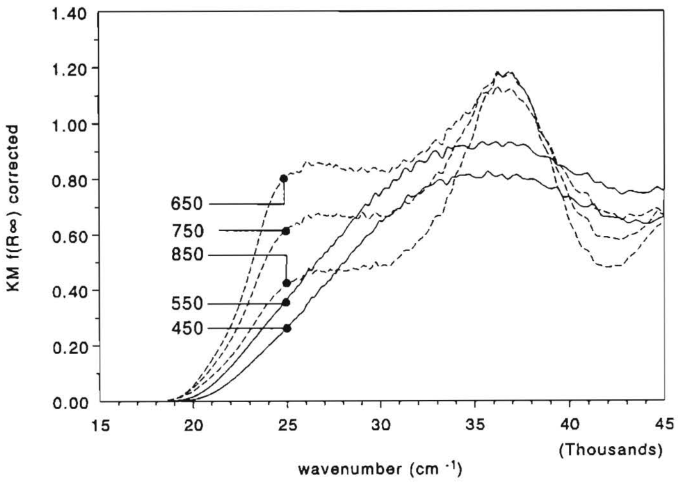


Figure 6: Effect of the calcination temperature (°C) on the DRUVVIS spectrum of VAPO.

A change in the absorption spectrum is observed above 550°C. Moreover, XRD shows that the molecular sieve structure collapses between 550-650°C, resulting in dense phase materials. In samples calcined between 650-850°C two bands are found: a relatively sharp band at 36000 cm^{-1} (four coordinated site) and a band at 26000 cm^{-1} (five coordinated site). While the intensity of the four coordinated site is not dependent on the calcination temperature (650°C-850°C), the intensity of the other band decreases. This suggests that during the calcination some vanadium is lost.

ESR

ESR gives information regarding the local structure of the vanadium(IV) ions in non-calcined samples [2-8]. In figure 7 an ESR spectrum of non-calcined VAPO is shown. This anisotropic spectrum with hyperfine structure is typical for the coupling of the single electron of vanadium(IV) with the nucleus (I=7/2; 8 lines). Two different types of vanadium species are observed (S_1 and S_2). Except for differences in the intensity the spectra of VAPOs are all comparable, whatever the origin of the samples. The observed spectra resemble those reported in the literature [2-7]. Calculation of the spectral parameters using a simulation program points to a square pyrimidal or (pseudo) octahedral oxovanadium(IV) ($V=O^{2+}$) species [4,6]. After calcining almost no signal can be detected, showing that the vanadium(IV) species are effectively oxidised to vanadium(V). The signal can be (partially) restored by reduction with dihydrogen above 350°C. Reduction of the vanadium sites is more readily achieved by treatment of the VAPO with aromatics (toluene, xylene) at low temperature 50-80°C. Note that after reduction only a single species is present.

The main problem of ESR spectroscopy is that not all vanadium(IV) species may be observed, due to paramagnetic coupling of spins. This coupling leads to broadening of the spectrum and eventually no signal is observed at all. An indication might be a deviation of the baseline of the spectrum. The spectrum of the non-calcined sample (VAPO-5-E4) has a nearly horizontal baseline (figure 7). This

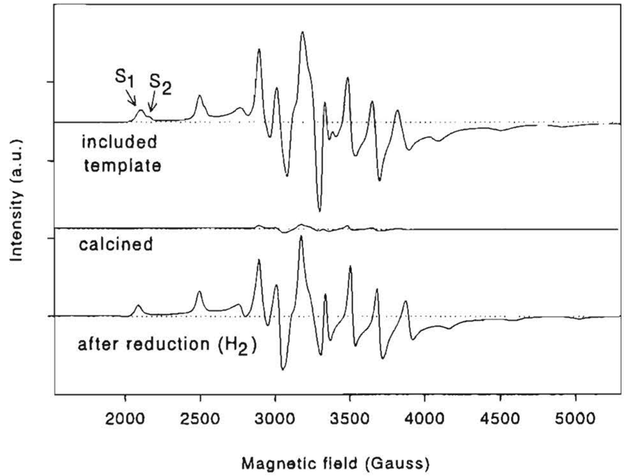


Figure 7: ESR spectra of as-synthesised, calcined and reduced VAPO-5-E4 (0.90 wt% V).

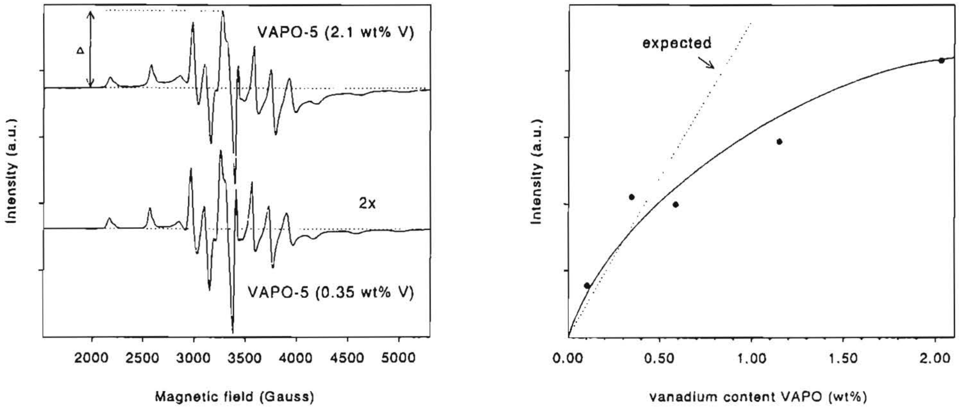


Figure 8: ESR-spectra of VAPO-5-P8 (2.1 wt% V) and VAPO-5-P0 (0.35 wt%) (left). Peak height (**Δ**) of the ESR spectrum as function of the vanadium content.

deviation is much stronger in the case of VAPO samples of poor quality. However, absence of this deviation is no proof for perfect incorporation of V(IV) in the framework. Results obtained by others show that the observed ESR signal corresponds to only 10% of the total amount of vanadium(IV), independent of the vanadium content of the VAPO [6]. Because it may provide some information about the clustering of vanadium ions the intensity of the ESR signal of the VAPOs was measured. In figure 8 the intensity of the spectra is shown as function of the vanadium content. At higher vanadium contents the intensity clearly deviates from linearity. While the vanadium content differs by a factor 6, the intensity differs only by a factor 2. This is consistent with a model where most of the vanadium(IV) is not visible by ESR, due to clustering. Note that such a comparison by peak height is only valid when the envelope of the signal remains the same upon increase of the vanadium content. As shown in figure 9 the shape of the spectrum is independent of the vanadium content. Our results give no definite answer about the absolute number of vanadium sites visible by ESR.

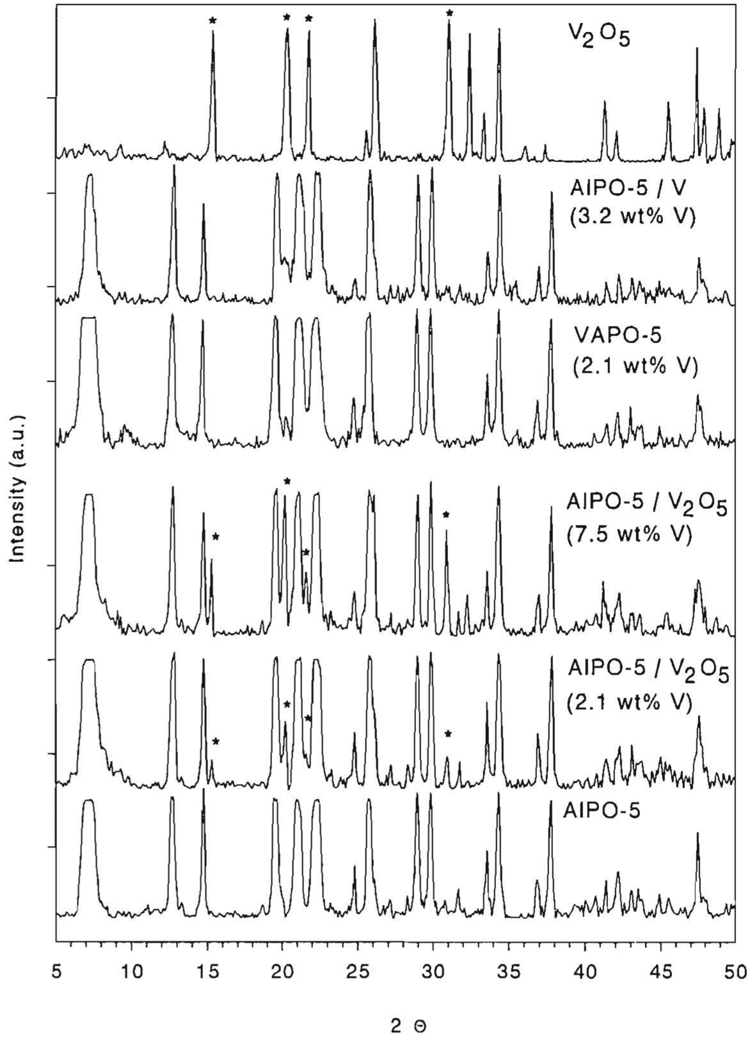


Figure 9: Powder diffractograms of V_2O_5, AlPO-5 physically mixed with V_2O_5, vanadium oxide supported on AlPO-5, VAPO-5 and AlPO-5 (reference). The highest peaks are cut off. The stars denote the main peaks of vanadium pentoxide.

XRD

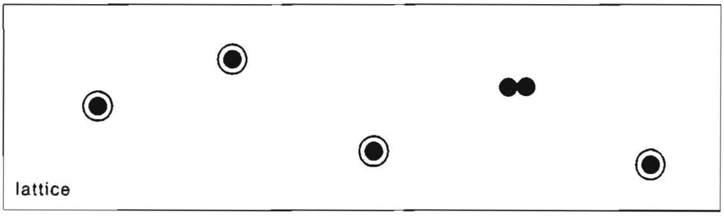
X-ray diffractograms may give some additional information about the formation of a crystalline vanadium pentoxide phase (figure 9). Main peaks of vanadium pentoxide at 2Θ = 15.5°; 20.3°; 21.9° and 31.0° that can be clearly distinguished from the $AlPO_4$-5 peaks are not present in the diffractogram of VAPO-5. On the contrary, in the diffractograms of physical mixtures containing vanadium pentoxide and AlPO-5 (2.1 and 7.5 wt%) the peaks of vanadium pentoxide can be easily indentified. Obviously VAPO-5-P8 (2.1 wt%) and vanadium impregnated AlPO-5 do not contain vanadium pentoxide, unless the crystallites are very small. Very small vanadium pentoxide particles (less than 10 vanadium ions) are not visible by XRD due to line broadening. Although the detection limit of XRD is nearly reached it seems possible to detect an amount of vanadium pentoxide corresponding to at least 1 wt% V, if the crystallites are large enough. On silica bulk vanadium oxide could only be identified above loadings of 8 wt% vanadium [17]. The results of XRD are in agreement with DRUVVIS and show that no bulk vanadium pentoxide is present in VAPO-5.

General aspects of the vanadium sites in VAPO

The DRUVVIS spectra of VAPO show a broading of the absorption spectrum rather than a linear increase of the absorption intensity. If all vanadium was incorporated in a similar manner no change in the shape of the absorption curve would be expected upon increasing the vanadium content (figure 3). Moreover, an abrupt change in the increase of the intensity would be expected when the maximum incorporation level of vanadium ions is reached. Note that this situation is different from CoAPO where the shape of the absorption curve between 14000 - 25000 cm^{-1} (400 - 700 nm) does not change upon increasing the cobalt content. In addition, the intensity of the absorption spectrum does increase lineary till about 3 wt% Co [18]. At higher amounts the intensity remains constant because no more cobalt can be tetrahedrally incorporated.

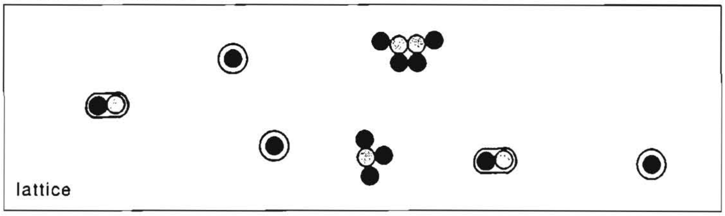
The results obtained can be explained by a model for calcined VAPO-5 where clustering of vanadium is important (figure 12). As deduced from DRUVVIS and ESR spectra all changes occur gradually. At low vanadium content (less than 1.0 wt% V) mainly monomeric, (pseudo) octahedral vanadium(IV) species are formed (S_1 and S_2), giving the relatively high intensity of the ESR spectrum. During calcination these species are oxidised and dehydrated. Two possibilities arise: a vanadium incorporated in a phosphate position or a species on a defect site. Our data do not permit exclusion of one of these models. Most likely both variants are present. Possibly, they show a difference in reducibility. An incorporated ion is probably much more difficult to reduce than species on the outer surface, because of a difference in accessibility. The ESR spectrum of VAPO-5s with a low vanadium content (< 0.3 wt% V) seems to be more difficult to restore than a VAPO with higher vanadium content, which could be an indication that at least some vanadium ions are incorporated. Note that an incorporated tetrahedral vanadium(V) species surrounded by phosphate groups is not possible because of the large charge excess. Besides, the elemental analysis, where a slight excess of aluminum over phosphorus had been found, does not exclude the occurence of a model were a phosphorus(V) ion is formally substituted for a vanadium(V) ion (see chapter 3). A two dimensimension representation may look as follows:

● four coordinated, attached. ; encircled: incorporated.

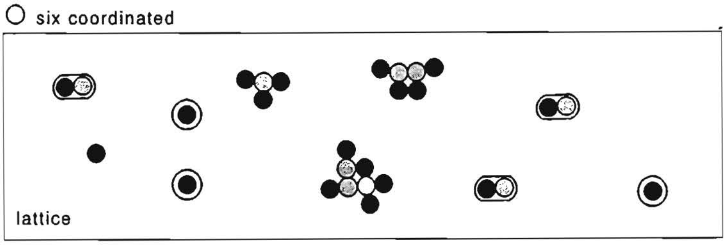


When the vanadium content increases the chance for dimeric and oligomeric sites increases. However, these sites are still tetrahedrally coordinated, but a minor amount of five coordinated species already emerge. This results in line broadening of the DRUVVIS spectrum. However, ESR spectra of non-calcined samples show that still monomeric species exist. Five coordinated species may point to the presence of a phosphorus surrounded oxovanadium(V) ion. Schematically this is:

○ five coordinated



The hypothetical substitution of both Al(III) and P(V) by an ESR-silent dimeric vanadium(IV) ion may also be possible and results in the dimeric site upon calcining Another variant is the growing of oligomers on a defect site on the outer surface, which may also result in the formation of five coordinated species. Upon further increasing of the vanadium content more five coordinated vanadium species are formed. The formation of a five coordinated oxovanadium(V) species is in agreement with the interpretation of the NMR experiments, performed with VAPOs containing more than 1% wt% of vanadium [4]. Above about 2.4 wt% V no pure VAPO can be obtained by hydrothermal synthesis, but impregnated VAPOs show that the formation of clusters carries through (figure 3). More interconnections between vanadium species are formed, finally resulting in six coordinated oxovanadium(V) species. However, as deduced from XRD and DRUVVIS at levels of 3.2 wt% V still no well defined vanadium pentoxide phase is formed. The results in:



A note should be made about the location of the vanadium clusters. Given the size of a VAPO-5 pore only small clusters can be accomodated (a few vanadium ions). Moreover, this should immediately influence the accessibility of the vanadium centers. The measured pore volumes point only to a slightly lower absorption capacity for n-butane compared with the theoretical value (less than 25% lower; see chapter 3). Even, the impregnated V/AlPO has still an appreciable pore volume (0.058 ml *n*-butane/g; about 40% lower than the pore volume of the starting material). Therefore, the clusters are small (only a few vanadium ions) or the clusters are located on the outer surface of the VAPO. By using EDX no enrichment or irregularities in the distribution of vanadium on the crystallite could be detected. Vanadium contents measured always correspond to less than 3 wt% vanadium. However, the nature of the sample (irregularity of the surface, inhomogeneity (pore structure) and the low conditivity) seriously limits the reliability of the results obtained by this technique.

It was found that during the gel preparation oxovanadium(IV) ions interact only weakly with the aluminophosphate [6]. Also the fact that the vanadium in VAPO changes gradually, relatively independent of the structure, supports this observation. Combining this with the idea that oxovanadium(IV) ions interact with the template [7] suggests that the monomeric or oligomeric vanadium ions are included in the pores during the synthesis and bind only in the later stage of the synthesis with the lattice, probably on lattice defects. Given the statement that the amount of vanadium(IV) observed with ESR corresponds to only 10% of the vanadium(IV) ions in the as-synthesised material, suggest that oligomeric species are already present before calcining. The pH of the crystallisation, (pH 5-7; see chapter 3) does certainly not exclude that multinuclear, ESR-silent, oxovanadium(IV) species are already present in the gel. These equilibria are complex. For example in this pH-range VO^{2+}, $VO(OH)^+$, $(VO)_2(OH)_5^-$ and $VO(OH)_3^-$ were reported to exist [11]. However, under actual conditions of the synthesis an excess of phosphate-, aluminate- and template ions is present, which certainly influences the equilibria between the various vanadium species. Moreover, the various vanadium species may have a different reactivity with the different gel components [19], which is not favourable when a well defined material is desired. The situation is even more complex when vanadium pentoxide instead of oxovanadium(IV) sulfate is applied as vanadium source because this oxide firstly has to be dissolved, leading to many different vanadium species [20]. This is expressed in the poor quality of the samples obtained with this vanadium source.

Conclusions

The coordination of the vanadium ions gradually changes upon increasing the vanadium content. The structure of vanadium is independent of the template used (tripropylamine or triethylamine). At low vanadium contents (< 1 wt% V) the sites are mainly tetrahedrally coordinated and probably monomeric. At higher vanadium contents clustering of the vanadium ions becomes more important.

Experimental

Instrumental

DRUVVIS measurements

For the DRUVVIS measurements a Hitachi 150-20 spectrophotometer equipped with a diffuse reflectance unit was used. Small amounts of dry sample (about 150 mg) were grounded in a ball mill for 45 minutes. If necessary (see appendix) the samples were diluted with $AlPO_4$-11 or $AlPO_4$-5 before grinding. After grinding the sample was dried at 200°C for at least 1 hour. The sample was cooled down in an exciscator and quickly transferred to the cell. This cell is made from non-absorbing suprasil glass, with dimensions 13x13x1 mm. The spectra were recorded in the range 200-900 nm. After baseline correction (absorbance λ=800 nm = 0) the spectra were converted to $f(R\infty)$ and wavenumbers.

ESR measurements

ESR 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.

XRD measurements

See chapter 3.

Preparation of an impregnated VAPO

Vanadium oxide on AlPO was prepared by reacting trimethoxyvanadiumoxide ($VO(OMe)_3$) with the AlPO-5. Trimethoxyvanadiumoxide was prepared according to a literature procedure [21]. The mass spectrum confirmed the structure of the prepared compound [22]. Under argon atmosphere about 0.1 g of the $VO(OMe)_3$ was dissolved in 25 ml of dry toluene. To the bright yellow solution 1.0 g dry AlPO-5 is added. The solution turns orange. After one hour the solid is filtered. The crystallites are dried and calcined according to the standard procedure. The resulting product is dark yellow.

Appendix

Without precautions the reflectance spectrum of a solid is not quantititive at all and even not qualitatively reliable, as shown in fig.10. In this spectrum it is shown that a pretreatment of the sample can change the shape of the spectrum completely which can give rise to wrong interpretations of the spectrum. This originates from the nature of the diffuse reflectance technique. The problem of obtaining the true spectrum or colour curve of a powder has been studied in much detail [23,24]. When light

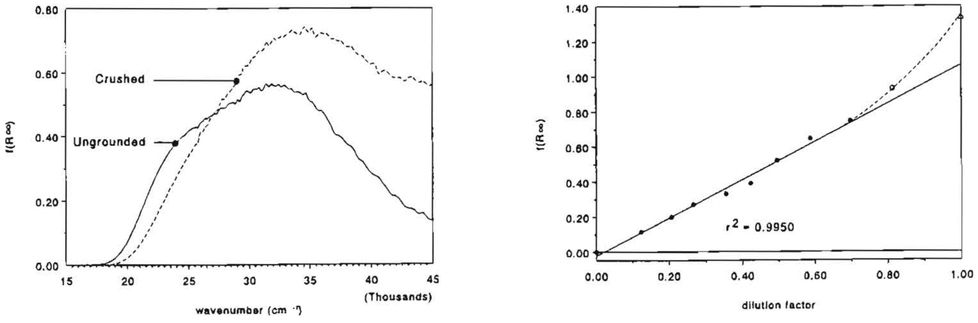


Figure 10: Influence of grinding on the DRUVVIS spectrum (left) and a dilution series of VAPO-5-P8 (right).

interacts with a surface, part of the light is reflected according to Fresnel laws and another part penetrates the material, where it can be absorbed or scattered diffusely. Both regular and diffuse reflectance parts are always present, the relative proportion of each depending on the nature of the reflecting medium. The diffuse part is coupled to the absorption. A compound that absorbs very strongly, has only a small contribution of diffuse reflectance to the measured total reflectance. The scattering properties of a sample depend also on the wavelength. Scattering becomes more prevalent when the particle size becomes small compared to the wavelength. Therefore the absorption at short wavelengths is more influenced than at large wavelengths, a reason for the changes observed in fig.10.

Theoretically, the behaviour of light interacting with absorbing powders is decribed by the Kubelka-Munk theory (K-M theory) [23,24]. The theory predicts relations for the observed final intensity as a result of the interplay between absorption and diffuse scattering of the incident light. The K-M theory allows to translate the diffuse reflectance spectrum to a spectrum similar to that obtained for a transmittance measurement by using the familiar equation [23,24]:

$$F\,(R_\infty) = \frac{(1 - R_\infty)^2}{2\,R_\infty} = \frac{K}{S}$$

R_∞ = Reflectivity of sample of infinite thickness
K = Absorption coefficient
S = Scattering factor

Note that this formula does not account for wavelength dependent scattering (Rayleigh scattering).

Quantitive results can only be obtained when only the diffuse reflectance component is measured. Therefore the regular component of the reflection should be minimised. In order to do so the following conditions have to be obeyed [25]:

- Use of sufficiently thick samples (recommended $\geq$ 1 mm).
- Random distribution of fine particles much smaller than the layer thickness.
- Samples with low absorption (dilution by a non-absorbing matrix).

The metal ion present in MeAPO can be regarded as a diluted solution of the metal ion in a non-absorbing aluminophosphate lattice. Before measurement all samples are thoroughly grounded, to minimise the regular component of the reflection by reducing the particle size. Straight lines, like in figure 14, can be obtained for $f(R_\infty) < 0.6$. Samples with a higher absorption ($A > 0.6$) are therefore diluted with optical white aluminophosphate. The absorption intensities obtained in this way are sufficiently well reproducable (± 5 %). The intensities found are corrected for the dilution. More diluted samples, however, show a slight red-shift of the absorption maximum (not shown). This is probably caused by a more intense scattering at higher wavenumbers, indicating the limitations of the theory.

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Reactions catalysed by VAPO

5

Introduction

Vanadium compounds are versatile stoichiometric as well as catalytic reagents for the oxidation of organic molecules in the liquid phase [1]. Environmentally friendly oxidants like hydrogen peroxide, organic peroxides and dioxygen can be applied with more or less success. Before the possible innovative role of VAPO can be discussed it is necessary to provide the reader with some background about vanadium oxidation chemistry. The major applications of vanadium-containing oxidation catalysts in the liquid phase can be found in the oxidation of alcohols, the epoxidation of alkenes and allylic alcohols, the hydroxylation of aromatics, oxidation of sulfides to sulfoxides or sulfones and the oxidation of ketones to diacids [1]. Some of these reactions will be discussed in more detail [2].

• Epoxidation of alkenes and allylic alcohols

Several vanadium compounds are able to catalyse the epoxidation of alkenes and allylic alcohols with high selectivity. Vanadium pentoxide shows activity for the epoxidation of alkenes [3-5] (see figure 1). Hydrogen peroxide as well as organic peroxides can be employed. A known procedure for the preparation of an epoxide of a higher alkene involves the use of vanadium pentoxide in combination with hydrogen peroxide in alcoholic solution (Milas reagents) [6]. The actual catalyst in this system is a vanadium peracid (HVO_4) that is formed by partial dissolution of the vanadium pentoxide due to interaction with hydrogen peroxide. Compounds like sodium *ortho*-vanadate (Na_3VO_4) also show epoxidation activity [6]. The decomposition of the peroxide is a strongly competing side reaction.

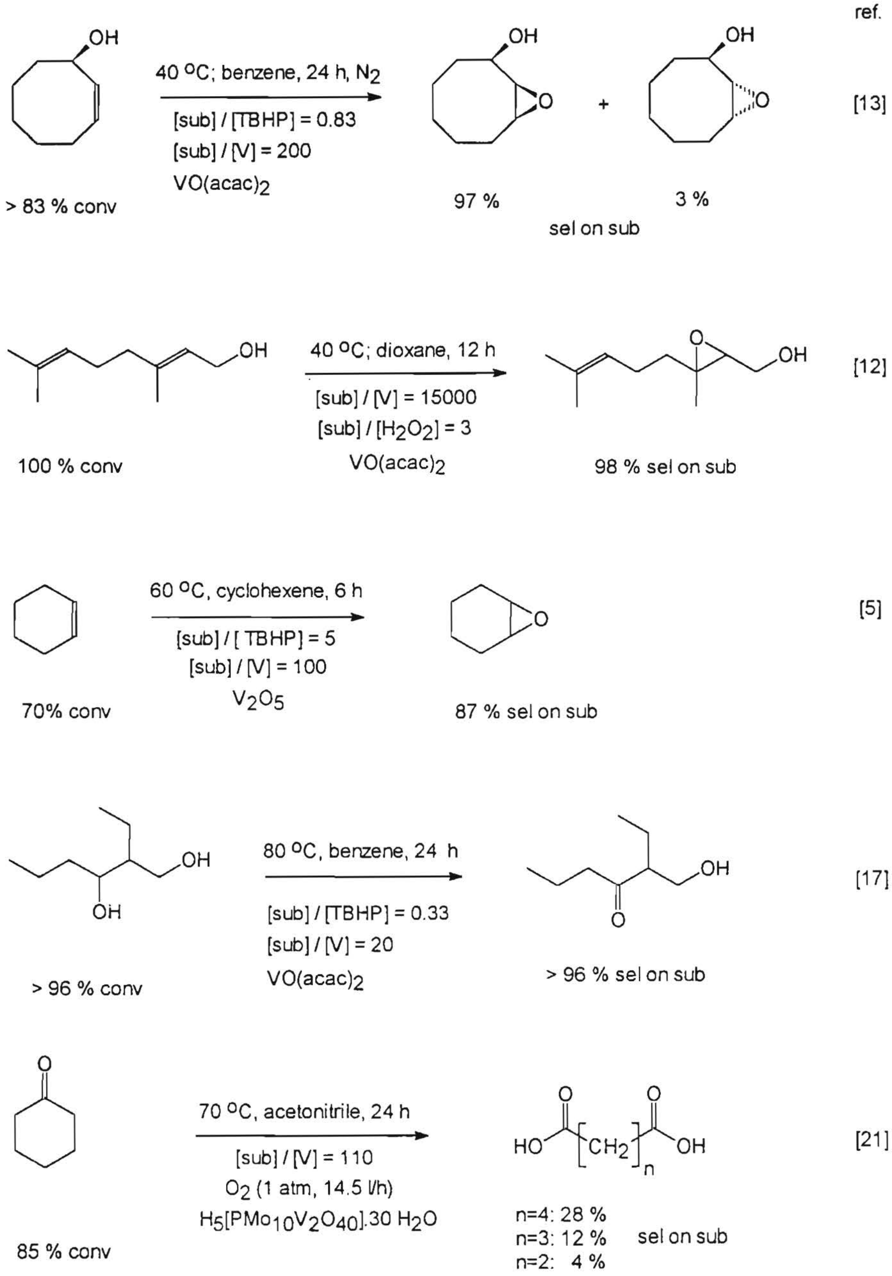


Figure 1: Typical examples of catalysis by vanadium complexes (see text).

The use of alkyl hydroperoxides under anhydrous conditions does not give much better results: a large excess of alkene over peroxide has to be used in order to get high selectivity based on peroxide [3,7]. On the contrary, the epoxidation of allylic alcohols proceeds actually more than one hundred times faster than the vanadium catalysed epoxidation of alkenes, because the reaction takes place intra- rather than intermolecular [6,8,9]. The use of oxo-bis(2,4-pentodionato)-vanadium(IV) ($VO(acac)_2$) in combination with TBHP gives in many cases, even at room temperature, a high yield of the epoxide, with high selectivity based on the substrate and the organic peroxide [6] (figure 1). The reaction is stereo-selective and an enantiomeric excess can be achieved when chiral ligands are used [10]. Compared with these complexes vanadium pentoxide is a poor catalyst.

Related to this reaction is the preparation of epoxy-alcohols from alkenes, by applying dioxygen as oxidant, a radical initiator and $VO(acac)_2$ as catalyst [11]. Hydrogen peroxide is usually not a suitable oxidant as it is rapidly decomposed by vanadium. An exception is the selective epoxidation of 3,7-dimethyl-2,6-octadien-1-ol (geraniol) that shows a high selectivity based on hydrogen peroxide (figure 1) [12].

The mechanism of the epoxidation reaction has been extensively investigated [5,13-15]. Comparable final results could be obtained with different vanadium compounds like vanadium(IV)tetrachloride (VCl_4), vanadyl(IV)sulfate pentahydrate ($VOSO_4.5\ H_2O$), tris(2,4-pentodionato)-vanadium(III) ($V(acac)_3$) and cyclopentadienyl tetracarbonyl vanadium(I) [13]. This is indicative of a common active species, although this is doubted by others [16]. It has been found that $VO(acac)_2$ is rapidly converted to a vanadium(V) peroxocomplex by interaction with an organic peroxide [15]. The ligands are rapidly destroyed under reaction conditions. On the other hand, the enantiomeric excess of epoxide that is found when a chiral complex is used shows that some vanadium complexes are sufficiently stable under reaction conditions [10]. However, a stable vanadium(V) *t*-butylhydroperoxide complex does not show any epoxidation activity and only one-electron transfer products are formed [14].

The most likely mechanism is shown in figure 2 [6,13]. Mechanistically the alkene and allylalcohol oxidation are related if not the same. An important step is the coordination of the substrate and the peroxide to the metal centre. This explains why

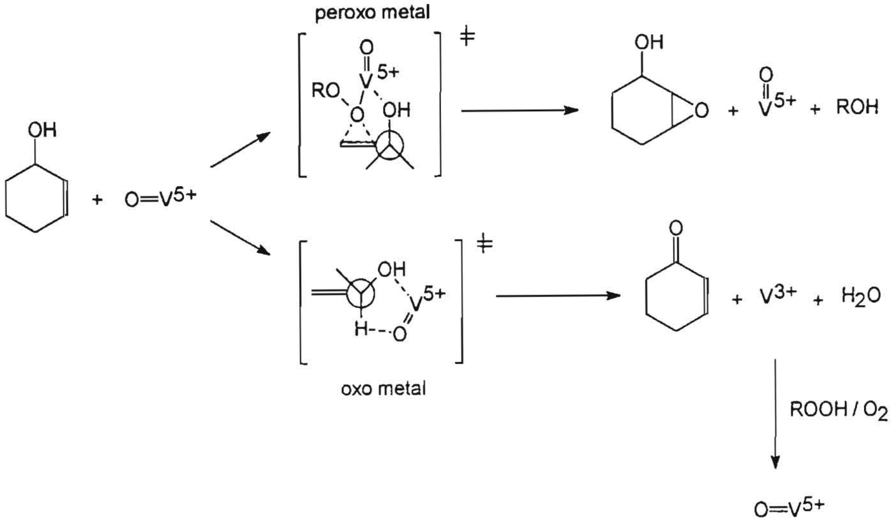


Figure 2: Different reaction pathways in the oxidation of allylic alcohols [13]

strongly coordinating allylic alcohols are much more reactive than weakly coordinating alkenes. Therefore the metal should be coordinatively unsatured. Thus the first requirement of a good epoxidation catalyst is that it should be a good Lewis acid (able to interact with electronrich molecules). This is in accordance with the observation that more nucleophilic alkyl substituted alkenes and allylic alcohols are more reactive. A second requirement is that the metal may not be a too strong oxidant, thus facilating electron transfer V(V) → V(IV) resulting in the formation of free radical species that lower epoxide selectivity. The reaction is strongly retarded by water and alcohols [6] due to competition with the substrate for available coordination sites.

In case of an allylic alcohol the alcohol group can also be oxidised. The choice for the epoxidation or the alcohol oxidation pathway is determined by the dihedral angle $\omega(C_3=C_2-C_1-O)$ of the allylic alcohol [10] (figure 2). An angle of about 90° favors the epoxidation. However, when this angle becomes larger the transition state for the epoxidation cannot be reached and only oxidation of the alcohol function is observed. It should be noted that the epoxidation pathway, if sterically possible, is more favorable than the direct oxidation of the alcohol. This is also reflected in the milder conditions used for the epoxidation.

· Oxidation of alcohols

Only a few studies deal with the catalytic oxidation of alcohols by vanadium complexes [17,18]. In acidic water the vanadylgroup ($V=O^{3+}$) is a moderately strong oxidising agent with E_0=+0.991 V, but it can also be used in organic solvents. Both acyclic and cyclic secondary alcohols give the corresponding ketones in good yields using $VO(acac)_2$ in combination with *t*-butylhydroperoxide (TBHP) in dry benzene [17]. Remarkably, primary alcohols hardly reacted. Competitive oxidation of 4-dodecanol and 1-dodecanol yields more than hunderd times more 4-dodecanone than dodecanenal. Diols with a primary and secondary hydroxyl function were oxidised to ketoalcohols in good yields (figure 4). However, although the product selectivity was generally high, the selectivity based on TBHP was probably low (less than 33%), indicating that the decomposition of TBHP is an important side reaction [17]. When 1,2-diols are oxidised cleavage of the diols prevailed [18]. It has been reported that triisopropoxyvanadium(V) shows catalytic activity in the oxidation of 2-propanol to propanone using hydrogen peroxide and dioxygen as oxidant [19].

The mechanism of the oxidation of alcohols is probably heterolytic (see figure 2) because a free radical mechanism cannot explain the high selectivity for the oxidation of secondary alcohols compared with primary alcohols. More likely is an oxo-mechanism in which coordination of the alcohol to the vanadium complex is an important step. It is known that secondary alcohols co-ordinate much better to the vanadium than primary alcohols [20]. Oxidation of the coordinated alcohol probably proceeds via a *β*-hydrogen elimination invoting a cyclic transition state (see figure 2). The oxovanadium(V) complex is regenerated by a peroxide.

· Oxidation of ketones

Vanadyl complexes like $VO(acac)_2$ show catalytic activity in the oxidation of ketones with dioxygen, in presence of a protic solvent [21]. Mechanistically it is believed that the Brønsted-acid is necessary to shift the keto-enol equilibrium to the more reactive enol [21]. An interesting improvement is obtained by the use of heteropolyacids as catalysts. These inorganic complexes combine a vanadium site with a Brønsted-acid and therefore a protic solvent is not a prerequisite. Indeed $H_5[PMo_{10}V_2O_{40}].30\ H_2O$ in acetonitrile shows activity in this reaction (figure 1), and is more active than the $VO(acac)_2/HAc$ system. Non-acidic $((n\text{-}Bu)_4N]_5[PMo_{10}V_2O_{40}].aq$ is not active. Non-catalytic activation of the cyclohexanone by shifting the equilibrium can also be accomplished by a strong Lewis acid complex like $VO(OEt)Cl_2$ [22].

VAPO as catalyst

VAPO can be regarded as a catalyst that should fit somewhere in the picture of catalysis by vanadium complexes. VAPO might be an unique catalyst if it is truly heterogeneous, the selectivity of the reaction could be influenced by the pore structure and if the non-productive decomposition of peroxides is minimal. The oxidation of alcohols and the epoxidation of allylic alcohols are interesting model reactions as they involve different mechanism (oxometaal *versus* peroxometal). The selectivity observed in the epoxidation of allylic alcohols is also an interesting tool to study the influence of the pore structure on the reaction. Assuming that the reactions take place in the pore system of the VAPO, a possible shape selective effect can be expected. The oxidation of ketones explores the possibilities of using dioxygen as terminal oxidant. As discussed earlier VAPO-5 showed activity as an epoxidation catalyst [23].

Results and discussion

Decomposition of organic peroxides

VAPO was tested as a catalyst for the decomposition of TBHP. The results are shown in figure 3. VAPO is able to decompose TBHP and the reaction product is t-butanol. While the amount of vanadium in each reaction is comparable, the rate of decomposition depends on the VAPO used. The decomposition is not influenced by the solvent. These results are different from the results reported by others [23,24]. It was reported that TBHP could not be decomposed on VAPOs prepared by the fluoride method ($[TBHP] \approx 1$ M; ≈ 0.08 mmol V; 70°C in chlorobenzene under

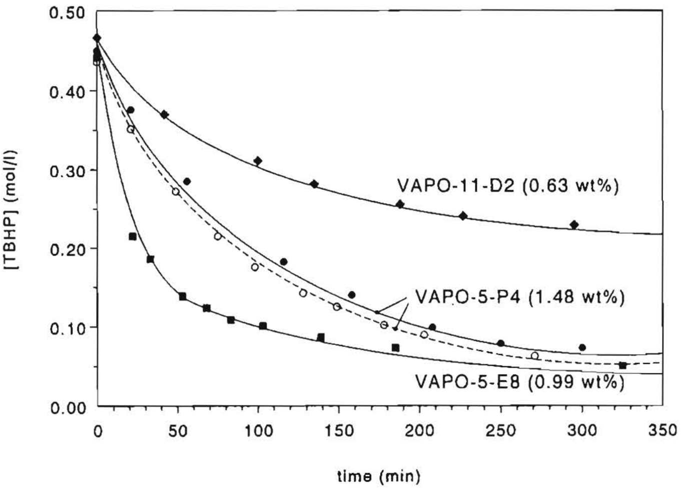


Figure 3: Decomposition of TBHP at 70°C catalysed by VAPO-5 (≈ 0.115 mmol V, T = 70°C). Dashed line: solvent chlorobenzene; Solid line: solvent acetonitrile.

dinitrogen atmosphere). On the contrary, cyclohexane hydroperoxide could be decomposed on VAPO-11 ([peroxide] ≈ 0.025 M; ≈ 0.03 mmol V; 70°C in cyclohexane), although the conversion after 5 h is low (about 17%). Note that cyclohexane hydroperoxide is more susceptible towards decomposition than TBHP. These VAPOs seem to be less active than our samples which suggest that the VAPOs might be different.

Another striking difference is observed between VAPO-5 and VAPO-11. When a dry VAPO-5 is added to the reaction mixture directly a strong colour change of the VAPO is observed from yellow to brown-red. Apparently there is a strong interaction between the vanadium sites and TBHP (probably formation of ROO-V(V) or ROO-V(IV)). During the reaction the colour fades slowly to yellow / white. Change of the colour is not observed for VAPO-11. These observations are an indication that the vanadium sites on VAPO-11 are different from VAPO-5, which is not supported by the results of the characterisation (see chapter 4). An alternative explanation might be that the vanadium sites in VAPO-11 are not accessible for reaction with TBHP due to the small pores.

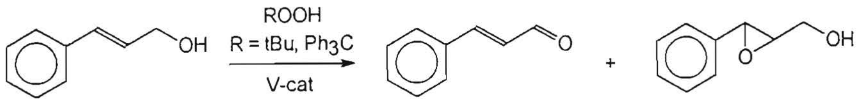
The red colour is also observed in case of oxo-bis(2,4-pentodionato)-vanadium(IV) and other vanadium complexes [15]. The origin of the colour has been subject to much speculation in literature [1,13,15]. In solution the red colour lasts only for about a few seconds, before the colour fades to yellow. It was argued that the red colour is caused by a vanadium peroxide complex. This combined ^{51}V-NMR and ESR study showed that in the initial stages also radical species are formed (RO•), which may start the further decomposition of the TBHP. Therefore it is not unlikely that these red coloured species are responsible for the much faster decomposition of TBHP in case of VAPO-5 compared with VAPO-11.

Oxidation of allylic alcohols

VAPO was used as a catalyst for the epoxidation of 3-phenyl-2-propen-1-ol and 2-cyclohexen-1-ol. The first compound can be considered as a model for larger molecules with more than one reactive group. Cyclohexen-1-ol is interesting because it possesses a much more reactive (secondary) alcohol function than 3-phenyl-2-propen-1-ol. As argued earlier, effects of the pore structure on the selectivity may be observed. Single component absorption experiments showed that both allylic alcohols are easily absorbed into the pores of AlPO-5 and AlPO-11. This shows that these molecules in principle have no steric restrictions to enter the micropore structure of VAPO-5 and VAPO-11. The main results of the vanadium catalysed oxidation of 3-phenyl-2-propen-1-ol by TBHP are summarised in table 1.

VAPO-5 shows activity in this reaction. However, the activity of the commonly used catalyst VO(acac)$_2$ is more than twenty times higher. Turnover numbers are calculated at an early stage of the reaction, which allows a fair comparison of the reaction rate. The VAPOs become relatively more active when the vanadium content increases. The samples prepared using triethylamine, like VAPO-5-E5, are even more active. No influence of the pore structure is found on the activity or selectivity (compare reaction 3 and 4). The epoxide is almost the sole product, only a small amount of aldehyde is formed (see figure 4). Secondary reactions such as the hydrolysis of the epoxide or oxidation of the aldehyde to the corresponding acid are the most likely cause of the low product selectivity sometimes observed. The observed selectivity based on TBHP was high in all cases studied (90-100%). In figure 4 the activity of many VAPOs is plotted as a function of the vanadium content

Table 1: The vanadium catalysed oxidation of 3-phenyl-2-propen-1-ol by peroxides.



				t = 100 min		
	Catalyst (wt% V)	V_{total} (mmol)	TOF (mol/mol.h)	Conv sub (%)	Sel prod sub (%)	Sel epox (%)
Solvent: acetonitrile; Oxidant: t-butylhydroperoxide						
1	-	-	-	1	-	0
2	$VO(acac)_2$ (19.2)	0.085	770	92	87	99
3	VAPO-11-D1 (0.32)	0.076	7.8	26	82	85
4	VAPO-5-P0 (0.35)	0.090	7.2	25	74	81
5	VAPO-5-P5 (1.41)	0.088	21	47	85	90
6	VAPO-5-P8 (2.05)	0.096	27	52	95	91
7	VAPO-5-E5 (0.92)	0.054	38	50	68	83
Solvent: benzene; Oxidant: t-butylhydroperoxide						
8	VAPO-5-P4 (1.48)	0.087	40	63	84	95
9	VAPO-5-P0 (0.35)	0.088	32	51	63	91
Solvent: benzene; Oxidant: triphenylmethylhydroperoxide						
10	-	-	-	3	-	-
11	VAPO-5-E5 (0.92)	0.053	47	47	95	98
12	VAPO-5-P (1.85)	0.120	20	62	100	99

Conditions and experimental errors: Acetonitrile; 50 ± 1 °C; [sub] = 0.30 ± 0.01 M; [sub]/[TBHP] = 1.05 ± 0.08; [TBHP]/[V] ≈ 38; conv: ± 2%; sel: ± 5%.

TOFs are calculated at 30% conversion of the substrate. The products epoxide and aldehyde are determined quantitatively.

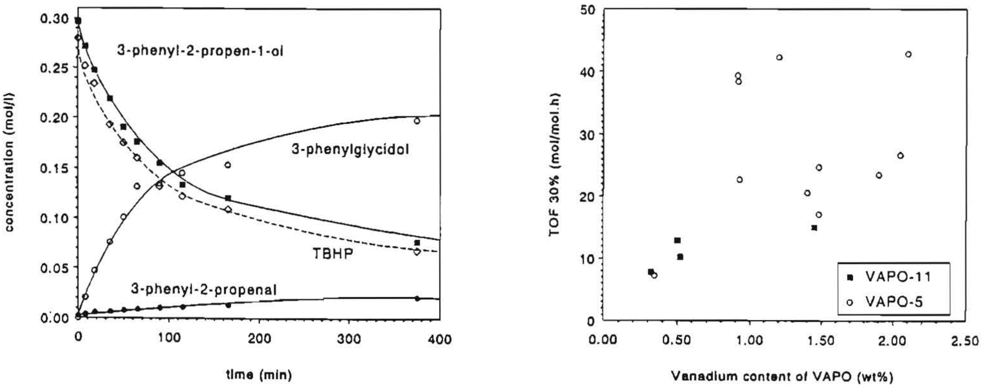


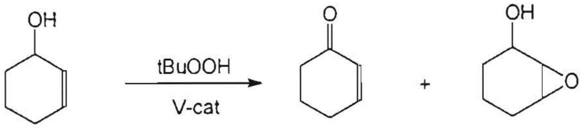
Figure 4: Oxidation of 3-phenyl-2-propen-1-ol with TBHP catalysed by VAPO: A typical time-concentration profile (left) and the activity of various VAPOs (right).

regardless of the synthetic procedure, purity and crystallite habit of the VAPO-5 or VAPO-11. The activity of VAPO varies, but non of the VAPOs shows an exceptionally high activity. The mean activity of VAPO-5 seems to increase with increasing vanadium content. VAPO-11s are less active than VAPO-5s. From a preparative point of view, VAPO-5 can be applied to prepare 3-phenylglycidol in high yield.

The low activity of VAPO raises some doubt about its catalytic behaviour. A small amount of vanadium (few percent) in solution may already be responsible for the observed activity. Another possibility is that the intrinsic activity of VAPO is low due to diffusion limitations of the reaction. The use of triphenylmethyl hydroperoxide (TPMHP) as oxidant, that cannot enter the pores of VAPO, can give some initial information about the location of the reaction. Theoretically, the VAPO catalysed oxidation with TPMHP should be very slow because the active sites cannot be reached. From table 1 it is clear that VAPO shows activity with TPMHP. This activity is comparable with that measured for TBHP under the same reaction conditions although a fair comparison is difficult to make because the reactivity of both peroxides is not equal. Another experiment that gives more information about the reaction is the removal of the catalyst from the reaction mixture after a short reaction time. The possible reactions in the filtrate are followed. The results of these experiments show that after filtration the reaction proceeded only a little slower. This points to at least a contribution of a reaction taking place in solution. The results of these experiments will be discussed in detail later.

Table 2 shows some main results of the oxidation of 2-cyclohexen-1-ol. The substrate is rather sensitive towards oxidation. Without catalyst an appreciable amount of ketone is formed. Upon adding a catalytic amount of $VO(acac)_2$ to the reaction mixture the epoxide becomes a major product. Again, VAPO-5 and VAPO-11 are less active than the homogeneous catalyst but the differences are smaller than

Table 2: Oxidation of 2-cyclohexen-1-ol by TBHP catalysed by vanadium compounds.



	Catalyst (wt% V)	V_{total} (mmol)	TOF (mol/mol.h)	t = 300 min Conv sub (%)	Sel prod sub (%)	Sel epox (%)
13	-	-	-	14	55	0
14	$VO(acac)_2$ (19.2)	0.085	132	80	87	65
15	VAPO-11-D1 (0.32)	0.079	2.7	22	75	55
16	VAPO-5-P0 (0.35)	0.086	3.7	21	65	48
17	VAPO-5-P4 (1.48)	0.080	6.3	43	84	68
18	VAPO-5-P5 (1.41)	0.084	6.3	42	87	67
19	VAPO-5-P8 (2.10)	0.083	9.6	49	93	76
20	VAPO-5-P10 (1.43)	0.079	34	65	60	62
21	VAPO-5-E4 (0.90)	0.053	9.8	32	70	59

Conditions and experimental errors: Acetonitrile; 51 ± 1 °C; [sub] = 0.29 M; [sub]/[TBHP] = 1.16 ± 0.08; [TBHP]/[V] ≈ 38; conv: ± 1%; sel: ± 5%.

The TOFs are calculated at 20% conversion of the substrate. Products are the ketone and the epoxide. TOFs are roughly corrected for the blank reaction.

is found for the oxidation of 3-phenyl-2-propen-1-ol. Also here VAPO-5s with a higher vanadium content are more active and show a higher selectivity towards the epoxide. Figure 5 shows a typical time-concentration profile of a reaction catalysed by VAPO-5. VAPO-5-P10 gives a different result from all the other VAPO-5s. The 2-cyclohexen-1-ol reacts about twice as fast compared with the reaction catalysed by VAPO-5-P5, a catalyst with a comparable amount of vanadium. However, the product selectivity towards the ketone and epoxide is much lower and many products are formed. Major side products found by GC-MS are 7-oxabicyclo-[4.1.0]heptane-2-one, 2-cyclohexen-1,4-diol and cyclohexen-*t*-butylperoxide. The reason for this different catalytic behaviour is not clear. The origin lies probably in the different preparation methods for the VAPOs. VAPO-5-P10 consists of small particles, while VAPO-5-P4 consists of dense agglomerates. Besides, the template in the preparation of the VAPO-5s does not have much influence on the final product, although VAPO-5-E4 is more active than VAPO-5-P5.

An interesting question is whether the results can be explained in terms of an influence of the pore structure on the reaction or not. Earlier, it was argued that such an effect was found in this reaction [25]. However, the direct comparison between VAPO-5-P0 and VAPO-11-D1, both with similar vanadium content do not confirm these earlier observations. Except for VAPO-5-P10, the activity and selectivity seems to be correlated: the more active the VAPO, the more selective the reaction towards the epoxide. If the selectivity was controlled only by steric hinderance no selectivity change is expected when the vanadium content of the VAPO is altered. VAPO-11-D1 neither shows a lower activity, nor a lower selectivity towards the epoxide than VAPO-5-P0, as would be expected because of the smaller pore size of VAPO-11. The relatively large contribution of the simultaneously occuring blank reaction to the total conversion decreases the real epoxide selectivity. Probably both VAPO-5 and VAPO-11 are highly selective towards epoxide formation, and thus no shape selectivity is observed under the applied reaction conditions.

A note should be made about the selectivity based on the peroxide which always appeared to be more than 100%. In the blank reaction a slow increase of the concentration of peroxide is found in time, rather than a decrease. Therefore, the participation of dioxygen from air in the reaction, resulting in the formation of

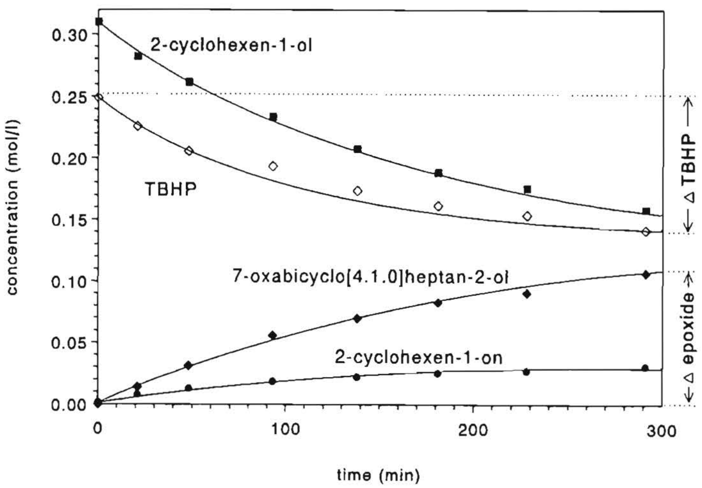


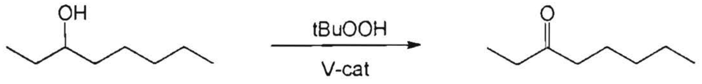
Figure 5: Oxidation of 2-cyclohexen-1-ol with TBHP catalysed by VAPO-5-P8.

peroxides, is obvious. However, there seems to be a correlation between thedisappearance of TBHP and the formation of epoxide (see also figure 5). Calculation of the TBHP selectivity on epoxide yield gives selectivities close to 100%. In contrast with the reactions catalysed by VO(acac)$_2$, the non-selective decomposition is not observed in the reactions catalysed by VAPO.

Oxidation of alcohols

The oxidation of simple alcohols by TBHP was used as model reaction. Substrates studied were 1-octanol, 2-octanol, 3-octanol and cyclo-octanol. These substrates were chosen for their reactivity. Among the series of simple linear alcohols C_6-C_9 possessing a hydroxylgroup on the 2-position, 2-octanol is the most reactive using TS-1 / H_2O_2 / acetone at 70°C [26]. All reactants are fast absorbed into AlPO-5 and AlPO-11. Although the dimensions of cyclo-octanol are comparable with the pore

Table 3: Oxidation of 3-octanol with TBHP catalysed by vanadium catalysts.



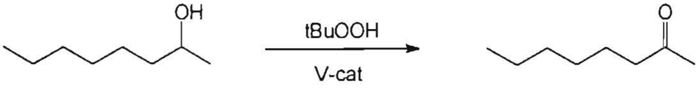
	Catalyst (wt% V)	V_{total} (mmol)	TOF (mol/mol.h)	t = 400 min Conv sub (%)	Sel sub (%)	Sel TBHP (%)
22	-	-	-	5	100	-
23	$VO(acac)_2$ (19.2)	0.088	18	46	85	35
24	V_2O_5 (56.0)	0.121	2.1	31	100	52
25	VAPO-11-D1 (0.32)	0.106	0.8	12	100	100
26	VAPO-11-D2 (0.63)	0.105	1.4	17	100	100
27	VAPO-5-P0 (0.35)	0.125	2.4	31	90	35
28	VAPO-5-P4 (1.48)	0.117	2.8	40	90	40
29	VAPO-5-P4 (1.48)	0.228	3.1	50	75	35
30	VAPO-5-P8 (2.10)	0.128	6.5	43	85	45
31	VAPO-5-P10 (1.43)	0.114	2.7	30	100	45

Conditions and experimental errors: Acetonitrile; 71 ± 1°C; [sub] = 0.3 M; [TBHP]/[sub] = 1.4 ± 0.05; [TBHP]/[V] ≈ 40; conv: ± 1%; sel: ± 5%. TOFs are calculated at 30% conversion of the substrate, and are roughly corrected for the blank reaction.

size of AlPO-11 single component absorption studies show that the maximum pore occupation at equilibrium is about 40%. The large pore AlPO-5 absorbs cyclo-octanol almost quantitatively.

Tables 3-5 shows some major results obtained with different catalysts. From these tables it can be seen that VAPO is able to catalyse the oxidation of alcohols. The rate of the oxidation decreases in the order 3-octanol ≈ 2-octanol > cyclo-octanol >> 1-octanol for VAPO-5 and the homogeneous catalyst $VO(acac)_2$.

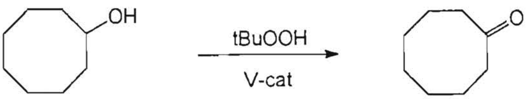
Table 4: Oxidation of 2-octanol with TBHP catalysed by vanadium compounds.



				t = 400 min		
	Catalyst (wt% V)	V_{total} (mmol)	TOF (mol/mol.h)	Conv sub (%)	Sel sub (%)	Sel TBHP (%)
32	-	-	-	10	100	-
33	VO(acac)$_2$ (19.2)	0.091	10.0	50	95	40
34	VAPO-5-P4 (1.45)	0.117	2.7	48	95	36

Conditions and experimental errors: acetonitrile; 71 ± 1 °C; [sub] = 0.3 M; [TBHP]/[sub] = 1.4 ± 0.1; [TBHP]/[V] ≈ 40; conv: ± 1%; sel: ± 5%. TOFs are calculated at 10% conversion of the substrate and TOFs are roughly corrected for the blank reaction.

Table 5: Oxidation of cyclo-octanol with TBHP catalysed by vanadium compounds.



				t = 400 min		
	Catalyst (wt% V)	V_{total} (mmol)	TOF (mol/mol.h)	Conv sub (%)	Sel sub (%)	Sel TBHP (%)
35	-	-	-	24	95	100
36	VO(acac)$_2$ (19.2)	0.104	11.8	72	90	55
37	VAPO-5-P4 (1.48)	0.115	2.5	56	98	90
38	VAPO-11-D1 (0.32)	0.113	1.2	45	100	100

Conditions and experimental errors: Acetonitrile; 71 ± 1 °C; [sub] = 0.3 M; [TBHP]/[sub] = 1.4 ± 0.1; [TBHP]/[V] ≈ 40; conv: ± 1%; sel: ± 5%. TOFs are calculated at 20% conversion of the substrate. The TOFs are roughly corrected for the blank reaction.

As expected, primary alcohols are hardly oxidized. In contrast to the results obtained with TS-1, 2- and 3-octanol have almost equal reactivities [26]. The activity of the catalysts show the following order: VO(acac)$_2$ > VAPO-5 > VAPO-11 >> none (blank). The differences in activity between the VAPO and VO(acac)$_2$ are much smaller than in case of allylic alcohols.

The selectivity to the expected product (octanone) is always high. On the other hand the selectivity based on TBHP with the VAPO-5 catalysts is low. VAPO-11 shows a high selectivity based on the peroxide. VAPO-5s with higher vanadium contents are more active. The crystallite habit seems not an important parameter influencing the activity. Note that the colour change observed during the reaction is remarkable. While VAPO-5-P0 turns dark red, VAPO-11-D1 stays yellow.

Removal of the VAPO-5 from the reaction mixture after a short reaction time resulted in a reduced rate of 3-octanol conversion which was more pronounced than observed during the oxidation of allylic alcohols. This suggests that a heterogeneous reaction takes place. This issue will be discussed in more detail in chapter 7.

Many attempts were made to increase the yield of 3-octanone. When one would like to prepare octanone *via* this method an high yield 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. Keeping the concentration of TBHP low would be expected to retard the decomposition. Therefore an experiment was performed where the peroxide was supplied to the reaction mixture in two portions. Figure 6 compares the results of the experiment where the peroxide was supplied in one single portion and in two portions. From the figure it can be seen that the two-step addition results in a lower reaction rate but does not give a higher overall yield. The yield of octanone is raised only another 10%, while the peroxide is decomposed at the same rate as in the first step. Thus, while the selectivity based on TBHP in the first step is higher (55% vs. 35% in the single step addition), it is lower in the second step (30%). Since only a little octanol is converted in the second step it could mean that deactivation of the VAPO occurs.

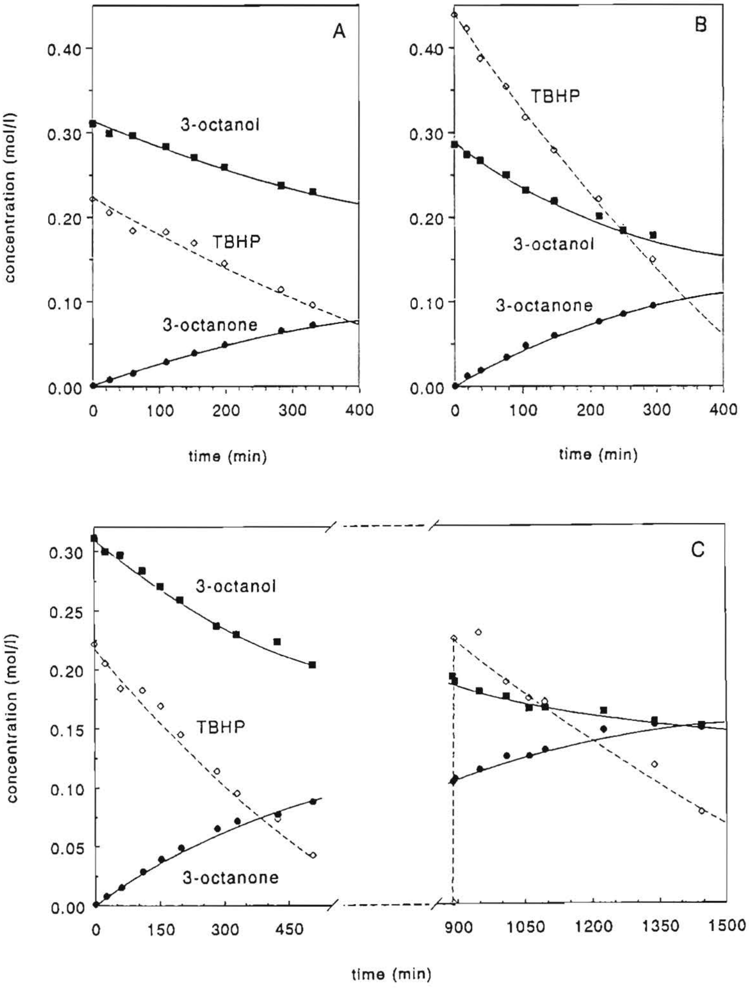


Figure 6: The oxidation of 3-octanol with TBHP catalysed by VAPO-5-P4.

A. Addition of TBHP in one portion ($[\text{TBHP}]_o$ = 0.22 M).

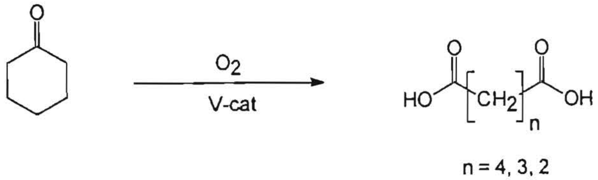
B. Addition of TBHP in one portion ($[\text{TBHP}]_o$ = 0.44 M).

C. Addition of TBHP in two portions ($[\text{TBHP}]_o$ = 0.22 M + 0.22 M).

Oxidation of ketones

The oxidation of cyclohexanone by dioxygen was used as a model reaction. A catalytic effect is observed when VAPO or VO(acac)$_2$ is added to the reaction mixture (see table 7 and figure7). However, activity is only observed when acetic acid is used as solvent. The vanadium complexes did not show any activity when acetonitrile / ethanol 1:1 was used as solvent, indicating that VAPO is unable to activate the substrate. Apparantly, VAPO is a too weak Brønsted-acid to shift the keto-enol equilibrium [21]. In acetic acid the homogeneous catalyst is more active than VAPO-5. Interestingly, a higher yield is obtained with VAPO-11. Under the applied reaction conditions degradation of the formed hexanedioic acid is observed. At higher reaction temperatures degradation becomes more pronounced.

Table 7: Oxidation of cyclohexanone with dioxygen catalysed by vanadium compounds.



n = 4, 3, 2

	Catalyst (%wt V)	V_{total} (mmol)	t = 1200 min Conv (%)	Sel C_6	Sel C_5	Sel C_4
39	-	-	5	31	25	-
40	VO(acac)$_2$ (19.2)	0.114	100 (600 min)	67	15	19
41	VAPO-5-P2 (1.2)	0.071	54	59	23	19
42	VAPO-11-P2 (1.2)	0.072	90	59	20	21

Conditions and experimental errors: glacial acetic acid; 70±1 °C; [sub] = 0.41 ± 0.01 M; 1 bar dioxygen; conv: ± 5%; sel: ± 5%. The total concentration of C_6, C_5 and C_4 add upp to more than 80% of all products formed.

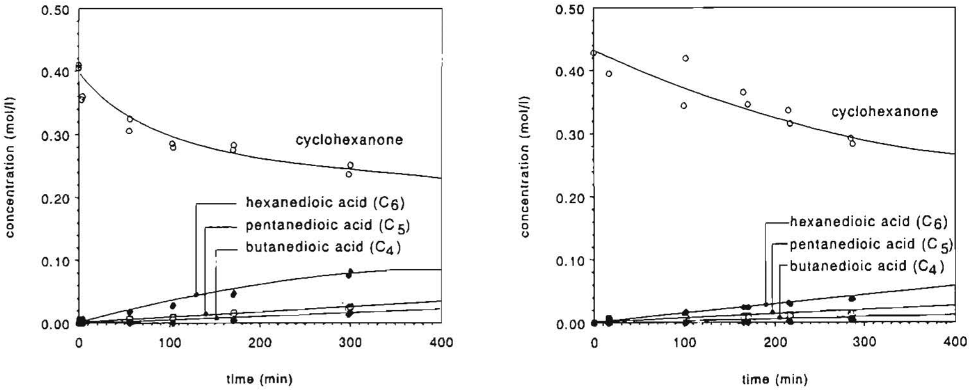


Figure 7: Oxidation of cyclohexanone by dioxygen catalysed by VAPO-11 (left) and VAPO-5 (right) in glacial acetic acid at 70°C.

The homogeneous complex VO(acac)$_2$ is also more selective towards hexanedioic acid than the VAPO. In the literature 98% conversion of the cyclohexanone after 16 hours and a selectivity of 32% (hexanedioic acid), 12% (pentanedioic acid) and 4% (butanedioic acid) for the VO(acac)$_2$ catalysed oxidation is reported [21], which is less active and selective than the result presented in table 7. Note that VAPO could be recovered from the reaction mixture after reaction in glacial acetic acid.

Conclusions

VAPO-5 shows activity as catalyst in various oxidation reactions: the epoxidation of allylic alcohols with TBHP, the oxidation of alcohols with TBHP and the oxidation of ketones with dioxygen. However, depending on the substrate and the reaction conditions, the activity per vanadium site is lower for VAPO than for VO(acac)$_2$. The difference is relatively small for the oxidation of alcohols and large for the oxidation of allylic alcohols. Therefore VAPO is more active as an oxometal rather than a peroxometal catalyst.

Within a series of VAPO-5 catalysts differences are observed, although none of the VAPOs show exceptional behaviour. Samples with a higher vanadium content are relatively more active. No clear correlation could be found between the activity and the crystallite habit.

In case of the oxidation of alcohols, differences are found between VAPO-5 and VAPO-11 regarding the decomposition of TBHP. An effect of the pore structure on the reaction rate in this reaction cannot be excluded.

Nevertheless, from experiments in which the catalyst was removed from the reaction mixture it cannot be excluded that the observed reactions partially take place in solution, rather than on the outer surface or inside the micropores of the VAPO.

Experimental Procedures

Chemicals

Reference samples were obtained from commercial suppliers (Aldrich, Janssen) in the highest available quality unless otherwise stated.

Glacial acetic acid, Merck, 100%;
1,3,5-Tri-*i*-propylbenzene, Aldrich, 97%;
1,3,5-Tri-*t*-butylbenzene, Aldrich, 97%;
t-Butyl hydroperoxide, Aldrich, 70% in water;
Triphenyl methylhydroperoxide, Aldrich;
3-Phenyl-2-propen-1-ol, 98%;
2-Cyclohexen-1-ol, Aldrich, 95+%;
2-Cyclohexen-1-on, Aldrich, 96%;
Oxo-bis(2,4-pentanedionato)-vanadium(IV), Aldrich, 95%.

Acetonitrile, 99%;
Benzene, Merck, P.A.;
2-Octanol, Janssen, 99%;
3-Octanol, Janssen, 99+%;
Cyclo-octanol, Janssen, 99%;
3-Hexanone, Janssen, 98%;
Acetophenone, Janssen, 99%;
Cyclohexanone, Janssen, 99.8%;

General Procedures

A waterfree stock solution of the substrate (0.45 M) in acetonitrile or benzene was prepared and stored on molsieves 3A. This stock solution also contains a standard. A TBHP solution (1.4 M) was prepared by dissolving 15 ml of TBHP (70% in water) in 70 ml of acetonitrile or benzene. The solution was made waterfree by drying on calcium sulfate. After filtration the solution was stored on molsieves 3A. In a similar way 0.9 M solutions were prepared. A 0.9 M TPMHP solution was prepared by dissolving 12.4 g TPMHP in 50 ml of benzene under gentle heating. VAPO catalysts were dried overnight at 150°C before use.

Reactions were carried out in a thermostatted glass reactor equipped with cooler and sampling port. Additionally, a gas inlet tube could be mounted. 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, the catalyst was added to the reaction mixture. The reaction was followed by taking samples with a syringe. Before analysis the samples (max 0.5 ml) were filtered using 0.45 μm brown-rim filters of Schleicher & Schuell. Part of the sample was subjected to analysis of the peroxide content, while an other part was used for GC-analysis.

The peroxide content was determined by jodometric titration. Typically 200-300 μl of the sample was added to a solution containing 2 ml of a saturated potassium iodide solution, 2 ml of sulphuric acid (2.5 M) and 25 μl ammonium hexamolybdate solution as catalyst. After storing the mixture in a refrigerator for 30-60 min the sample was titrated with 0.01 M of sodium thiosulfate. Starch was used as indicator.

Gaschromatographic analyses were carried out on a Carlo Erba GC 6000 vega series 2 equipped with autosampler. Depending on the colomn split or splitless was used. Columns (DB-1 and DB-23) were obtained from J&W Scientific. If necessary, the peroxides were destroyed before analysis by adding a triphenylphosphine solution (1.2 g PPh_3/4 ml of benzene; typically 100 μl of this solution was added to 200 μl of sample). The peroxide needs to be destroyed to prevent reactions in the injection port of the GC.

Single component absorption experiments

In order to check the accessibility of the VAPO for the components liquid phase absorption experiments were conducted. About 350 μl or 350 mg of the substrate was dissolved in 50 ml triisopropylbenzene, a solvent that cannot enter the micropores. Also 300 mg of an internal standard (tri-*t*-butylbenzene) was added to the reaction mixture. AlPO-5 or AlPO-11 was well dried (200°C, overnight) and stored in an exciscator. The absorption was carried out between 50°C (allylic alcohols) or 70°C (alcohols) in a thermostated glass reactor. About 1 g of AlPO was added to the solution. The volume of absorbate corresponds to the maximum amount that can be absorped into the pores of AlPO-5. Samples were taken regulary and the absorbed amount was determined by GC (Column DB-1, split injection, T_{inj}=300°C, T_{det}=250°C, T_{column}=150°C → 180°C). Generally the maximum absorbed amount was reached within 30 minutes.

Oxidation of 3-phenyl-2-propen-1-ol

The stock contained acetophenone as internal standard (substrate : standard ration = 6-10). The reaction was carried out for 8 hours at 50°C. About 0.3 g of VAPO (1.50 wt% V) (0.088 mmol V) or an equivalent amount of vanadium present in other vanadium catalysts were added to the reaction mixture. Samples were analysed by iodometric titration and GC. Triphenylphosphine was added to the samples (Colomn: DB-1; split injection; T_{inj}=300°C; T_{det}=250°C; T_{colomn}=170°C). Calibration curves for 3-phenyl-2-propen-1-ol, 3-phenyl-2-propenal and 3-phenylglycidol were constructed ($r^2 > 0.998$).

Oxidation of 2-cyclohexen-1-ol

The reactions were carried out for 8 hours at 50°C. The conditions used for the analysis were colomn: DB-1; split injection; T_{inj}=300°C; T_{det}=250°C; Temperature programmed analysis, starting at 120°C up to 150°C. For quantitative analysis the stock solution contains 3-hexanone. Calibration curves for 2-cyclohexen-1-ol, 2-cyclohexen-1-on and oxabicyclo[4.1.0]heptan-1-ol were constructed ($r^2 > 0.9995$). 7-Oxabicyclo[4.1.0]heptan-2-ol was prepared by direct reaction of m-chloro-perbenzoic acid with 2-cyclohexen-1-ol [27]. The epoxide was found to be sufficiently pure (more than 97% by GC) to be used for calibration.

Oxidation of 2-octanol and 3-octanol

The reaction was conducted for 8 hours at 70°C. The reaction mixture contained about 0.12 mmol of vanadium. The peroxide content was determined. GC analyses were performed on a DB-1 column at T_{inj}=250°C; T_{det}=250°C; T_{colomn}=150°C. It was not necessary to add triphenylphosphine to the samples. Authentic samples of the substrate and products were used to verify peak positions and for calibration. As internal standard 3-hexanone was present (substrate:standard=6-10).

Oxidation of cyclo-octanol

The procedure used to oxidise cyclo-octanol was similar to the procedure described to oxidise the linear alcohols. Triphenylphosphine was added to the sample before analysis. The samples were analysed on a DB-1 colomn at T_{colomn}=150°C, T_{inj}=300°C, T_{det}=250°C.

Oxidation of cyclohexanone

A standard solution containing 10.6 g (0.107 mol) of cyclohexanone and 1.50 g (0.0129 mol) of hexanoic acid (standard) in 250 ml glacial acetic acid was prepared. From this solution 20 ml was transferred into the glass reactor. The reaction was carried out at 70°C. Dioxygen (1 bar) was bubbled through the reaction mixture for 20 h. About 0.3 g of well dried VAPO or 0.03 g $VO(acac)_2$ were added to the reaction mixture.

During the reaction samples of about 300 μl were taken and the VAPO containing samples were filtered. The samples were esterified with 3 ml of a diluted solution of sulphuric acid in ethanol (5 volume%). The samples, in tight closing vessels, were heated overnight at 40°C. Then 2 ml of water was added to the solutions and the samples were extracted with 2 ml of heptane. This heptane solution was analysed by GC. The samples were splitless injected on a DB-23 colomn: T_{inj} = 300°C; T_{det} = 250°C; T_{column} = 70°C → 190°C. Calibration curves of cyclohexanone, hexanedioic acid, pentanedioic acid and butanedioic acid were constructed using the same derivatisation procedure. The calibration curves were found to be linear ($r^2 > 0.998$).

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Regeneration and Stability of VAPO-5

6

Introduction

A catalyst must possess a high stability so that it can be used several times without losing its activity. Stability refers not only to the active site of a heterogeneous catalyst but also to the structure as a whole. A limited stability of the catalyst under reaction conditions is a fundamental problem in oxidation chemistry. Relatively little attention is paid to the stability of oxidation catalysts under reaction conditions. Obviously there is a paradoxical situation when considering the stability of the catalyst since a catalyst with a too stable structure is not active (an example is mentioned on page 87). Therefore a compromise should be sought between a good performance and high stability. The reasons for deactivation of homogeneous catalysts have been summarised [1]. The most common deactivation mechanisms are: degradation of the ligands, formation of inactive oligomers, dead-end species and inhibition by strong binding of reactants and products to the sites. However, heterogeneous catalysts might also lose their activity by other deactivation mechanisms like leaching of active sites and in case of porous catalyst by blocking of the pores. These mechanisms are discussed below in more detail.

· Degradation of the ligands

The organic ligands of the catalyst are thermodynamically unstable with respect to carbon dioxide and water. The ligand itself is a substrate for the reaction. Well known is the degradation of porphyrin ligands when hydrogen peroxide is employed as an oxidant [2], although it should be noted that the resulting metal complex may retain some activity. It is less likely that a similar degradation mechanism occurs when metal containing molecular sieves are used as catalyst, because the inorganic framework is much less susceptible towards oxidation.

- **Formation of inactive oligomers**

Usually oxo-bridged oligomers are formed that show marginal or no activity. Many transition metal ions like Ti^{4+} and Cu^{2+} tend to oligomerise under reaction conditions. In metal containing molecular sieves the metal ion is located at fixed positions in the framework and therefore the occurence of this mechanism is less likely.

- **Formation of dead-end species**

Many metal ions have various oxidation states. Common oxidation states for vanadium are tri-, tetra and pentavalent while for chromium all oxidation states between tri- and hexavalent can be obtained. In case of chromium the trivalent state is thermodynamically most stable. In the catalytic cycle ($O{=}Cr^{6+} \rightleftharpoons Cr^{4+}$) an electron uptake by the relatively unstable Cr^{4+} results in the formation of the kinetically stable Cr^{3+}. For the resulting Cr^{3+} it is difficult to re-enter the catalytic cycle. There is no reason why this mechanism should not occur when using metal containing molecular sieves.

- **Inhibition**

The reaction can be inhibited by substrate-, product- or solvent molecules. The catalytic reaction may be seriously retarded by molecules that strongly bind to the catalyst. For example reactions catalysed by titanium- and vanadium complexes in solution are seriously inhibited by water and alcohols. The inhibition mechanism can be minimised by tuning the absorption and desorption characteristics of the sieve.

- **Leaching**

Active species can be lost by lysis from the framework of the catalyst. This is probably a mechanism that acts is more common than expected. Although this is not always the case the dissolved species may show catalytic activity. For example the catalytic action of vanadium on silica (V_2O_5 on SiO_2) is thought to be partially caused by dissolved vanadium [3]. Aluminophosphates are known to be less stable than aluminosilicate based molecular sieves [4], therefore the occurrence of this deactivation mechanism can not be excluded. Leaching of metal ions is reported in case of CoAPO-5 (for examples see page 29).

- **Pore blocking**

The pores of the catalyst might be simply blocked by molecules in such a way that transport in the pores is no longer possible and the active site is no longer accessible. The fact that it is nearly always necessary to calcine a MeAPO after the reaction to restore its activity could indicate that the pores become blocked during the reaction.

In this chapter the properties of regenerated VAPO catalysts will be discussed in detail. The VAPOs are recovered from the reaction mixture and characterised. The purpose of this chapter is to gain information about the stability of the VAPO under the applied reaction conditions. Therefore two different reactions, the oxidation of 3-phenyl-2-propen-1-ol and 3-octanol, were studied in more detail. Because regeneration seems to be required, different regeneration procedures will be discussed. From an industrial point of view calcination is not an attractive way of regeneration. A much better method would be removal of the molecules from the sieves by washing with an appropriate solvent.

Results and discussion

Oxidation of 3-phenyl-2-propen-1-ol

Recycling and characterisation of a VAPO after reaction

A VAPO-5 with medium vanadium content (≈ 1.2 wt% V) was re-used several times. Two different pretreatments were applied. The first procedure involved only washing and drying after removal of the catalyst from the reaction mixture by filtration. In the second procedure an additional calcination step was included (heating in air at 500°C for 3 h). After work-up the VAPO was characterised by XRD, DRUVVIS, ESR and by thermogravimetric methods.

Recycling without intermediate calcination gives a VAPO that becomes less and less active after each cycle (figure 1). The TOF drops from 40 mol substrate/mol V.h for a fresh catalyst to 11 mol/mol.h after 3 cycles. The selectivity towards the epoxide remains high. Calcination (500°C in air) of the VAPO between successive reaction cycles restores the activity of the VAPO almost completely.

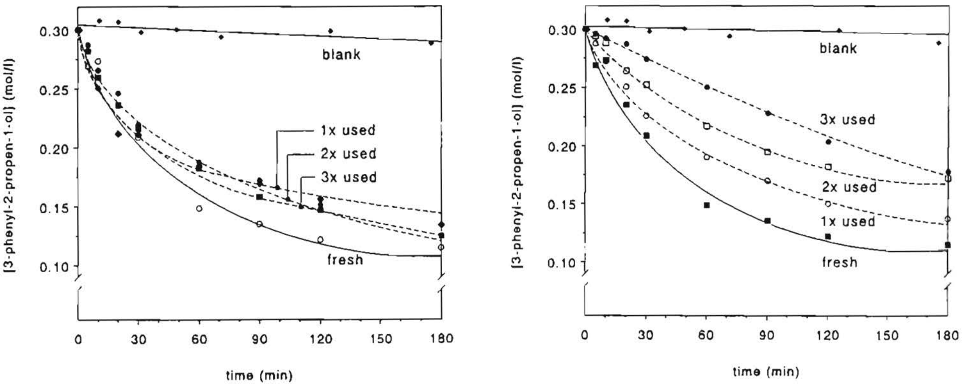

Figure 1: Activity of VAPO-5-P2 after successive regenerations.
Left: Re-use of the VAPO after washing and drying.
Right: Re-use of the VAPO after washing, drying the VAPO is calcined in air at 500°C.

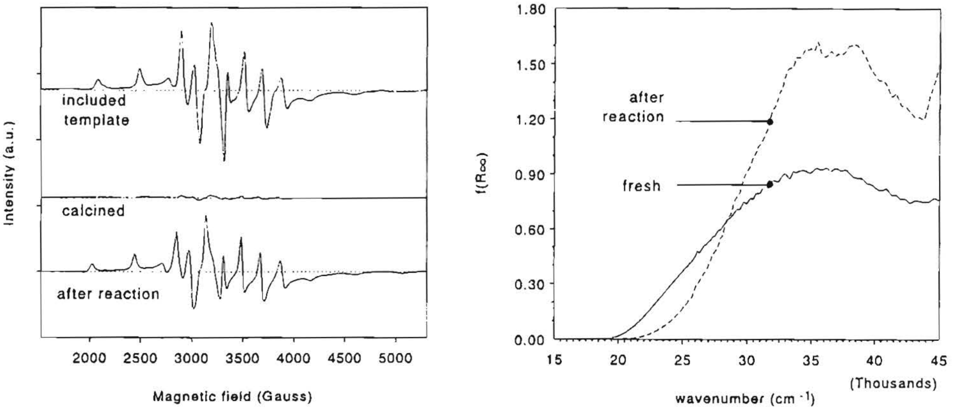

Figure 2: Characterisation of VAPO catalysts after reaction.
Left: ESR of as-synthesised, calcined and VAPO-5-P2 after reaction. The spectra are drawn on the same scale. Right: DRUVVIS spectra.

Characterisation of a VAPO after reaction revealed that some changes occur, although the overall microporous structure was not destroyed. The differences before and after reaction are mostly related to the structure of the vanadium sites. After reaction the VAPO is green. The DRUV/VIS spectrum shows a much more intense band in the region 30000-40000 cm^{-1} which is attributed to absorbed organic species. No new absorption bands can be found in the visible region. ESR shows that again the characteristic V(IV) signal, which means that the vanadium sites are reduced from V(V) to V(IV) during the reaction (figure 2). Although it is difficult to quantify the ESR results the number of reduced vanadium ions seems to increase after more reaction cycles (not shown). The expected weak d-d transitions of V(IV) in the DRUV/VIS spectrum are not visible, probably because the amount of V(IV) is too low.

The VAPO is not accessible for *n*-butane anymore, indicating that the pores are obstructed by organic material (reactants, solvents or products).

Role of calcination

Earlier experiments showed that calcining between successive reaction cycles could restore the activity of the VAPO-5 almost completely. For the total regeneration of the VAPO a minimum calcination temperature of about 400°C is required. Above this temperature the original yellow color of the sample is restored, indicating that the oxidation state of the vanadium is again pentavalent state. However, the calcination temperature should not be too high. Upon calcining the particular sample (VAPO-5-P7, 1.90 %wt V) above 600°C, the microporous structure collapsed and a VAPO with tridymite structure was formed. The structure of the vanadium sites also changes, as is shown on page 72. Note that an AlPO-5 (without vanadium) has a much higher thermal stability. AlPO-5 is destroyed only at temperatures above 1000°C [5]. The lower stability of VAPO-5 can possibly be attributed to the presence of more defect sites in the aluminophosphate framework.

The effect of the calcination temperature on the activity of the VAPO was studied. As can been seen in figure 3 the activity of the VAPO tends to be become higher when the calcination temperature rises. This is surprising because the samples calcined above 600°C lost their pore structure. *A priori* one would expect a decrease in activity when using a dense phase VAPO, but no decrease is observed. This might be an indication that the pores are actually not used in the oxidation of 3-phenyl-2-propen-1-ol or only for a short time (deactivation by pore obstruction). In all further regeneration experiments the VAPO was calcined at 500°C before re-use.

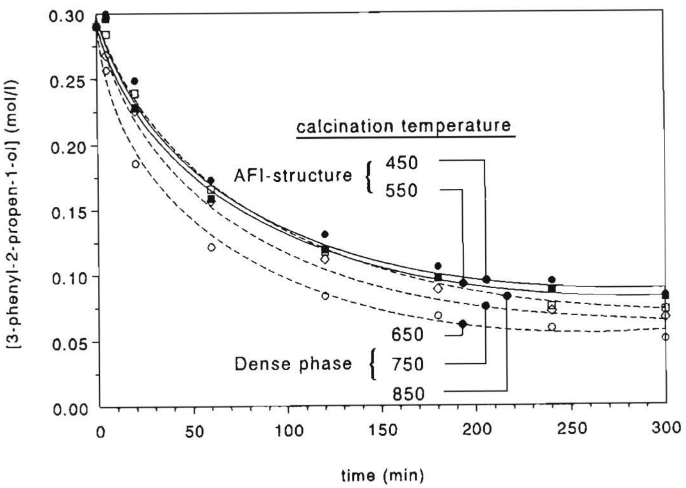

Figure 3: Activity of VAPO-5-P7 calcined at different temperatures (450-850°C).

Long term recycling of VAPO with intermediate calcining

Earlier regeneration experiments (using a VAPO several times) also made clear that small changes in the structure of the VAPO occurred. For example a small loss of vanadium was found (less than a few procent). To examine this changes more accurately, a more extensive long term experiment was carried out, starting with several grams of catalyst. If characterisation of the VAPO was desired a small amount of VAPO was kept apart, while the other part was used for a new reaction cycle. The VAPO-5 was recycled fourteen times and characterised after the first, second, fourth, seventh, tenth and fourteenth reaction cycle. After calcining the VAPO was characterised by XRD, SEM, PV (n-butane and dinitrogen), DRUVVIS, AAS and a reaction with 3-phenyl-2-propen-1-ol under standard conditions. The data was compared with that of the freshly calcined VAPO. The results are shown in figure 4.

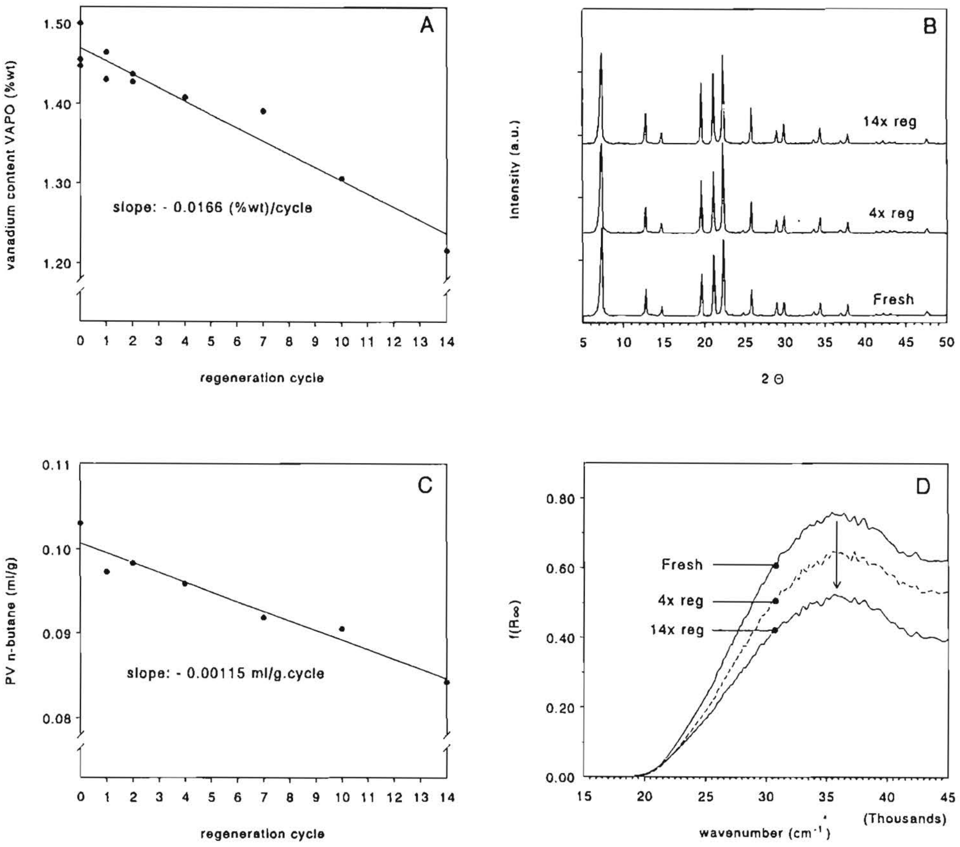

Figure 4: Characterisation of recycled VAPO-5-P3 regenerated by calcining.

A: Vanadium content of the catalyst (AAS).

B: Pore structure and crystallinity (XRD).

C: Pore volumes (*n*-butane sorption).

D: The vanadium sites (DRUVVIS).

XRD-analysis (figure 4) shows that the crystalline structure is not disturbed under the reaction conditions. The intensity of the peaks are more or less the same for all samples, indicating that no transformation towards non-crystalline phases occured.

Pore volume determination, using *n*-butane as sorbate, showed a slight decrease of the pore volume after successive regenerations (figure 4). While the pores are filled with molecules during reaction, they are opened again upon calcination. The fresh catalyst had a pore volume of 0.103 ml *n*-butane/g. The pore volume reduced to 0.084 ml *n*-butane/g after fourteen regenerations, a decrease of about 18%. A steady decline is observed of about -0.0012 ml/g.cycle. After fourteen regenerations still no stable plateau value is reached. This could mean that the pore structure is slowly destroyed under reaction conditions, but not in a way that it has an effect on the XRD spectrum. However, it should be emphasized that only a minor blockage of the pore can prevent a *n*-butane molecule to enter it.

Like the pore-volume the vanadium content of the samples also showed a downward trend after repeated regenerations (figure 4). This loss of vanadium seems to be continuous. A small mean loss of 0.017 wt% vanadium per reaction cycle is observed (1.1 % after one reaction). More alarming is the fact that after several regeneration cycles still vanadium is lost during the reaction. This points to an intrinsic instability and not to a limited and definite amount of loosely bonded vanadium that is removed after a few reaction cycles leaving a stable catalyst. At this point it is not known how important this dissolved vanadium is and how it influences the reaction. This aspect will be discussed in detail in the next chapter. Moreover, it should be noted that the loss of vanadium can only be measured accurately after many regenerations. If only a few regenerations are carried out the loss of vanadium could be easily disregarded. At best, the AAS results are 1% accurate.

In accordance with the declining vanadium content, DRUVVIS measurements show a decrease in vanadium absorption intensity too (figure 4). However, quantitatively the observed decrease in intensity (about 30%) is more than would be expected from the AAS measurements (18%). Except for a decrease of intensity the shape of the absorption curves did not change. No signal could be detected by ESR spectroscopy, indicating that all vanadium tetravalent is re-oxidised to pentavalent vanadium (no figure shown).

SEM photographs (figure 5) show some attrition of the catalyst particles after repeated regenerations. The outer surface of the regenerated VAPO-5 particles seemed to be worn off, while other particles are simply split.

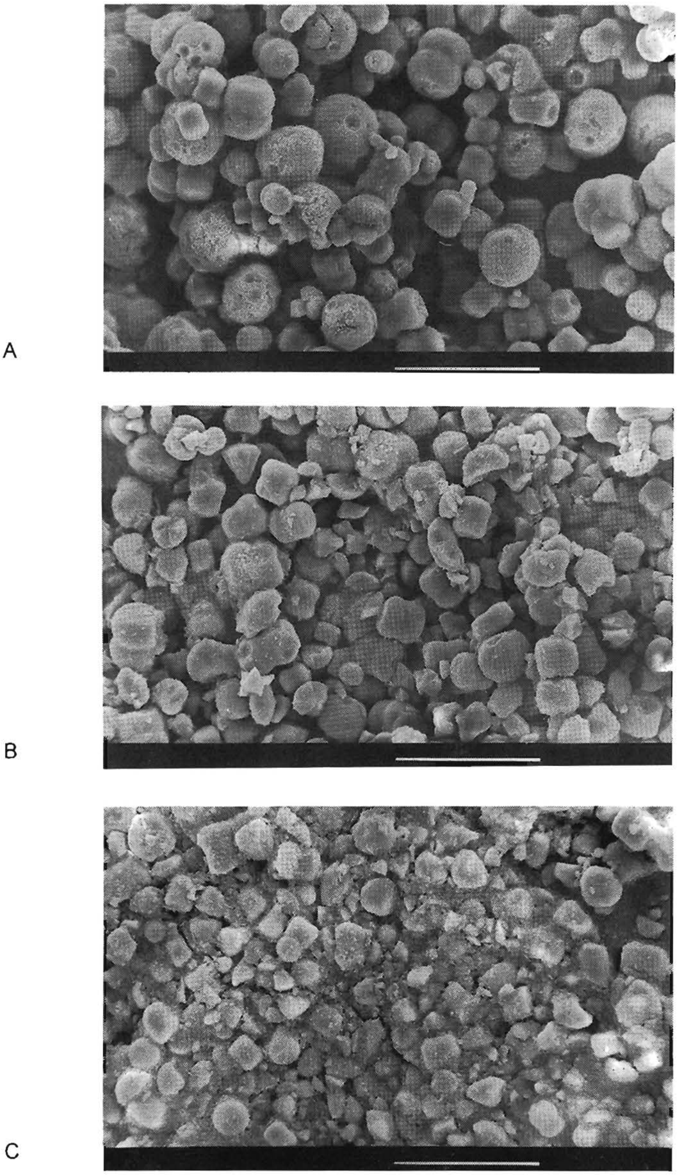

Figure 5: Morphology of VAPO-5-P2 after several regenerations compared with the fresh catalyst. The enlargement of the pictures is 800x, bar = 10 μm.
A. fresh; B. 4x used (96 hours); C. 14x used (336 hours).

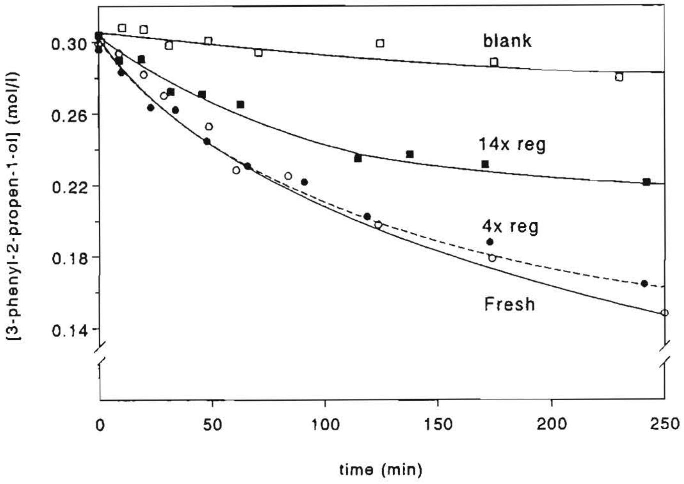

Figure 6: Activity of VAPO-5-P2 after successive regenerations.

Reactions (figure 6) with the regenerated VAPOs show that no significant loss in activity is observed after four regenerations. After fourteen regenerations the activity is decreased by about 50%. Only a small selectivity loss from 90% to 85% is observed. The vanadium loss alone can not explain this activity loss. Assuming that the concept 'reaction in micropores' holds, this decrease in activity can be a combined effect with the decreased pore volume. Note that this VAPO is less active than the VAPO used for earlier experiments.

Oxidation of 3-octanol

In order to see if the observed effects are more general a short study was made of the regeneration of VAPO used for the oxidation of 3-octanol. A VAPO with 1.48 wt% V was recovered from the reaction mixture, washed and dried. Part of the catalyst was calcined at 500°C in air. The activity and selectivity of the both catalyst batches were determined and compared with the performance of a fresh catalyst. The results are presented in table 1 and figure 7. Without calcining only a small activity results, but the selectivity based on the TBHP is very high. Upon calcining most of the original activity is restored and also the selectivity based on the peroxide drops again to a level of about 50%.

The VAPOs were recovered from the reaction mixture after a reaction time of twentyfour hours. After washing and drying the used VAPO-5s were characterised by standard techniques. The main results are shown in table 2. XRD shows no changes in the structure. After reaction the VAPOs with a high vanadium content are light green, while the VAPOs with a low vanadium content are white. ESR confirms that most of the vanadium sites are in the reduced state after reaction. The micropores of the VAPO are not accessible after reaction.

It was not possible to make the pores accessible by extracting the VAPO with an organic solvent (acetonitrile). After Soxhlet extraction for 5 days, less than 5% of the absorbed molecules were removed from the pore structure. In the filtrate minor amounts of 3-octanol, 3-octanone, 3-hexanone (standard) and *t*-butanol could be detected. The fact that the pore structure cannot be made accessible by washing, is

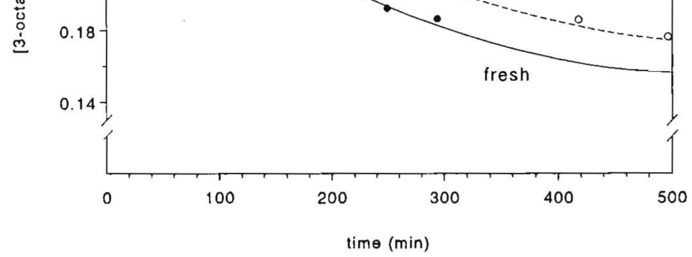

Figure 7: Activity of VAPO-5-P4 after use as catalyst for the oxidation of 3-octanol.

Table 1: Oxidation of 3-octanol catalysed by regenerated VAPO-5.

				t = 400 min		
	Catalyst (wt% V)	V_{total} (mmol)	TOF (mol/mol.h)	Conv substrate (%)	Sel substrate (%)	Sel TBHP (%)
28	VAPO-5-P4 (fresh)	0.117	2.8	40	90	40
43	VAPO-5-P4 (used, washed and dried)	≈ 0.11	1.1	19	100	100
44	VAPO-5-P4 (used, calc)	0.123	2.4	38	90	50

Conditions: acetonitrile; 71 ± 1 °C; [sub] = 0.3 M; [TBHP]/[sub] = 1.4 ± 0.1; conv: ± 1%; sel: ± 5%. TOFs are calculated at 20% conversion of the substrate. The TOFs are roughly corrected for the blank reaction.

Table 2: Characterisation of VAPO-5 used for oxidation of 3-octanol.

Catalyst	V content (%wt)	PV (ml/g) *n*-butane	Amount of organics inside the pore (%wt)
VAPO-5-P4 (fresh, calcined)	1.48	0.095	-
VAPO-5-P4 (used, calcined)	1.37	0.072	-
VAPO-5-P4 (used, dried)	-[a]	0.0[b]	7.2
VAPO-5-P4 (used, Soxhlet[c])	-[a]	0.0[b]	6.7
VAPO-5-P0 (not calcined)	-[a]	0.0	10.3
VAPO-5-P0 (calcined)	0.345	0.096	0.4
VAPO-5-P0 (used, calcined)	0.340	0.085	-
VAPO-5-P0 (used, dried)	-[a]	0.0[b]	4.9

[a]: Not determined.

[b]: Weight loss after drying at 120°C;

[c]: Soxhlet extraction for 5 days with acetonitrile.

a strong indication that the catalyst deactivates due to strongly absorbed molecules in the pore structure. Transport of molecules and reaction in the micropores become probably become impossible. TGA results show that the absorbed molecules (about 5 wt%) can only be removed thermally above 350°C which indicates that these molecules are strongly absorbed.

The VAPO loses 8 wt% of vanadium in case of VAPO-5-P4 after one reaction cycle. In addition, even a VAPO with a vanadium content as low as 0.35 wt% seems to lose some vanadium during the reaction.

General aspects of the recycling of VAPO

The VAPOs used for the oxidation of 3-octanol and 3-phenyl-2-propen-1-ol showed many similarities. In both reactions the VAPO changes during the reaction. Important differences compared with the fresh catalyst are the reduction of some vanadium sites, the loss of vanadium and the obstruction of the pore system.

The reduction of vanadium during the reaction shows that one-electron transfer steps do take place, possibly by direct reaction with the substrate. Remember that a VAPO is rather easily reduced by aromatic compounds (see chapter 4). The formation of (free) radical species during the reaction can therefore not be excluded. The always observed formation of V(IV) might be an indication that this species is the most stable oxidation state. It is known that vanadium(IV) complexes are active in the decomposition of peroxides. However, after a reaction VAPO is not active in this reaction (a high selectivity based on peroxide is always found) which can be attributed to the inaccessibility of the pore system for reactants. It appeared to be impossible to perform a reaction with a V(IV)-VAPO with accessible pores. Reduction by dihydrogen (which should give a VAPO with accessible pores) appeared not to be very effective. ESR suggests that VAPO can be reduced by dihydrogen only partially.

A VAPO used for the oxidation of 3-phenyl-2-propen-1-ol looses much less vanadium (-1%) per reaction cycle than a VAPO used for the oxidation of 3-octanol (-8%). This can be ascribed to the more severe reaction conditions (70°C instead of 50°C and $[TBHP]_o$ = 0.45 M instead of 0.3 M) in case of 3-octanol. However, after fifteen cycles the VAPO-5-P3 has lost about 20% of the initially present amount of vanadium. This suggests that a certain amount of potentially extractable vanadium (more than 20%) is already present in the fresh VAPO. Because VAPO-5-P3 and VAPO-5-P4 are very similar this also suggest that after one run still weakly bonded vanadium is present on the VAPO.

However, the influence of the calcination procedure on the formation of loosely bonded vanadium sites cannot be completely excluded. For example, during the high temperature treatment of gallium containing ZSM-5, migration of the incorporated gallium ions is observed at higher temperatures [6]. In the case of VAPO-5 no evidence can be found for the formation of loosely bonded sites other than by interaction with the substrate. If calcination is responsible for the formation of loosely bonded vanadium, it would be expected that a higher calcination temperature generates more weakly bonded sites. Calcination at 550°C, instead of 450°C, does not result in a more active VAPO and also no spectroscopic differences can be found.

Assuming that the extractable vanadium is present after preparation, the question why a VAPO does not lose all its extractable vanadium in one run is still open. The mild reaction conditions offer an explanation but another explanation assumes protection of the VAPO against leaching by strong absorption of the substrate. This latter hypothesis is strenghtened by the fact that calcining at high temperature is necessary to remove strongly bonded molecules from the pores. Literature gives also some indications. The heat of absorption of molecules into molecular sieves is high and increases with decreasing poresize. While for the absorption energy of *n*-decane on SiO_2 (aerosil) values of about 57 kJ/mol are reported [7], the same molecule absorbed into silicalite gives a heat of absorption of 112 kJ/mol. For polar molecules, like 3-octanol and 3-phenyl-2-propen-1-ol even higher heats of absorption can be expected due to an additional dipole-dipole interaction with the polar AlPO-lattice [8]. For acetonitrile absorbed on CoAPO-5 and CoAPO-11 the initial absorption energy is between 90-100 kJ/mol [9]. Moreover, it is likely that a strong absorption of molecules retards the transport (diffusion) of molecules present into the micropore.

Conclusions

The main conclusion that can be drawn is, that although the microporous structure is conserved, the VAPO-5 deactivates under the applied reaction conditions. This deactiviation is due to the irreversible absorption of molecules into the pore system of VAPO. Leaching of vanadium is also observed, which depends on the applied reaction conditions. Some of the vanadium present in VAPO is reduced during the reaction. Regeneration of the VAPO is only possible by calcination in air at elevated temperatures. Upon calcining the pore all organic compounds are removed from the pores and the vanadium(IV) species are oxidised towards vanadium(V). The results give strong indications that VAPO is not suitable as heterogeneous catalyst for oxidation reactions in the liquid phase.

Experimental Procedures

General

For more details about the preparation and characterisation of the VAPO molecular sieves see the preceeding chapters 3, 4 and 5. The origin of the chemicals used for the reactions is mentioned in chapter 5.

Recycling of VAPO as catalyst for the oxidation of 3-phenyl-2-propen-1-ol

In 500 ml of acetonitrile 30.0 g (0.220 mol) 3-phenyl-2-propen-1-ol and 5.00 g acetophenone (0.042 mol) were dissolved. The solution was dried on molsieves 3A. A solution of 29.0 g (0.225 mol) TBHP 70% in 250 ml acetonitrile was dried on Drierite and stored on molsieves after filtration. VAPO-5-P3 was carefully dried overnight at 120°C and cooled down in an dessicator. For a typical reaction 3-phenyl-2-propen-1-ol, TBHP and vanadium were used in a 1:1:0.0033 molar ratio. For the first cycle 70 ml of 3-phenyl-2-propen-1-ol and 35 ml of TBHP solution were heated at 50°C. VAPO-5 (12.5 g) was added and allowed to react for 24 h at 50°C. After each reaction the VAPO was filtered off at 50°C and washed with acetonitrile. The VAPO was dried at 80°C. Then the VAPO was used again in a new cycle or calcined at 500°C in air for 3 hours using a standard temperature program. In a new cycle the amount of reactants used were adapted to the amount of VAPO. After the first, second, fourth, seventh, tenth and fourteenth cycle a calcined sample of about 0.8 g was kept apart for analysis by XRD, SEM, PV (*n*-butane and nitrogen absorption), DRUVVIS, ESR, AAS and a test reaction with 3-phenyl-2-propen-1-ol under standard conditions.

Recycling of VAPO as catalyst for the oxidation of 3-octanol

To obtain a used catalyst a standard reaction was carried out with twice as much catalyst (about 0.8 g) without sampling. After 24 hours the VAPO-5 was filtered off at 70°C, washed with acetonitrile and dried. Part of the recovered VAPO was calcined at 500°C for 3 hours in air using a standard temperature program. Another part was first Soxhlet extracted with acetonitrile for 5 days and then dried at 80°C. The VAPO's were characterised by standard methods.

Instrumental

TGA measurements where carried out using a Shimadzu TGA-50 thermogravimetric analyser. The sample cup was slowly heated in air to burn off the organic residues (temperature program: 20→700°C; 1°C/min). Afterwards the VAPOs were bright yellow.

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VAPO-5: A Heterogeneous Catalyst ?

7

Introduction

Metal containing molecular sieves are unique catalysts because they possess a metal ion embedded in a uniform microporous structure. The participation of all the active sites inside the pores during the catalytic reaction is an essential part of the concept. The catalyst should accelerate the reaction inside the pore system and not on the outer surface and/or in the solvent. If only the outer surface of the MeAPO is involved this system can be simply regarded as an aluminophosphate supported catalyst. Moreover, the outer surface area is about two orders of magnitude smaller than the inner one and in case of a homogeneous distribution of active sites only a very small part of them is involved in a reaction. However, it is even more important that the MeAPO does not lose active material during the reaction. Obviously, loosely bonded vanadium sites are the least acceptable, because they can catalyse an undesired reaction in solution. The vanadium compounds which remain in the reaction mixture may also influence the quality and toxicity of the desired reaction product.

Surprisingly, in the search for heterogeneous liquid phase oxidation catalysts hardly any attention is paid to determine the possible role of surface attached or loosely bonded metal ions. Attention is mainly paid to the performance of these catalysts, rather than the fundamental question whether the catalyst is truly heterogeneous or not. In the scarce examples where leaching is recognised the possible contribution of dissolved metal ions to the observed activity is neglected. For example, bis(2,4-pentodionato)oxovanadium(IV) has been anchored to a crosslinked polystyrene polymer. When this catalyst was used for the oxidation of dimethylsulfoxide with TBHP a loss of 30% of vanadium was observed [1]. Comparable results were obtained with other immobilised vanadium complexes [2].

Only a few reports are known in which the measured concentration of the metal ion in solution has been correlated with the total performance and/or similar amounts of homogeneous catalyst [3,4]. The first report, about the use of CoAPO, has been discussed before (see page 31). The latter one is fascinating because it seems that an active heterogeneous oxidation catalyst can be prepared. This system consists of a molybdenum ion complexed with a polymer bonded, strongly chelating ligand (N-(2-hydroxypropyl)amino-methyl-2-pyridine). In the solutions molybdenum concentrations corresponding with less than 0.2 wt% of the total amount were found. At these low molybdenum concentrations in solution the activity of the heterogeneous catalyst is maintained at 60 mol/mol Mo.hour. This is a rather poor catalyst because it is well known molybdenum complexes are very active catalysts in this reaction (probably more than 1000 mol/mol.h) [4].

In the case of VAPO-5 arguments in favor of an intraporous reaction were presented [5]. However, in the preceeding chapters doubts about the catalytic activity of solid VAPO have been expressed:

- After removal of the VAPO from the reaction mixture there is a continuation of the reaction in case of 3-octanol and 3-phenyl-2-propen-1-ol (chapter 5), which proves that active species are present in solution.
- The recovered one has lost a small amount of vanadium (chapter 6).
- The pores of a VAPO are blocked after reaction. Calcining is necessary to restore the activity (chapter 6). Moreover, a dense phase vanadium aluminophosphate shows activity comparable with VAPO-5.

These arguments point to a major contribution of dissolved vanadium and justify a more thorough approach to prove the validity of the concept. To identify the location(s) where the reactions take place the first step is the determination of the contribution of the dissolved vanadium to the observed activity of the VAPO. If it is ensured that the reaction is truly heterogeneous the contribution of the outer surface can be determined by using large reactants that cannot enter the pores and thus only can react on the outer surface.

In this chapter the role of vanadium that has been extracted from the framework of the VAPO will be investigated. The oxidation of 3-phenyl-2-propen-1-ol and

3-octanol are used as model reactions. According to the long term recycling experiment with 3-phenyl-2-propen-1-ol about 5 mg/l of vanadium will be present in solution after reaction. The concentration of vanadium in solution is determined by GF-AAS. Whether these minute amounts of vanadium are responsible for the observed activity or not will be investigated too. Therefore reactions with small amounts of homogeneous catalyst $VO(acac)_2$ have been performed. The results are compared with the activity of VAPO. In this respect the experiments where the VAPO is removed after a short residence time in the reactor are discussed in more detail. Finally, conclusions will be drawn about the role of VAPO in the catalytic process.

Results and discussion

Analysis of trace amounts of vanadium and aluminium

The concentration of vanadium in the solution is expected to be low (< 5 mg/l). Moreover the vanadium is dissolved in an organic matrix and the available volume of the sample is small (less than 1 ml). Several techniques are known to determine low concentrations of vanadium in solution: AAS, GF-AAS and ICP-MS. GF-AAS and ICP-MS have a useful detection limit of 0.2 μg/l [6], while standard AAS has a detection limit for vanadium of only 40 μg/l. AAS would probably be suitable, but a large amount of sample is needed (> 10 ml). ICP-MS needs very expensive equipment. Given our requirements, GF-AAS seems to be the most suitable technique. Disadvantages of GF-AAS are the difficulties faced during the development of the method, the relatively long time required for analysis (typically 4 min/run) and only a single element per run can be analysed [7]. Moreover, it is known that the analysis of vanadium is interfered by many factors. Relatively little is known about the analysis of vanadium in reaction mixtures comparable with ours. This justifies a more thorough approach towards the analysis to check the quality of the measurements. A detailed discussion of the analysis can be found in the appendix.

For aluminium, originating from the aluminophosphate framework, a semi-quantitative analysis is satisfying. In principle no aluminium is expected to be present in solution and otherwise the filtration technique should be improved. GF-AAS has a detection limit of 0.01 μg/l. More information about the technique is available in the appendix.

Oxidation of 3-phenyl-2-propen-1-ol

Several experiments were conducted to determine the vanadium concentration in solution (see figure 1). VAPOs with a vanadium content between 0.35 - 2 wt% vanadium were tested. In all cases the total amount of vanadium present in the reaction mixture was kept at a constant level. From figure 1 several trends can be derived. Firstly, the higher the vanadium content of the VAPO, the higher the loss of vanadium. VAPOs containing a large amount of vanadium are relatively less stable. Secondly, the maximum concentration of vanadium is reached within 30 minutes. The almost 15 times higher concentration observed in case of VAPO-5-P8 shows that the solution in case of VAPO-5-P0 is not satured. Thus, the leaching process ceases quickly. A possible cause may be pore blocking of the VAPO due to the strong absorption of polar molecules. The small difference observed between VAPO-5-P3(2) and VAPO-5-P5 shows that VAPOs prepared according to the same recipe give comparable results. The concentration of vanadium in a reaction mixture with VAPO-5-P3(2) corresponds reasonably with the mean decrease found earlier (see

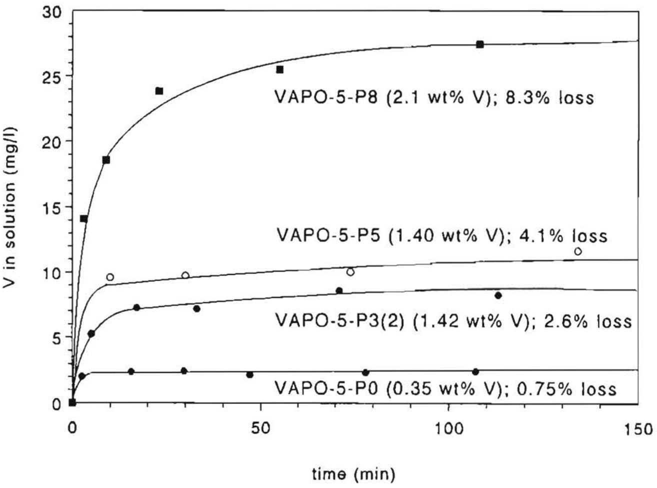

Figure 1: Concentration of vanadium in solution during the oxidation of 3-phenyl-2-propen-1-ol with TBHP catalysed by VAPO. The number between parentheses gives the initial vanadium content of the VAPO.

chapter 6). In solution a concentration corresponding to a loss of about ≈2.6% of the initial amount of vanadium present in the VAPO was found.

The concentration of aluminium in the solutions appeared to be very low and never exceeded 2 mg/l, which corresponds with an aluminium loss below 0.2%. Therefore, the vanadium did not originate from small VAPO-5 particles that passed the filter during sample preparation.

In order to gain information about the activity of this dissolved vanadium a series of experiments with $VO(acac)_2$ was conducted. The concentration of vanadium was varied between 0-300 mg/l. Figure 2 shows that vanadium in solution is a very active catalyst for the oxidation of 3-phenyl-2-propen-1-ol. The reaction is highly selective towards the epoxide. Only above 70% conversion of the substrate deviations are observed, due to consecutive reactions of the products. The calculated turnover frequency at 30% conversion of the substrate varies from 750-1800 mol/mol V.h. Thus even at a vanadium concentration of 3 mg/l (0.06 mmol/l) within one hour 30% conversion of 3-phenyl-2-propen-1-ol can be obtained.

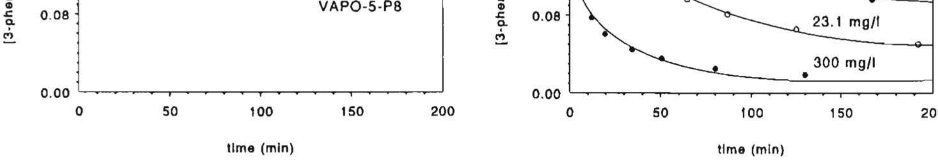

Figure 2: Epoxidation of 3-phenyl-2-propen-1-ol with TBHP catalysed by VAPO-5s (300 mg V/l) (left) and $VO(acac)_2$ (0-300 mg V/l) (right). Conditions: 50°C; dry acetonitrile; $[sub]_0$ = 0.30 M; [TBHP]/[sub] ≈ 1.0.

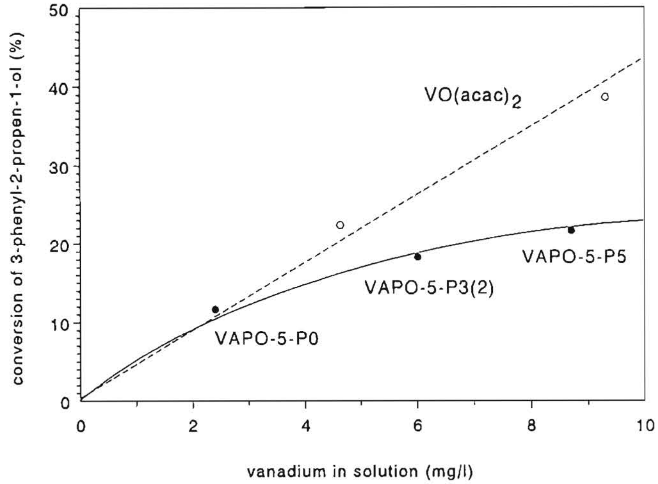

Figure 3: The observed conversion of 3-phenyl-2-propen-1-ol vs. [vanadium] in solution. The results obtained with VO(acac)2 and VAPO-5 are shown.

In figure 3 the conversion of 3-phenyl-2-propen-1-ol after a reaction time of 30 minutes *versus* the concentration of vanadium in solution is displayed. For a fair comparison the reference point (30 minutes) needs to be at low conversion of the substrate to ensure that the reaction rate is not too much influenced by the reaction products. The relation between the concentration of vanadium in solution and the conversion seems to be linear. When the conversion after 30 minutes is plotted against the vanadium concentration a deviation from linearity is observed above 30 mg V/l (not shown). During the reactions with VAPO-5 the concentration in solution is also measured. In figure 3 the measured conversion of 3-phenyl-2-propen-1-ol obtained with VAPO is shown. The concentration of vanadium in solution is equal to the mean concentration of vanadium measured during the first 30 minutes of the reaction. It appears that the conversions obtained with VAPO are comparable with or even lower than the conversions obtained with the equal amounts of VO(acac)$_2$ present in solution. Therefore the observed activity can be explained by the amount of dissolved vanadium and the solid VAPO does not contribute significantly to the reaction. Given the loss of a few percent of vanadium, more than 95% of all the vanadium present in the reactor does not take part in the reaction. However, this claim is only valid when the vanadium in solution has similar reactivity, regardless of it originates from $VO(acac)_2$ or VAPO. When $VO(acac)_2$, a tetravalent vanadium compound, is added to the reaction mixture it is immediately converted into a vanadium peroxo complex (VOO*t*Bu). Moreover, only small differences in activity were observed in the oxidation of cyclohexene with TBHP catalysed by different vanadium complexes [8]. The difference in reaction rate between the least active catalyst, $VO(acac)_2$, and the most active one $(n\text{BuO})_3VO$ is 3.7. It is likely that the vanadium leached from the VAPO is present in solution as a peroxo complex because of the excess of peroxide in the reaction mixture.

As mentioned in chapter 5 a simple experiment to prove whether the reaction is heterogeneously catalysed or not is the removal of the catalyst from the reaction mixture after a certain time and following the reaction in the filtrate. The leaching profiles of VAPO in figure 1 show that, the maximum concentration of vanadium is reached after a short reaction time. Nevertheless the point of removal of the catalyst needs to be carefully determined, otherwise a wrong conclusion can be drawn. This is illustrated in figure 4. In this example it is assumed that the reaction takes place only in solution. Case A illustrates the situation where the maximum metal concentration in solution is nearly reached at the point of removal. As expected, after removal of the catalyst the reaction continues at the same rate as the non-filtered reaction mixture. Case B shows a regular but relatively slow leaching process. The reaction rate is initially low. When the catalyst is filtered-off the metal concentration in solution is relatively low and the reaction hardly proceeds. With the catalyst present initially a reaction with an increasing rate is observed. The striking difference between both reactions leads to the (wrong) conclusion that the reaction is heterogeneously catalysed. Therefore, to interpret these experiments correctly the concentration of the metal ion in time needs to be measured. Moreover, to observe a change in reaction rate a balance should be sought between the point of filtration and the maximum attainable conversion of the substrate that can be reached. In the case of the oxidation of 3-phenyl-2-propen-1-ol case A occurs; the point of removal is estimated at 40 minutes. At this point the vanadium concentration in solution is almost at a maximum and the conversion of the substrate is about 20%, while the maximum conversion that can be reached is more than 70%.

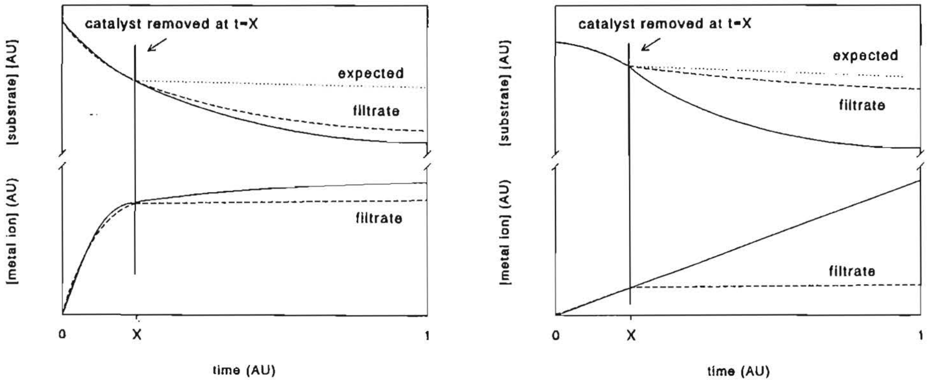

Figure 4: Effect of leaching profiles on the reactions were the catalyst is removed at t=X. It is assumed that only dissolved metal is active as catalyst.

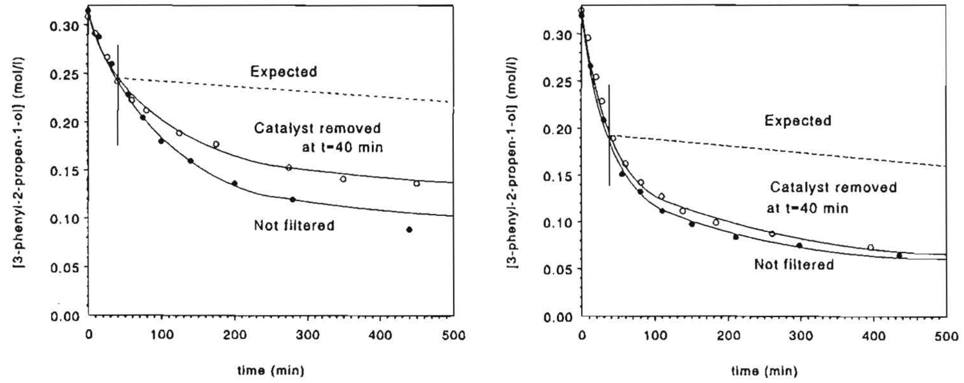

Figure 5: Removal of VAPO-5-P4 from the reaction mixture after 40 minutes on the conversion of 3-phenyl-2-propen-1-ol. The experiment was carried out in acetonitrile (left) as well as in benzene (right).

Figure 5 shows the results of experiments where VAPO-5-P4 (1.48 wt% V) was removed from the reaction mixture at t=40 minutes. The experiment was carried out in acetonitrile and benzene. When acetonitrile is used as solvent the reaction is somewhat slowed down after filtration, while removal of the VAPO does not influence the reaction in benzene. In addition the reaction rate in benzene is higher. A similar result was obtained with VAPO-5-P0, which has a low vanadium content (0.35 wt%) (no figure). As shown in figure 1 the solvent contains vanadium already after a short reaction time. The results always point to a large contribution of dissolved vanadium to the observed activity, regardless the vanadium content of the VAPO-5.

Oxidation of 3-octanol

The concentration of vanadium in solution was followed in time during the oxidation of 3-octanol by TBHP. Three representative VAPO-5 catalysts were compared: a VAPO-5 with low, medium and high vanadium content. The total vanadium content in the reaction mixture was kept constant. In figure 6 the concentration of vanadium in solution is shown. The activity, expressed as decrease in substrate concentration in time, is also shown (figure 7). The loss is calculated from the amount of vanadium measured in solution. As observed in the oxidation of 3-phenyl-2-propen-1-ol the VAPO loses a higher amount of vanadium during the reaction. This can be explained by the more severe reaction conditions (higher temperature and higher [TBHP]). It was found that the vanadium content of VAPO-5-P4 decreased by about 8% during the reaction, which is in good agreement with the amount of vanadium found back in solution (see page 120).

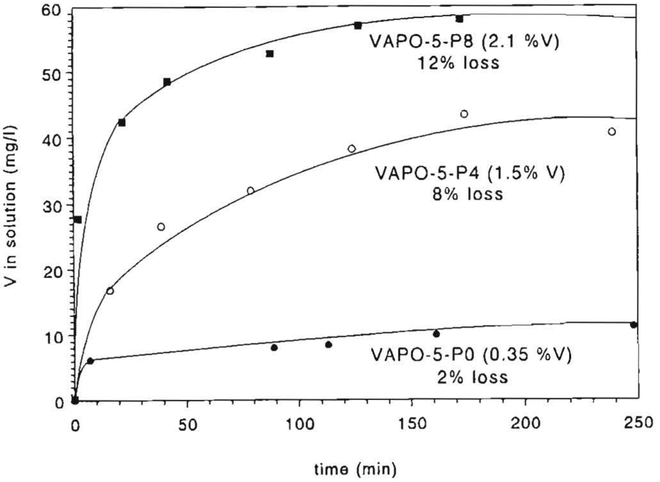

Figure 6: Concentration of vanadium in solution during the oxidation of 3-octanol with TBHP catalysed by VAPO-5. The amount of vanadium lost is indicated between parentheses.

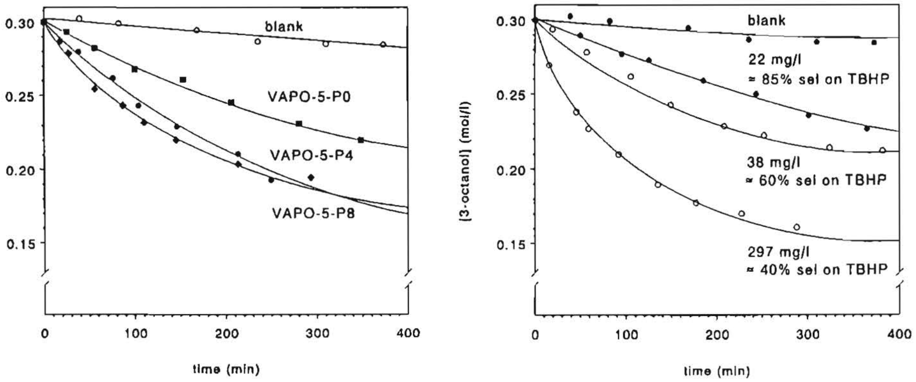

Figure 7: Oxidation of 3-octanol with TBHP catalysed by VAPO-5s (400 mg/l) (left) and VO(acac)$_2$ (0-300 mg V/l) (right). Conditions: Dry acetonitrile, 70°C, [octanol] = 0.3 M, [TBHP] = 1.4 M.

Most of the vanadium is released in the early stages of the reaction. After about 30 minutes the concentration in solution increases only slowly. As in case of the oxidation of 3-phenyl-2-propen-1-ol the concentration of aluminium in solution never exceeded 2 mg/l.

In a series of experiments the activity of VO(acac)$_2$ was measured at concentrations between 0-300 mg/l (figure 7). VO(acac)$_2$ is a much less active catalyst for the oxidation of 3-octanol than for the oxidation of 3-phenyl-2-propen-1-ol. TOFs at 30% conversion of the substrate are about two orders of magnitude lower. Values between 8.6-18 mol/mol.h are found. The selectivity of the alcohol oxidation based on the product is close to 100%. The selectivity on peroxide tends to rise at lower concentrations of vanadium. Below 50 mg V/l the selectivity on TBHP is estimated to be higher than 60%.

A direct comparison between the concentration/time curves of VAPO-5 and VO(acac)$_2$ shows that not all activity can be explained by the vanadium ions in solution. It is assumed that vanadium ions have similar activity regardless of their

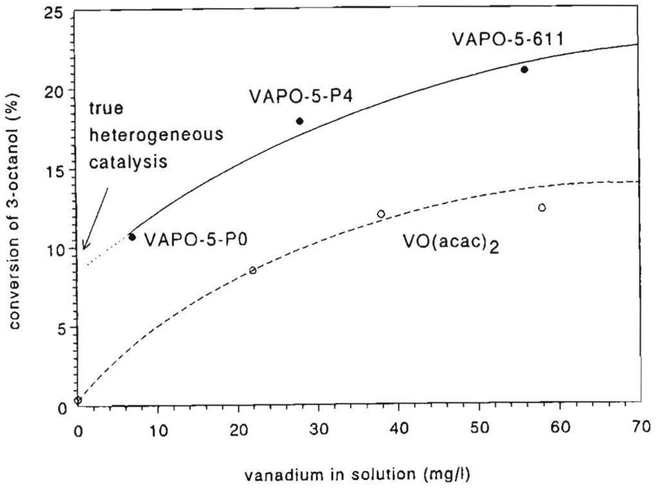

Figure 8: Activity of vanadium in solution compared with the activity of VAPO-5 after 100 minutes.

origin, which has been made feasible earlier. This should mean that VAPO shows activity as heterogeneous catalyst in the reaction. This hypothesis was investigated in more detail. In figure 8 the vanadium concentration in solution (figure 6) is plotted against the conversion of the substrate (figure 7). The conversion and concentration of vanadium at t=100 min is taken. After this time the activity is not much influenced by byproducts and deactivation of the catalyst. The results obtained for $VO(acac)_2$ and VAPO-5 are shown in the same graph. As expected, the more $VO(acac)_2$ in solution, the higher the substrate conversion. At concentrations more than 60 mg V/l the curve flattens off. At a similar vanadium concentration in solution the conversion obtained with VAPO is always higher. When the amount of dissolved vanadium is extrapolated to zero, the contribution of the true heterogeneously catalysed reaction can be calculated. At this point the conversion of the substrate is certainly not zero, indicating that solid VAPO is active. The calculated TOF is 2.2 mol/mol.h (9 % substrate ($\equiv$ 0.405 mmol) is converted in 1.67 h using 0.11 mmol V). The parallel curves in figure 10 suggest that the activity of solid VAPO is independent of the vanadium content. Note that the amount of leached vanadium is small (less than 15%), leading to a comparable total amount of heterogenised vanadium present in all reaction mixtures. A heterogeneously catalysed reaction is responsible for about

50% of the observed conversion of 3-octanol when VAPO-5-P8 (with a high vanadium content) is used as catalyst.

The role of VAPO-5 in this reaction can be derived from the experiments where VAPO-5 has been removed from the reaction mixture after a certain time. Considering the conditions decribed earlier filtration after 60 minutes at about 10% conversion gives useful results. A typical result is shown in figure 9. These graphs show that after removal of the catalyst (VAPO-5-P8) from the reaction mixture 3-octanol is still converted to 3-octanone, although that the consumption of the substrate is slower than in the case when VAPO-5 is present. On the other hand, TBHP reacts much slower after filtration 9. Consequently, because 3-octanone is still formed the selectivity of the product on TBHP rises from 45% to 75%. Therefore, the vanadium species responsible for the non-productive decomposition of the peroxide is probably present on the VAPO-5.

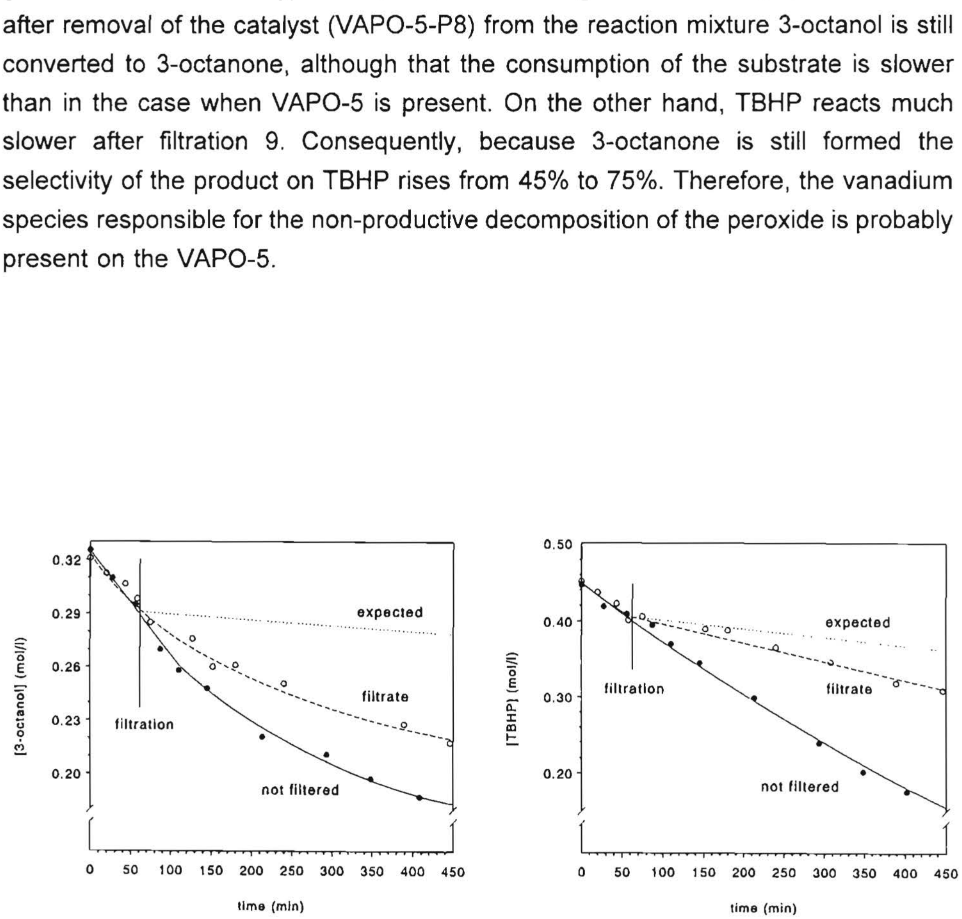

Figure 9: Removal of VAPO-5-P8 (2.1 wt%) from the reaction mixture after 60 minutes. Shown is the decrease of substrate in time (left), and the TBHP consumption in time (right).

From these experiments it is clear that in the oxidation of 3-octanol more reactions occur simultaneously. VAPO-5-P0 loses a small amount of vanadium but the observed selectivity based on TBHP is only 35%, which can almost solely be attributed to the heterogeneously catalysed reaction. The reaction catalysed in solution is probably very selective on the peroxide (> 80%), according to the results from the $VO(acac)_2$ catalysed reactions. Therefore, on VAPO-5 the non-productive decomposition of the peroxide prevails. The larger contribution of dissolved vanadium in case of VAPO-5-P8 is reflected in a higher selectivity based on peroxide (45%). However, the favourable contribution of vanadium in solution to the selectivity on TBHP is expected to be limited because the selectivity drops when more vanadium is present in solution (figure 8).

General aspects of the behaviour of VAPO as catalyst in the reactions

In both reactions it was shown that the VAPO-5 has at best a weak activity. At this point of the discussion it is interesting to ask whether this observation also holds for other reactions with VAPO-5 or not. VAPO-5 was shown to catalyse the epoxidation of 2-cyclohexen-1-ol with TBHP (see page 95). Although it was not investigated the conclusion that also in this case dissolved vanadium is responsible for the observed activity seems to be justified. An argument that supports this conclusion is the large difference between the $VO(acac)_2$ and VAPO catalysed reaction. Another argument is the decrease in activity per vanadium site when VAPOs with a lower vanadium content are used. These VAPOs are more stable towards leaching and the lower activity is explained by a lower concentration of vanadium present in solution.

Earlier it was concluded that VAPO-5 is an active catalyst for the epoxidation of alkenes with TBHP. It was argued that this reaction is intraporous [5]. This conclusion was drawn on the basis of a shape selective poisoning experiment. The VAPO catalysed epoxidation of 2,3-dimethyl-2-butene with TBHP was studied in the presence of triethylamine or triphenylamine. Triethylamine, which is easily absorbed by large-pore molecular sieves poisons all active sites, while triphenylamine can only poison the sites present on the outer surface. It was found that triethylamine blocked the epoxidation reaction for about 2 hours, in which only triethylamine N-oxide is formed. When all amine was consumed the epoxidation reaction started with a rate higher than that of the unpoisoned reaction. Triphenylamine did not affect the rate of epoxidation.

However, there is an alternative explanation for the results of the poisoning experiments. It is well known that vanadium complexes catalyse the oxidation of tertiary amines towards N-oxides [9]. The reactants are added in a ratio alkene : TBHP : amine = 40 : 20 : 1 mmol. It is assumed that also in this experiment the vanadium concentration in solution is less than 10 mg/l (excess [amine] / [V] > 100). Under reaction conditions the amine competes with the alkene for a coordination site. Although the alkene is present in large excess over the amine, the latter is still expected to coordinate and react with the site. The product, the N-oxide, does not compete with the vanadium site. Thus, only when all amine has reacted the alkene reacts. Thus if triphenylamine would be more reactive than triethylamine the epoxidation of 2,3-dimethyl-2-butene would be hardly influenced [10]. It would have been more conclusive if experiments with a homogeneous catalyst were carried out for comparison.

Conclusions

During a reaction VAPO-5 loses vanadium. The amount of vanadium that is lost depends on the substrate, the reaction conditions and the amount of vanadium present in the VAPO. From VAPO-5s with a higher vanadium content more vanadium is leached. After a relatively short reaction time the concentration of vanadium in solution reaches a constant level.

Refering to the title of the chapter, the answer to the question depends on the type of reaction. VAPO shows a low but significant activity as heterogeneous catalyst in the oxidation of 3-octanol. VAPO is a poor catalyst regarding the selectivity on the peroxide. Moreover, also dissolved vanadium contributes to the observed reaction. The epoxidation of 3-phenyl-2-propen-1-ol with TBHP is mainly catalysed by dissolved vanadium. This reaction occurs so efficiently in solution that the influence of the solid VAPO is only very small and cannot be determined. In this case more than 95% of all vanadium present in the VAPO is not active.

Experimental procedures

Chemicals

Bis(2,4-pentodionato)-oxovanadium(IV), VO(acac)$_2$, Aldrich, 95% (recrystallised from chloroform);
Bis(2,4-pentodionato)-oxovanadium(IV), VO(acac)$_2$, Janssen, 99%;
Triisopropoxyvanadium(V)oxide, VO(iOPr)$_3$, Aldrich, >95% (AAS);
1-Propanol, C_3H_8O, Riedel-de Haën, P.A.;
Nitric acid, Merck, 65% (Suprapur);
Vanadium standard solution 1000 mg/l, Merck, Titrisol;
Aluminium standard solution 1000 mg/l, Merck;
Aluminiumtriisopropoxide, Janssen, 98+%;

Instrumental

Samples were diluted using a Metrohm 725 Dosimat. The analyses were carried out using a Perkin Elmer 3030 atomic absorption spectrophotometer equipped with a Model HGA-600 graphite furnace and an AS-60 autosampler. Pyrolytic coated tubes (Perkin Elmer, B0 135653) were used.

Analysis of vanadium

Several dilutants and procedures were tested to obtain reliable results. Reference compounds for vanadium were VO(acac)$_2$ and VO(*i*OPr)$_3$. Solutions of VO(*i*OPr)$_3$ in propanol were prepared under argon atmosphere. After injection of the sample (20 μl) on the tube wall the sample was heated to 90°C (propanol) or 120°C (water) in 20 seconds. After drying for 25 seconds the sample was heated to 1150°C in again 20 seconds. This temperature was kept constant for 20 seconds. The vanadium was instantaneously atomised at 2650 °C. The vanadium signal was measured for five seconds at λ=318.4 nm and a slit of 0.7 nm. Finally, the oven was heated to 2680°C for three seconds to remove all residual products. Except for the period during the measurement an argon flow of 300 ml/min is passed through the oven.

Analysis of aluminium

All glasswere was thoroughly rinsed with 2% nitric acid before use. All analyses were carried out in 1-propanol. Al(*i*OPr)$_3$ was used as reference compound. The sample (20 μl) was directly injected on the tube wall and after drying, heated to 1300°C for 20 seconds. Then the oven was heated instantaniously to 2400°C, which appeared to be the optimal atomisation temperature. The signal was measured for two seconds at λ = 309.3 nm and a slit of 0.7 nm. Afterwards the oven was heated for three seconds at 2700°C.

Reactions and removal of the catalyst from the reaction mixture

Reactions were carried out according to procedures described in chapter 5. At a certain point (see text) the content of the reactor was removed with a syringe and filtered hot (0.45 μm brown-rim filters of Schleicher & Schuell) into a pre-heated reactor. The total reactor contents could be transfered within a few minutes. The solutions are clear.

Appendix

Analysis of vanadium

The analysis of vanadium in the reaction mixtures was thoroughly studied to check the reliability and duplicity of the method. The analysis of vanadium by the GF-AAS technique is complex and interfered by many factors [11]. Besides, for our samples (organic solvent with complex organic molecules and peroxides) no method of analysis was available.

After introduction of the sample and passing through the drying and ashing steps of the temperature program the vanadium signal is detected (figure 10). The shape of the signal is comparable to that mentioned in literature [11]. Since the signal suffers from some tailing, the peak area is used for calibration. Two typical calibration curves are shown in figure 12, using two different solvents (1-propanol and 0.2 % HNO_3 / water). A commercial solution of vanadium was used to obtain this calibration curves. Both curves are similar, indicating no interference of the solvent on the signal. To avoid solibility problems of the reaction mixtures, 1-propanol was used as dilutant for all measurements.

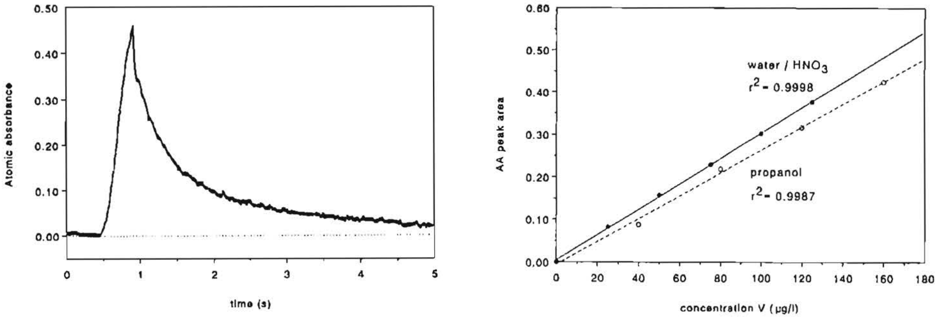

Figure 10: Signal observed for vanadium (left) and calibration curve (right).

Analysis of reference compounds showed a large difference between the absolute values found by different methods (table 1). In acidified water slightly higher values than theoretical are found. However, when 1-propanol is used only about 50% of the theoretical amount is recovered. Addition of HNO_3 to the 1-propanol has a large positive effect on the signal, however still too low values are found.

Given these results a series of experiments was conducted to check the effect of different solvents on the accuracy of the results. Some samples were analysed in different ways. The results are shown in figure 11. Clearly, the obtained results show a wide variation. In all cases propanol as solvent gives

Table 1: Analysis of vanadium content in reference compounds via different methods

Reference compound (wt% V)	Results (wt% V) Propanol	Propanol / HNO_3 (0.2%)	Water / HNO_3 (0.2 %)
$VO(acac)_2$ (19.2)	9.2 ± 0.4	16.5 ± 0.2	20.8 ± 0.7
$VO(iOPr)_3$ (20.9)	10.3 ± 0.6	19.6 ± 0.9	-[a]

All values are obtained using a calibration curve. Values are based on several measurements.

[a]: not measured

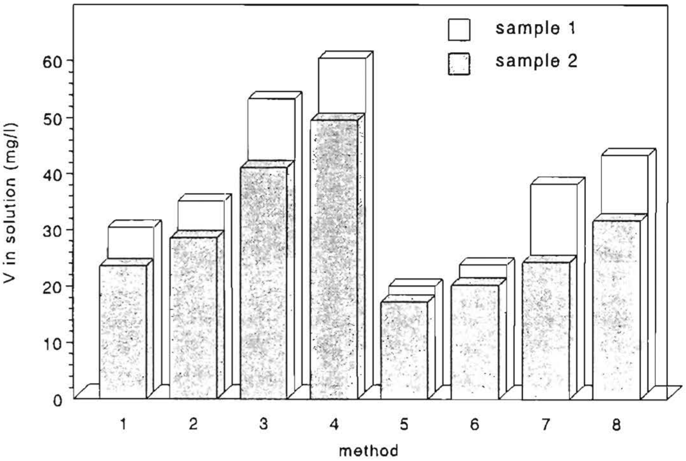

Figure 11: Comparison between different methods of analysis

The reaction mixtures contain 3-octanol, 3-octanone, TBHP, *t*-butanol, 2-hexanone and acetonitrile. Method 1 is commonly used for the analysis (figure 1 & 6).

Unless otherwise stated the solvent indicated is also used for rinsing.

Calibration curve.

1. Solvent 1-propanol.
2. Solvent 1-propanol + 0.2 % HNO_3; 1-propanol used for rinsing.
3. Solvent water + 0.2 % HNO_3; 1-propanol used for rinsing.
4. Solvent water + 0.2 % HNO_3.

Standard addition.

5. Solvent 1-propanol.
6. Solvent 1-propanol + 0.2 % HNO_3; 1-propanol for rinsing.
7. Solvent water + 0.2 % HNO_3; 1-propanol used for rinsing.
8. Solvent water + 0.2 % HNO_3.

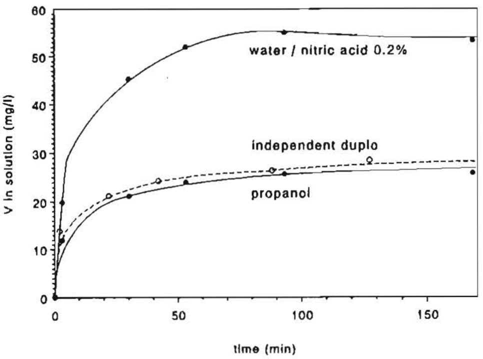

Figure 12: Analysis of the reaction mixture of the VAPO catalysed oxidation of 3-octanol. Two independent series are measured in propanol. One of these series is also measured in water/HNO_3.

the lowest value, which is about 50% of the highest value. Acidified water as solvent gives the highest value. results. The concentration of nitric acid added to the 1-propanol was varied between 0-0.5% HNO_3.

Surprisingly, while the signal of the reference samples increased (table 1), the signal of the reaction mixtures increased only slightly (figure 12). The optimum concentration of nitric acid added to propanol is about 0.2%. Above this concentration no further increase of the signal is observed.

Note that there is also an effect of the solvent used for rinsing of the autosampler and the method of measurement (via a calibration curve or the standard addition method). Combining this with the results obtained for the reference compounds, the absolute value found when 1-propanol is used as standard is too low (about 50%). Figure 13 shows the results of two independantly carried out reactions, which show that the results obtained by using 1-propanol as solvent are well reproducable, although these results are systematically to low. The systematic error appeared also to be dependant on the contents of the reaction mixture. For 3-octanol a mean deviation of about 50% was found (compare method 1 and 4), for 3-phenyl-2-propen-1-ol the deviation from the absolute value was about 35% (no figure, but measured). Because the concentrations measured in acidified water were closer to the absolute value than those measured in propanol, all concentrations mentioned in the text were multiplied by 2 in case of 3-octanol and by 1.5 in case of 3-phenyl-2-propen-1-ol.

The too low values obtained when 1-propanol is used as solvent suggest that some of the vanadium is lost during the measurement. Mechanisms for the vanadium loss can be the formation of volatile vanadium compounds during the ashing step and the formation of very stable non-volatile vanadium carbides that bind irreversibly to the wall of the oven [11]. Variation of the ashing temperature between 90-1150°C did not influence the results of the measurements. When volatile compounds are formed during this step a higher signal would be expected at lower ashing temperature. To check if carbides were formed the signal was measured during the cleaning step. The absorption peak of vanadium shows some tailing, which may be an indication for some slow vanadium release. However, during the cleaning step no more vanadium can be detected. Moreover, blanc samples (propanol) always give a zero signal which also indicates that no vanadium is left in the oven.

Analysis of aluminium

The analysis of aluminium was less extensively examined. The solvent (1-propanol) seems to give no problems. The absorption profile of aluminium is sharp and almost without tailing (figure 13), therefore the peak height, rather than the peak area was used for the measurement of the atomic absorption value. The calibration curve was linear up to 80 μg Al/l propanol (figure 13). Aluminium contents found for the standard corresponded to 13.0 wt% Al and 11.8 wt% Al (theoretical for $Al(\mathit{i}OPr)_3$ 98+%: 12.9-13.2 wt% Al). These results were obtained with independent calibration curves.

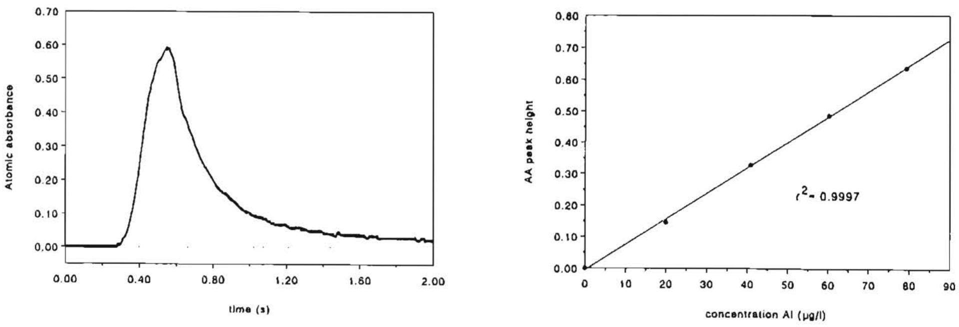

Figure 13: Signal observed for aluminium analysis (left) and calibration curve (right).

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8

Intrinsic Activity of VAPO-5

Introduction

VAPO molecular sieves loose small amounts of vanadium during the reaction. Therefore the direct determination of the intrinsic activity of VAPO-5 is difficult. To determine the activity of solid VAPO a material has to be prepared that loses only very small amounts of vanadium during the reaction. For the oxidation of 3-octanol this would mean that a concentration of 1 mg V/l in solution is acceptable to neglect the contribution of dissolved vanadium. During the oxidation of 3-phenyl-2-propen-1-ol only 0.2 mg V/l in solution is tolerable.

Pretreatment of the VAPO before the reaction can be a possible method to make a more stable VAPO. To remove vanadium from the lattice, several procedures are reported. Vanadium could not be removed from the framework by ion exchange with an 1 M solution of sodium chloride [1]. Others found that VAPO-5, compared with VS-1, V-ZSM-5 and V/SiO_2, is relatively resistant towards a treatment with 30 wt% H_2O_2 at room temperature [2,3]. Upon treatment of VAPO-5 with hydrogen peroxide at reflux temperature the vanadium content decreased from 0.9 → 0.55 wt%, a loss of about 40% [3]. However, the residual VAPO did not show activity anymore [3].

In this chapter the extraction of vanadium from various VAPO-5 samples will be discussed. Several solvents were tested as extracting agents. The limited stability of VAPO against aqueous acid or basic media requires a careful choice of the extraction agent. The products were calcined, characterised and applied as catalyst. In chapter 7 it was argued that VAPO-5 is at least partially active as a true heterogeneous catalyst for the oxidation of 3-octanol with TBHP, while the epoxidation of 3-phenyl-2-propen-1-ol is (almost) completely catalysed by vanadium in solution. Therefore, in this chapter emphasis is put on the oxidation of 3-octanol.

Results and discussion

Preparation and characterisation of extracted VAPOs

VAPO-5-P7 was treated with different solvents. Water, glacial acetic acid and acetonitrile were tested. These solvents were chosen because of their polarity. It is expected that polar molecules are the most effective extracting agents to remove the weakly bonded vanadium ions from the lattice. The samples were extracted by the Soxhlet technique for 7 days in order to be sure that all weakly bonded vanadium was removed from the lattice. Alternatively, vanadium was extracted from the lattice with TBHP in acetonitrile for 24 h at 70°C.

Table 1 shows the results of these experiments. Water proves to be the most effective extraction agent. By using water relatively much vanadium is extracted (17%) while the micropore structure is preserved. Although glacial acetic acid removes vanadium more effectively, the micropore structure collapses. On the contrary acetonitrile does hardly remove any vanadium at all. By extraction with TBHP only 10% of the vanadium is removed but the micropore structure is preserved. Measurement of the pore volume showes that all samples are slightly damaged during the extraction procedure.

Table 1: Removal of vanadium from VAPO-5-P7 with different extraction agents.

		Soxhlet Extraction			Extraction
	Fresh	water	glacial acetic acid	acetonitrile	TBHP in acetonitrile
Pore volume(ml/g)	0.086	0.069	0.022	0.082	0.073
Vanadium content (wt%)	1.89	1.58	0.61	1.86	1.77
Structure	AFI	AFI	Tridymite + AFI	AFI	AFI

Samples were Soxhlet extracted for 7 days and calcined. The extraction with TBHP was carried out with 0.45 M TBHP for 24 h at 70°C.

Several VAPOs, with varying vanadium content, were extracted with water and subsequently calcined. The results are shown in table 2. Compared with a fresh sample the extracted samples have a lower absorption capacity for *n*-butane. The extent of the decrease of pore volume seems to be related to the vanadium content of the sample. The more vanadium is present in the VAPO, the more vanadium is extracted and the more the sample is damaged. Contrary to the observed vanadium loss, the DRUVVIS spectra of extracted samples with a low vanadium content show a small increase of intensity (figure 1). Only when the amount of extracted vanadium is large (33%) a relatively small decrease of the absorption intensity is measured (20%). In all cases the shape of the spectrum does not alter, which suggests that no specific vanadium sites are removed. A possible explanation for this discrepancy between the expected and measured intensity could be a small increase of the extinction coefficient of the vanadium site, due to a change of the coordination sphere around the vanadium ion.

VAPO-11-D1 (0.32 wt% V) was also extracted with water. After extraction a hydrated VAPO-11 with contracted pores was left [4]. Only drying or calcining could dehydrate the VAPO-11. The pore volume of the residual material was decreased by about 25%. The vanadium content was not determined.

Table 2: Soxhlet extraction of several VAPO-5s with water.

Sample	PV (ml/g) *n*-butane		Δ (%)	V-content (wt%)		Δ (%)
	before	after		before	after	
VAPO-5-P0	0.090	0.080	11	0.345	0.303	12
VAPO-5-P10	0.100	0.087	13	1.33	1.17	12
VAPO-5-P5	0.086	0.070	18	1.40	1.18	16
VAPO-5-P7	0.086	0.069	19	1.89	1.58	16
VAPO-5-P8	0.081	0.071	12	2.10	1.41	33

Samples were Soxhlet extracted for 7 days and calcined.

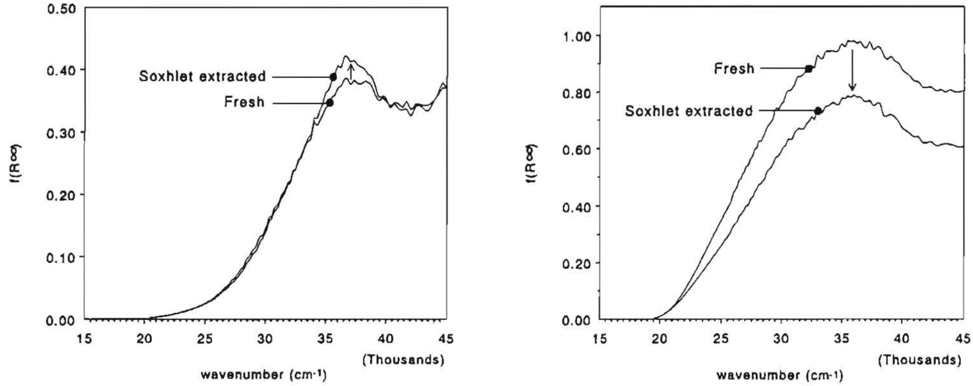

Figure 1: DRUVVIS spectra of the extracted and fresh samples: VAPO-5-P0 (left) and VAPO-5-P8 (right).

Reactions catalysed by extracted VAPO-5s

Oxidation of 3-phenyl-2-propen-1-ol

The extracted VAPOs were less active as catalyst for the oxidation of 3-phenyl-2-propen-1-ol with TBHP than the corresponding fresh VAPOs. For example an extracted VAPO-5-P5 was about three times less active than VAPO-5-P5. In chapter 7 it was concluded that only dissolved vanadium is responsible for the observed activity. To check this conclusion the vanadium content in the reaction mixture of the extracted VAPO was determined by GF-AAS. About 3 mg/l vanadium could be detected in the reaction mixture, which is about 60% less than was found in the reaction mixture of the fresh VAPO-5-P5. Because also a much lower activity was found, the conclusion that VAPO-5 is not an active catalyst is supported. The experiments with extracted VAPO-5s show that vanadium still is removed from the VAPO during reaction.

Oxidation of 3-octanol

Some of the extracted VAPOs were tested as catalysts for the oxidation of 3-octanol with TBHP. VAPO-5-P3(15), which was extensively used as catalyst for the oxidation of 3-phenyl-2-propen-1-ol (chapter 6) and already lost an appreciable amount of vanadium was also tested too. The results are shown in table 3. All samples are less active than the fresh samples (see page 98). The calculated turnover frequencies are less than 0.5 mol/mol.h, which is 10-20 % of the original activity. Contrary to the observations for the fresh VAPO-5s, the activity is, within the error of measurements, not dependent on the vanadium content of the VAPO-5. The reaction seems to be more selective based on the TBHP, although due to the low conversion the precision of the numbers is not high. These results suggest that there is almost no non-productive TBHP decomposition. Interestingly, while the fresh VAPO-5s immediately turn red when they are contacted with the reaction mixture, this color change is much less intense or even absent when extracted VAPO-5s are used.

Table 3: Oxidation of 3-octanol with TBHP catalysed by extracted VAPO-5s.

				t=400 min		
	Catalyst (wt% V)	V_{total} (mmol)	TOF (mol/mol.h)	Conv sub (%)	Sel sub (%)	Sel TBHP (%)
22	-	-	-	5	100	-
45	VAPO-5-P0 Sox(0.30)	0.111	0.4	11	100	52
46	VAPO-5-P5 Sox(1.18)	0.175	0.5	18	100	70
47	VAPO-5-P10 Sox(1.17)	0.233	0.2	13	100	60
48	VAPO-5-P7 Sox(1.58)	0.120	0.5	15	100	85
49	VAPO-5-P3(15)(1.24)	0.115	1.0	20	86	60

Conditions and experimental errors: Acetonitrile; 71 ± 1 °C; [sub] = 0.3 M; [TBHP]/[sub] = 1.4 ± 0.1; [TBHP]/[V] ≈ 40; conv: ± 1%; sel: ± 5%; sel on TBHP: ± 10%. TOFs are calculated at 10% conversion of the substrate and roughly corrected for the blank reaction.

The reaction catalysed by fresh and extracted VAPO-5-P0 was studied in more detail. In chapter 7 it was concluded that VAPO-5-P0 was active as a heterogeneous catalyst. Figure 2 shows the direct comparison between extracted and the fresh VAPO-5-P0. The actual concentration of vanadium in solution was also determined (figure 2). To start with the latter figure, it is clear that the amount of leached vanadium is about 70% lower. Apparently, leachable vanadium is still present in the extracted VAPO or generated during the initial stages of the reaction. As observed for the fresh sample the leaching soon stops. The comparable low activity found for all samples suggests that most of the loosely bonded vanadium is removed with water. It is not unlikely that the observed low activity is caused by these tiny amounts of vanadium in solution.

Figure 2 shows that the extracted VAPO has lost almost all activity. Thus, the residual vanadium present in the VAPO (88% of the original amount) is hardly active. This leads to the important conclusion that the removed vanadium sites (12% of the total amount present) are responsible for the observed activity of the fresh VAPO-5. Recalculation of the TOF for VAPO-5-P0 (see page 98) leads to 20 mol/mol.h (2.4 x (100/12)).

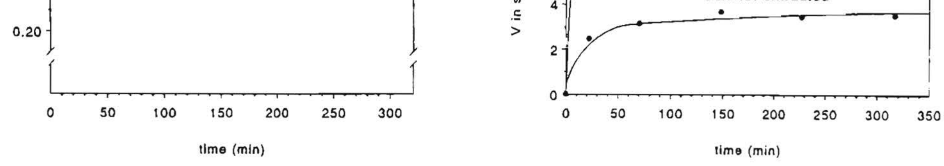

Figure 2: Comparison between VAPO-5-P0 and the Soxhlet extracted VAPO-5-P0 as catalyst for the oxidation of 3-octanol with TBHP: Consumption of 3-octanol in time (left) and concentration of vanadium in solution (right).

Conclusions

Vanadium can be effectively removed from the VAPO-5 by Soxhlet extraction with water, without destroying the micropore structure. The amount of vanadium that can be extracted is in the range 10-35%. VAPOs with a high vanadium content contain more extractable vanadium. The residual VAPO is hardly active as catalyst in the oxidation of 3-octanol with TBHP. The extracted VAPO is not absolutely stable but still loses small amounts of vanadium during the reaction. Comparison between the performance of a fresh VAPO-5 and an extracted VAPO-5 shows that only 10-15% of the total amount of vanadium present in VAPO is active, while the remaining 85-90% is not active.

Experimental procedures

Reaction conditions and characterisation methods were decribed in the previous chapters. Extractions of VAPO were carried out in a Soxhlet-apparatus for 5-7 days. Typically 5 g of VAPO was extracted with 200 ml of solvent. After extraction the samples were dried at 120°C overnight before calcining. About 1.5 g of VAPO was also extracted by suspending the material in 75 ml of a 0.45 M TBHP solution in acetonitrile at 70°C for 24 h. After this period no more peroxide could be detected in the solution. The VAPO was filtered, washed with acetone, dried and calcined.

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General Discussion and Industrial Relevance

9

Introduction

At the start of the project two main objectives were formulated: the preparation of well defined microporous VAPOs and the application of these materials as catalyst for liquid phase oxidation reactions. The first objective could be achieved. Well defined VAPO-5 (maximum about 2 wt% vanadium) and VAPO-11 (maximum about 0.6 wt% vanadium) were prepared. The second objective could not be achieved. The phrasing gradually changed from *'in which liquid phase oxidation reactions can VAPOs be used as catalyst?'* to *'do these systems really work in the way it is desired ?'*. From the work reported in the proceeding chapters it has become clear that the application of VAPO in liquid phase oxidation reactions suffers from many problems. A survey of this work leaves the reader with some unanswered questions:

- What is the reason for deactivation of VAPO during a reaction ?
- Why does leaching of vanadium stop after a short period ?
- Why is so much (more than 80%) of the vanadium inactive ?

An attempt will be made to unify the answers into a single model. Before the industrial relevance of the MeAPOs as liquid phase oxidation catalyst will be discussed the results of a side project will be treated briefly. This project involved the application of MeAPOs as catalyst for the selective isomerisation of 1-butene towards isobutene in the gasphase and was carried out in cooperation with L. Gielgens and prof. V. Ponec from Leiden University.

A model of catalysis by VAPO

In chapter 7 it was shown that leaching of vanadium plays an important role in the liquid phase oxidation reactions. The amount of extracted vanadium depends on several factors: vanadium content, type of substrate and reaction conditions. Figure 1 schematically shows the loss of vanadium observed for three VAPO-5 samples after different treatments. As can be seen VAPO-5 becomes less stable when the vanadium content is increased. It is also clear that during the oxidation of 3-octanol and 3-phenyl-2-propen-1-ol the loss of vanadium is smaller than after extraction with water. Earlier (chapter 6) it was proposed that strong irreversible absorption of polar molecules into the VAPO-5 pore could be responsible for this behaviour. Thus, strongly absorbed molecules protect the VAPO against further leaching. Several arguments support this proposition:

- From the same VAPO different amounts of vanadium can be extracted, depending on the reactant, indicating a different protecting power of the substrates.
- A VAPO with obstructed pores is less active. Due to sorbed molecules it loses less vanadium.
- The micropore system cannot be made accessible by treatment with a solvent at low temperature (81°C). The poresystem can only be opened by thermal treatment between 400-550°C.
- After a short time the maximum concentration of vanadium in solution is reached, while the reaction mixture is certainly not satured with vanadium.

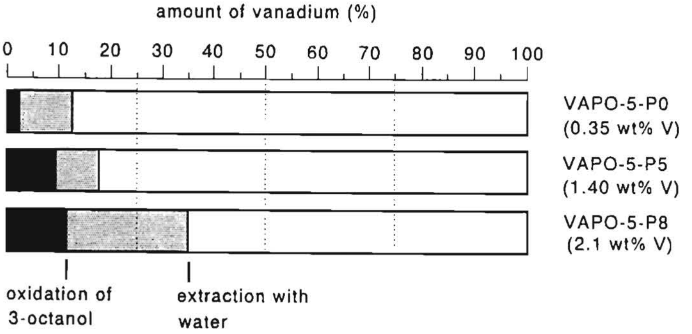


Figure 1: Amount of vanadium extracted from various VAPOs by different methods.

Extraction of VAPO-5-P8 with water results in 34% loss of vanadium. It seems improbable that this large amount of vanadium originates only from the outer surface. Characterisation of VAPO shows that the vanadium species (monomers and small clusters) are homogeneously dispersed which should mean that less than a few percent of the total amount of vanadium is present on the outer surface (see page 55). However, during a reaction the amount of vanadium extracted from the outer surface may be relatively larger, because pore plugging prevents intraporous vanadium from leaching. In case of 3-octanol the activity is almost lost already after one cycle, while a VAPO used for the oxidation of 3-phenyl-2-propen-1-ol did only show a small loss in activity. This can be explained by the more severe reaction conditions and probably also the less protecting power of 3-octanol compared with 3-phenyl-2-propen-1-ol. After one reaction cycle the VAPOs are not accessible anymore because the pores are obstructed and the outer surface is covered with molecules. In the next cycle vanadium can only be extracted from the outer surface, where molecules are less strongly absorbed. Results with the large peroxide TPMHP show that at least some vanadium should be present on the outer surface. When the vanadium on the outer surface is exhausted, no more vanadium dissolves and the reaction stops. As shown in chapter 8 TBHP is responsible for the extraction of vanadium during a reaction.

Experiments with extracted VAPOs show that still vanadium can be removed from the lattice of VAPO-5 during a reaction. In addition the long term regeneration experiment with 3-phenyl-2-propen-1-ol did after 20% loss of vanadium still not provide indications that a minimum level of vanadium is reached. Even an extracted VAPO-5-P0, with a low vanadium content (0.30 wt%), loses some vanadium during the reaction. This indicates that most of the residual vanadium ions are rather tightly bonded to the lattice.

The extracted VAPO does hardly show any activity although it is accessible to reactants. The reasons for this observation can be:

- The reaction inside the pore system is strongly diffusion controlled and the pore systme is blocked. Moreover, probably all vanadium on the outer surface is removed during the extraction with water and no reaction can take place there. All residual vanadium inside the pores is not accessible anymore.

- The vanadium site has an intrinsically low activity and is not accessible for sterical reasons. This could be an argument in favour of an incorporated tetrahedral VO_4^{3-} species on a phosphate position (see page 77).

Based on our results, the first reason seems to be the most likely one.

A model for catalysis by VAPO consists of three parts (figure 2). Initially a fresh, dry VAPO contains accessible vanadium(V) sites. When the VAPO is contacted with the reaction mixture several processes occur. The substrate and oxidant are absorbed. Due to interaction with these molecules some vanadium is extracted from the lattice and comes into solution. Also vanadium sites are reduced to V(IV) (not shown).

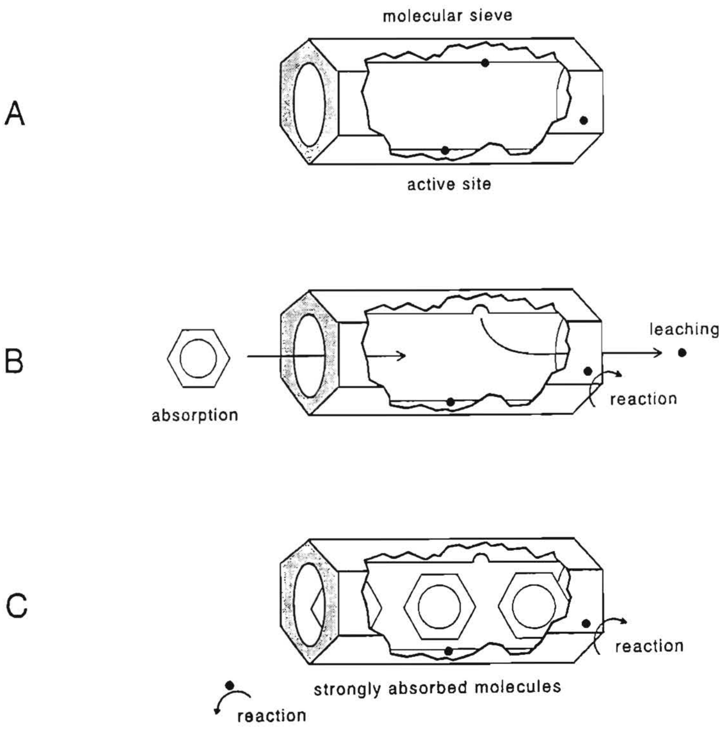


Figure 2: Catalysis by VAPO. For a model description see text. The benzene molecules drawn represent organic molecules (solvent, reactants and products) interacting with the VAPO.
A) Before reaction; B) After a short reaction time; C) Final situation.

Gradually the final situation is reached where the pores are irreversibly blocked and transport of the molecules inside the pores is not longer possible. Vanadium cannot longer be extracted. Reactions can only take place in solution or on the outer surface of the VAPO.

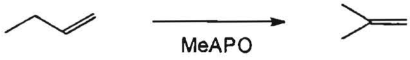
Application of MeAPO as catalyst for the gasphase isomerisation of *n*-butene towards isobutene.

Recently, the selective isomerisation of n-butene towards isobutene received considerable attention [1]. Isobutene is an important starting material for the production of methyl-*t*-butylether (MTBE) and ethyl-*t*-butylether (ETBE). These ethers are used as octane enhancers in gasoline [1]. One possible route to produce isobutene is via skeletal isomerisation of n-butene. The aluminosilicate ferriete (FER), which has a two dimensional poresystem consisting of a 10- and 8-membered rings, proved to be a highly stable and selective catalyst for this reaction [2]. However, modified AlPOs appeared also to be good catalysts for this reaction [3-5].

Several MeAPO-5 and MeAPO-11 (Me = Co, Mn, Mg and V) were tested for this reaction. The main results are presented in table 1 [6,7]. Contrary to pure AlPO-11, which shows only a very low selectivity towards isobutene, MnAPO-11 appeared to be an excellent catalyst for this reaction. The selectivity towards isobutene is close to the maximum value as predicted by the thermodynamic equilibrium [2]. Similar results are obtained for CoAPO-11 and MgAPO-11. In this series VAPO-11 falls apart. Surprisingly, all MeAPO-5s were found to be poor catalysts, while the active sites of MeAPO-5 and MeAPO-11 are similar.

The results show that on one hand MeAPO-11 (Me = Co, Mn, Mg) are selective catalysts. On the other hand VAPO-11 is a non-selective catalyst. Under reaction conditions the cobalt and manganese ions are present in the divalent state. It has been shown that the active site of these MeAPOs consists of a Lewis-centre (coordinately unsatured metal ion) together with a weak Brønsted-centre (P-OH). Apparently these features are critical to obtain a high selectivity. The combination of these two centres is probably not present in VAPO-5 (see chapter 4). In this respect, an important observation is that vanadium in VAPO shows a much weaker interaction

Table 1: Selective isomerisation of *n*-butene towards isobutene catalysed by MeAPO [6,7].



	Product composition (wt%)				
Products	Ferriete[a][6]	MnAPO-11[b]	VAPO-11[b]	MnAPO-5[b]	VAPO-5[b]
C_1, C_2	0.04	0.1	<1	<2	12
C_3	1.8	3	12	<2	
butane	1.3	0.2	<2	<2	<2
n-butene	40	54	65	92	66
isobutene	**37**	**42**	**10**	**2**	**9**
C_5	20	1	9	<2	10

Conditions:

[a]: T = 350°C; P *n*-butene = 1.4 bar; 48 h. MHSV = 2 mol/mol.hour

[b]: T = 400°C; total pressure: 1 bar; 1-butene pressure: 0.1 bar; dilutant: dinitrogen; total flow: 20 ml/min; time on stream: MeAPO-11: 16 h, MeAPO-5: 5 h, WHSV = 2 kg/kg.hour.

with acetonitrile than for example cobalt in CoAPO, which indicates that the Lewis acidity of VAPO is weak [8].

The differences between MeAPO-5 and MeAPO-11 (Me = Co, Mn, Mg) can be explained by the shape selectivity properties of these materials [6,7]. The absorption behaviour of several MeAPO-5 and MeAPO-11 was studied at different temperatures [6,7]. The main results are shown in table 2. While all MeAPO-5s accumulated carboneous material during the reactions the MeAPO-11s pores remained accessible. After reaction the MeAPO-5s were all black and the pores were blocked. The applied MeAPO-11s (Me = Mn and Co) showed the colour of the reduced MeAPO. Thus, on MeAPO-5 side reactions (dimerisation, finally resulting in aromatisation and carbon deposits) deactivate the catalyst. On MeAPO-11 these reactions do not occur. Apparently, the 10-membered pores of MeAPO-11 are too small for these

Table 2: Absorption behaviour of n-butene on some selected MeAPOs during reaction [6,7].

	Absorption of 2-butene			Pore volume n-butane (ml/g)		Color change
	G_{start}	G_{end}	Δ	PV_{start}	PV_{end}	
MnAPO-5	26.63	27.86	1.23	0.091	0.0	Purple → black
CoAPO-5	21.54	22.30	0.76	0.106	0.0	Green → black
MnAPO-11	25.26	25.28	0.02	0.060	0.053	Purple → white
CoAPO-11	22.51	22.60	0.09	0.043	0.025	Green → blue

Reaction conditions: T = 400°C; 2-butene, diluted in a helium stream (total He-flow: 135 ml/min; 2-butene flow: 18 ml/min), was passed over the sample for 1 hour in an Cahn 2000 Electrobalance.

G_{start} : weight of the catalyst before reaction.
G_{end} : weight after reaction.
PV_{start} : porevolume before reaction.
PV_{end} : residual pore volume after reaction.

deactivation reactions to occur. The results show that a small modification of the pore structure may have a large effect on the catalytic behaviour of the molecular sieve catalyst.

Industrial relevance of MeAPOs

The industrial relevance of the VAPO as catalyst for liquid phase oxidation reactions is limited. Leaching of vanadium and pore blocking by a too strong absorption of reactants and products are major problems. It can be expected that the problems described here are much more general and occur also with other MeAPOs. While leaching is dependent on the direct interaction between the reactants and the metal ion, pore plugging depends much more on the properties of the molecular sieve and the pore geometry. Thus even when a MeAPO could be prepared which is stable against leaching, a too strong absorption of reactants results in a catalyst with a low activity. The problems concerning the too strong absorption are expected to become more severe when molecules relevant for fine chemistry would be used. Molecules of interest have generally a large size (> C_8) and possess more polar groups than the molecules tested in our experiments. The high heat of absorption suggest that only the least polar molecular sieves are potentially suitable as catalyst for the oxidation of large and polar molecules. Among molecular sieves the silicalites are the most apolar (hydrophobic). This property combined with a relatively high stability of the metal site, explains the relatively succesfull application of TS-1. Moreover, the three dimensional pore system and the use of small crystallites improves the performance of this catalyst even more.

Nevertheless, the application of MeAPO for gas phase reactions is certainly still an interesting topic, as demonstrated by the results obtained for the selective isomerisation of *n*-butene. The problem of leaching of metal ions is not relevant. In principle pore blocking plays a less important role because the reactants are small, non-polar molecules which have a relatively low heat of absorption. Moreover, the higher reaction temperature has a positive effect on the mobility of molecules inside the micropore.

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Summary

Oxidation in the liquid phase is an important method used in fine chemistry to prepare oxygenated products. However, the use of stoichiometric oxidants and the often low selectivity lead to large amounts of waste that is difficult to process. The use of clean oxidants like dioxygen and peroxides in combination with a catalyst may contribute to the solution of these problems. Metal containing molecular sieves may be attractive catalysts as already demonstrated by the use of titanium silicalite (TS-1). Modified porous solid materials may have several advantages over conventional catalysts: easy removal from the reaction mixture, an improved stability and improved selectivity due to sterical constraints provided by the pore structure. Microporous aluminophosphates are new materials which are tolerant to the incorporation of many catalytically interesting metal ions. Several different pore geometries are known. The most common structures are AlPO-5 (straight pores 0.71 x 0.71 nm) and AlPO-11 (straight pores 0.43 x 0.62 nm). The first objective is the preparation of well defined microporous vanadium substituted aluminophosphates (VAPO). Vanadium has been chosen because vanadium complexes are known to be versatile catalysts for liquid phase oxidation reactions employing dioxygen, hydrogen peroxide or organic peroxides. The second and main objective of the thesis is to explore the possibilities and limitations of VAPO as heterogeneous catalyst for liquid phase oxidation reactions.

For the synthesis of VAPO-5 and VAPO-11 conventional hydrothermal preparation methods were used. The products were characterised by X-ray diffraction, scanning electron microscopy, elemental analysis, absorption methods, electron spin resonance and diffuse reflection electronic absorption spectroscopy. VAPO-5 with a well defined pore structure and a vanadium content up to about 2 wt% could be prepared. It was shown that the vanadium sites are mainly monomeric and tetrahedral at low vanadium contents (< 1 wt%). At higher vanadium content also small vanadium oxide clusters are formed. A maximum of 0.5 wt% vanadium could be incorporated into the AlPO-11 structure. Higher amounts of vanadium resulted in the formation of impure VAPO-11. The structures of the vanadium sites of VAPO-11 and VAPO-5 are similar.

VAPOs were tested as catalyst for reactions with t-butyl hydroperoxide (TBHP) as oxidant: the epoxidation of 3-phenyl-2-propen-1-ol and 2-cyclohexen-1-ol, the oxidation of 2-octanol, 3-octanol and cyclo-octanol to the ketone. Also the VAPO catalysed oxidation of cyclohexanone by dioxygen towards hexanedioic acid was investigated. The results (activity and selectivity) were compared with that of a homogeneous catalyst, bis(2,4-pentodionato)-oxovanadium(IV) (VO(acac)$_2$). Some general features can be recognised for VAPO catalysed reactions:

- Employing the same amount of vanadium the reactions proceed slower. The rate differences are much smaller in case of the oxidation of alcohols (about 2-18x) than in case of the epoxidation reactions (between 20-100x).
- VAPO-5s with a higher vanadium content are more active.
- No clear change of the selectivity patterns is observed when VAPO-11 is used instead of VAPO-5.

An important property of a applicable catalyst is that it is stable and can be recycled. The stability was investigated by re-using a VAPO-5 several times. The epoxidation of 3-phenyl-2-propen-1-ol and the oxidation of 3-octanol were used as model reactions. It appeared that VAPO-5 deactivates. The VAPO-5 needs to be calcined to restore activity. Repeated recycling with intermediate calcination of a VAPO showed that the pore structure remains intact. However, during the reactions a small amount of vanadium is lost. The amount depends on the reaction and the reaction conditions (for the epoxidation an average loss of 1.1 wt%/cycle was found, while for the alcohol oxidation a loss of 8 wt%/cycle was found). It appeared not to be possible to regenerate a VAPO by extensive extraction with acetonitrile, indicating that molecules are strongly absorbed into the pores.

The role of extracted vanadium was studied in more detail. Removal of the catalyst from the reaction mixture showed a continued reaction. The actual amount of vanadium present in the solution was determined by graphite furnace atomic absorption spectroscopy. Vanadium is leached rapidly and a steady state concentration is reached generally after 30 minutes. The amount leached is dependant on the vanadium content of VAPO. VAPO-5s with low vanadium content were most stable. Reactions were performed with equal amounts of vanadium as VO(acac)$_2$, which appeared to be active already at low concentrations (< 5 mg V/l). Correlation between the activity of VAPO-5 and VO(acac)$_2$ showed that all epoxidation activity observed can be explained by the vanadium dissolved in solution. It is argued that the active species in solution are similar, so that a fair comparison is possible. A different situation was observed in case of 3-octanol. Although measured concentrations of vanadium are higher and a homogeneously catalysed reaction takes place, there is obviously a contribution of a heterogeneously catalysed reaction. However, this reaction is fairly unselective with respect to the selectivity based on the peroxide (40%).

Loosely bounded vanadium ions could be removed by Soxhlet extraction with water. The pore structure was only a little damaged by this treatment. The extracted amount varied between 12-33%. Unexpectedly, the extracted VAPO-5 showed almost no activity as catalyst for the oxidation of alcohols. Apparently, the active sites were removed and the residual vanadium is not active.

The results are unified into a model for catalysis by VAPO. During the initial stage of the reaction substrate and oxidant are absorbed. Due to interaction with these molecules some vanadium is extracted from the lattice and comes into solution. Later on in the reaction no leaching or transport of molecules inside the pore is possible anymore due to pore blocking. This shows that the substrate and oxidant also protect the sieve against further leaching. Reactions only take place on the outer surface or in solution. It is argued that this model is not only valid for VAPO, but also for also for other MeAPOs.

Another possible application of MeAPOs is the use as catalyst for the gas phase isomerisation of n-butene towards isobutene. MeAPO-11 (Me = Co, Mn, Mg) are selective and stable catalysts, while MeAPO-5 deactivates rapidly. VAPO does show a low selectivity towards isobutene. Leaching of the MeAPO does not play a role.

The conclusion of this work is that VAPO, and other MeAPOs, cannot be used for the proposed application as catalyst for the oxidation of organic molecules in the liquid phase. Main problems are strong irreversible absorption and leaching of metal ions that may catalyse homogeneous reaction in solution.

Samenvatting

Vloeistoffase-oxidatie is in de fijnchemie een belangrijke methode om gefunctiona-liseerde moleculen te bereiden. Echter het gebruik van stochiometrische oxidanten en de vaak lage selektiviteit naar het gewenste produkt leiden tot grote hoeveelheden moeilijk te verwerken afval. Het gebruik van schone oxidanten zoals zuurstof en peroxides in combinatie met een katalysator kan tot een verbetering van de bestaande processen leiden. Metaal bevattende molekulaire zeven kunnen aantrekkelijke katalysatoren zijn voor dit soort reakties. Een bekend voorbeeld is het gebruik van titaan silicaliet. Microporeuze materialen hebben mogelijk een aantal aantrekkelijke voordelen ten opzichte van andere katalysatoren: ze zijn gemakkelijk te verwijderen uit het reaktiemengsel, bezitten een hogere stabiliteit en beïnvloeding van de selektiviteit is mogelijk door middel van de poriestruktuur. Microporeuze aluminofosfaten zijn nieuwe materialen die tolerant zijn ten opzichte van het aanbrengen van verschillende katalytisch interessante metaalionen. Verschillende poriestrukturen zijn bekend, waaronder AlPO-5 (met rechte poriën van 0.71 x 0.71 nm) en AlPO-11 (met rechte poriën van 0.43 x 0.65 nm). De eerste doelstelling van het projekt is het bereiden van goed gedefinieerde microporeuze vanadium bevattende aluminofosfaten (VAPO). Vanadium is gekozen vanwege de veelzijdige katalyse in de vloeistoffase. De tweede doelstelling is het onderzoeken van de mogelijkheden en beperkingen van VAPO als vloeistoffase oxidatie katalysator.

Voor de synthese van VAPO-5 en VAPO-11 zijn uit de literatuur bekende synthese technieken gebruikt. De produkten zijn gekarakteriseerd met röntgendiffraktie, scanning elektronen microscopie, element analyse, sorptiemethoden en diffuse reflektie elektronen absorptie spectroscopie. VAPO-5 met een goed gedefinieerde poriestruktuur en een vanadiumgehalte tot 2 gew% kan worden bereid. Uit de karakterisering van deze materialen blijkt dat VAPO-5 bij lage belading monomeer tetraëdrisch vanadium bevat. Bij hogere belading ontstaan ook kleine vanadiumoxide clusters. VAPO-11 met een goed gedefinieerde poriestruktuur kan alleen worden bereid als het vanadium gehalte laag wordt gehouden (< 0.5 gew%). De struktuur van de vanadium site in VAPO-5 en VAPO-11 is vergelijkbaar.

VAPO's zijn getest als katalysator voor reakties met *t*-butylhydroperoxide (TBHP) als oxidant: de epoxidatie van 3-phenyl-2-propen-1-ol, 2-cyclohexen-1-ol, de oxidatie van 2-oktanol, 3-oktanol en cyclo-oktanol tot het corresponderende keton. Ook is de VAPO gekatalyseerde oxidatie van cyclohexanon met zuurstof tot adipinezuur onderzocht. De behaalde resultaten zijn vergeleken (aktiviteit en selektiviteit) met die van de homogene katalysator bis-(2,4-pentodionato)-oxovanadium(IV) ($VO(acac)_2$). De VAPO gekatalyseerde reakties vertonen enige algemene kenmerken:

- Vergeleken op basis van een gelijk vanadium gehalte verlopen de reakties trager. De verschillen zijn kleiner in het geval van de oxidatie van alkoholen (ongeveer 2-18x) dan in het geval van de epoxidatie-reakties (tussen 20-100x).
- VAPO-5 met een hoger vanadium gehalte vertoont een hogere aktiviteit.
- Er wordt geen verschuiving in de selektiviteitspatronen waargenomen als VAPO-11 in plaats van VAPO-5 wordt gebruikt.

Een hoge stabiliteit en de mogelijkheid tot recyclen zijn belangrijke eisen aan een toepasbare katalysator. De stabiliteit van VAPO-5 is onderzocht door de VAPO herhaaldelijk te gebruiken. De epoxidatie van 3-phenyl-2-propen-1-ol en de oxidatie van 3-octanol zijn daarbij gebruikt als modelreakties. Het blijkt dat een gebruikte VAPO minder aktief is. De aktiviteit kan grotendeels worden hersteld door de geabsorbeerde molekulen bij hogere temperatuur met lucht te verwijderen (calcineren). Herhaalde recycling laat zien dat de poriestruktuur grotendeels intakt blijft, maar dat de VAPO een kleine hoeveelheid vanadium verliest. Het vanadiumverlies hangt af van de reaktie en de reaktiecondities (voor de epoxidatie reaktie wordt een verlies van 1.1 gew%/cyclus wordt gevonden, terwijl voor de alkohol oxidatie een verlies van 8 gew%/cyclus wordt gevonden). Het bleek niet mogelijk om de geabsorbeerde moleculen te verwijderen door langdurige extraktie met acetonitrile, wat laat zien dat de moleculen sterk geabsorbeerd zijn.

De rol van het opgeloste vanadium is in meer detail bestudeerd. Verwijdering van de katalysator uit het reaktiemengsel laat een doorgaande reaktie zien. Vanadiumdeeltjes in oplossing vertonen dus aktiviteit. De vanadium concentratie in oplossing is bepaald met grafiet oven atomaire absorptie spectroscopie. Het blijkt dat gedurende de reaktie het vanadium snel uit de VAPO in oplossing gaat. In het algemeen wordt de maximum concentratie na ca. 30 minuten bereikt. De hoeveelheid vrijgekomen vanadium hangt af van het vanadium gehalte van de VAPO-5. Een

VAPO met een laag vanadium gehalte blijkt het meest stabiel. Ter vergelijking zijn experimenten met een lage concentratie $VO(acac)_2$ uitgevoerd. Het blijkt dat deze homogene katalysator al bij lage concentraties aktief is (< 5 mg V/l). Vergelijking tussen de aktiviteit van VAPO-5 en $VO(acac)_2$ laat zien dat alle epoxidatie aktiviteit verklaard kan worden door vanadium in oplossing. Er zijn argumenten gegeven om aan te tonen dat een eerlijke vergelijking mogelijk is. In tegenstelling tot de epoxidatie reakties wordt bij de oxidatie van 3-oktanol wel een heterogeen gekatalyseerde reaktie waargenomen, alhoewel de gemeten concentraties vanadium in oplossing hoger zijn. Echter, de selektiviteit op basis van het peroxide is van de heterogene reaktie is laag (40%).

Zwak gebonden vanadium kan vooraf verwijderd worden door Soxhlet extractie met water. De poriestruktuur blijft intakt door deze behandeling. De geëxtraheerde hoeveelheid varieerd van 12-33%. Het resultaat is dat de VAPO-5 nauwelijks nog aktiviteit als katalysator voor de oxidatie van alkoholen vertoont. Blijkbaar worden door de extraktie de aktieve vanadiumdeeltjes verwijderd.

Alle resultaten kunnen worden samengevat in een model voor de katalyse met VAPO-5. In het begin van de reaktie worden substraat en oxidant geabsorbeerd. Door interaktie met het rooster wordt een kleine hoeveelheid vanadium geëxtraheerd dat in de oplossing terecht komt. Later in de reaktie zijn de poriën verstopt en kan geen lekkage meer optreden. Dit laat zien dat de reaktanten de VAPO ook beschermen tegen vanadium verlies. Reakties kunnen alleen nog in oplossing optreden of op het buitenoppervlak. Deze resultaten kunnen worden geëxtrapoleerd naar andere MeAPO systemen.

Een andere toepassing van MeAPO is die als katalysator voor de isomerisatie van buteen tot isobuteen in de gasfase. MeAPO-11 (Me = Co, Mg, Mn) zijn selektieve en stabiele katalysatoren, terwijl MeAPO-5 snel deaktiveerd. VAPO laat slechts een lage selektiviteit naar isobuteen zien. Doordat deze reaktie zich in de gasfase afspeelt, is hierbij geen gevaar voor het in oplossing gaan van het metaalion aanwezig.

De conclusie van dit werk is dat VAPO niet kan worden gebruikt voor de toepassing als katalysator voor de oxidatie in de vloeistoffase. De belangrijkste problemen zijn irreversibele absorptie en verlies van vanadium.

Dankwoord

Traditiegetrouw is er aan het einde van het proefschrift een dankwoord voor degenen die een rol hebben gespeeld bij het tot standkomen hiervan. Iedereen die direkt en indirekt een bijdrage heeft geleverd bedank ik hiervoor. Zonder deze hulp was het niet gelukt.

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Curriculum vitae

Martien Haanepen werd geboren op 9 mei 1967 in Haarlem. In juli 1985 werd het HAVO diploma behaald aan het Eerste Christelijk Lyceum te Haarlem. Daarna is hij gestart met de opleiding tot laboratoriummedewerker (HLO) aan het Bakhuis Roozeboom Instituut te Beverwijk.

Na het behalen van de propaedeuse is de auteur begonnen met de studie scheikunde aan de Rijksuniversiteit Leiden. Op 31 mei 1991 werd het doctoraal examen afgelegd in richting coördinatie-chemie. Het afstudeeronderwerp, uitgevoerd in de groep van prof.dr. J. Reedijk, had betrekking op de ontwikkeling van chelerende ionenwisselaars op basis van silica voor de selektieve verwijdering van koperionen uit afvalwater. Van 1 september 1990 t/m 31 maart 1991 heeft de auteur 7 maanden stage gelopen bij DSM-research te Geleen onder leiding van dr. H. Oevering. Daar heeft hij gewerkt aan een onderwerp uit de homogene oxidatie katalyse.

Op 1 juli 1991 trad de auteur in dienst als assistent in opleiding aan de Technische Universiteit Eindhoven. In de vakgroep Anorganische chemie en Katalyse werd het in dit proefschrift beschreven promotie-onderzoek uitgevoerd onder leiding van prof.dr.ir. J.H.C. van Hooff in samenwerking met prof.dr. R.A. Sheldon (TU Delft).

Uur U nadert.....

De laatste loodjes van een AiO in stress op weg naar voltooiïng van zijn proefschrift. t=0 is gedefinieerd als het tijdstip waarop dit proefschrift (met auteur) volgens planning naar de drukker zou vertrekken. Het begin is willekeurig gekozen en alles is naar waarheid genoteerd op een white board.

t-1215 min	Begin logboek
t-1170 min	Netwerk vliegt eruit, werken (printen) is nu onmogelijk!!!!!!!!!!!!!!!!!!!!!!!!
t-1155 min	Lokale printer met WP gevonden
t-1150 min	Blijkt niet te werken door ontbreken van printerfile
t-1145 min	Netwerk doet het weer en nieuwe toner in HP 4 Si
t-1140 min	Test door printen hoofdstuk 6
t-1135 min	Het werkt, **HOERA!!!!!!!**
t-1065 min	Eten in Mensa
t-1020 min	Terug met nieuwe energie, snel verbeteren, printen en plakken
t-990 min	Algemene copy van proefschrift naar Henk
t-900 min	Alleen nog hoofdstukken 4, 5 en 6 plakken en voorkant, inlegvelletje, inhoudsopgave, verklarende woordenlijst, bladzijde 162 maken en printen
t-840 min	Gone Home! We have left the building. Hoofdstuk 5 is nu ook gereed
t-270 min	Return of Tinus
t-210 min	Henk hervat plakwerk
t-70 min	Plakken is klaar
t-30 min	Kopiëren is klaar
t-10 min	Laatste check klaar
t-5 min	Inlegvelletje klaar
t-1 min	Idee om dit logboek in proefschrift op te nemen
t+9 min	Logboek is volledig uitgetypt
t+30 min	Tinus vertrekt naar drukker in Wageningen met slechts een kleine vertraging

Corrections
Thesis 'M.J. Haanepen - Application of VAPO as catalyst for liquid phase oxidation reactions'.

Despite careful corrections soms errors still remained. Because they may confuse the reader corrections are given. Moreover some additional information is provided.

- The definition for the conversion of the substrate is:

$$\text{Conv Sub} = \frac{S_0 - S_t}{S_0}$$

- Sel on Ox: Selectivity on oxidant, which is a measure for the efficiency of the oxidant (Ox_0 = amount of oxidant t=0; Ox_t = amount of oxidant t=t).

$$\text{Sel on Ox} = \frac{Ox_0 - Ox_t}{S_0 - S_t}$$

- All TOFs for the catalysed oxidation of 3-octanol are calculated at 10% conversion of the substrate (see page 98 / page 120).

Martien Haanepen

Eindhoven, February 26th, 1996

Stellingen behorende bij het proefschrift: 'M.J. Haanepen - Application of VAPO as catalyst for liquid phase oxidation reactions'.

1. Als er meer dan twee jaar ligt tussen aanbieding en acceptatie van een artikel is dit geen goed teken voor de kwaliteit hiervan.

   R. Roque-Malherbe et al., Zeolites, 13 (1993) 481
   Z. Gao et al., Zeolites, 16 (1996) 70-78

2. Door het niet expliciet vermelden van bepaalde reaktie parameters zoals substraat conversie of selektiviteit op basis van oxidant kan je een schijnbaar goede katalysator maken.

   K. Ramesh Reddy, et al., J. Cat., 143 (1993) 275-285
   T. Selvan and A.P. Singh, J. Chem. Soc. Chem. Commun, (1995) 883-884

3. Gezien de enorme complexiteit van het mechanisme van de homogeen gekatalyseerde vloeistoffase oxidatie van p-xyleen is het niet zo vreemd dat dit proces met heterogene katalysatoren niet goed werkt.

   W. Partenheimer, Cat. Today, 23 (1995) 69-158

4. Het bereiden van goed gedefinieerde heterogene katalysatoren is niet zo gemakkelijk als in vele literatuurvoorschriften wordt gesuggereerd.

   De meeste literatuurverwijzingen naar de synthese van moleculaire zeven.

5. Het bereiden van goed gedefinieerde heterogene katalysatoren wordt door veel organisch synthetici als een minderwaardige vorm van synthese ervaren.

   Eigen ervaring.

6. De homogeniteit van heterogene katalysatoren wordt veelal overschat.

7. Het wegbezuinigen van gekwalificeerd ondersteunend personeel (technici en analisten) leidt er toe dat het type onderzoek zoals in dit proefschrift wordt beschreven in de toekomst steeds minder gedaan kan worden.

8. De echte selektie van studenten vindt plaats aan de bedrijfspoort in plaats van op de universiteit waar deze selektie eigenlijk zou moeten plaatsvinden.

9. De symbiose tussen hard- en software industrie leidt ertoe dat de economische levensduur van de produkten steeds korter wordt. Dit heeft tot gevolg dat de financiële belasting van de consument/gebruiker steeds groter wordt.

10. Voor de meeste lezers van een proefschrift volstaat een veel kortere uitgave (curriculum vitae, dankwoord, samenvatting en stellingen).

Martien Haanepen

Eindhoven, 1 februari 1996