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Liquid phase oxidation at metal ions and complexes in constrained environments

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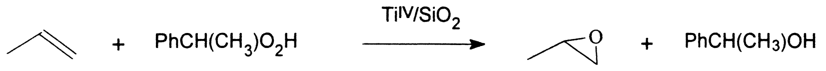
Abstract

Various approaches towards the rational design of novel catalysts based on the concept of confinement (site-isolation) of redox active metal centres in molecular sieves are reviewed. These comprise (a) substitution of T elements (Si, Al and P) in the framework of silicates, zeolites, AlPOs and SAPOs, (b) encapsulation of metal complexes in intrazeolite space (ship-in-a-bottle catalysts) and (c) grafting or tethering of metal complexes to the internal surface of the molecular sieves. Related materials - redox pillared clays, clay intercalated metal complexes, redox aerogels and metal complexes incorporated in aerogels - are also reviewed. The advantages and limitations of the various materials with regard to activity and selectivity as catalysts for liquid phase oxidations with O_2, H_2O_2 and RO_2H and stability towards leaching, are discussed. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction and background

Catalytic oxidation is widely used in the manufacture of bulk chemicals from hydrocarbons [1] and, more recently, as an environmentally attractive method for the production of fine chemicals [2]. Both gas phase and liquid phase processes are operated in practice and the latter generally employ transition metal salts or complexes as homogeneous catalysts. However, solid catalysts possess several advantages compared to their homogeneous counterparts, e.g. ease of recovery and recycling and amenability to continuous processing. Moreover, site-isolation of discrete redox metal centres in inorganic matrices can afford oxidation catalysts with unique activities and selectivities by circumventing the oligomerization of active monomeric oxometal (M=O) or related species to inactive μ-oxo complexes. The propensity of oxometal complexes for undergoing such a transition is a major cause of low activities observed, with e.g. titanium (IV) catalysts, in solution.

Conventional methods for immobilizing metal catalysts generally involve the incorporation of the redox metal centre into the surface of an oxide support. A noteworthy example is the heterogeneous Ti^{IV}/SiO_2 catalysts [3] used by Shell for the epoxidation of propylene with ethylbenzene hydroperoxide (reaction 1).



(1)

Another approach to design stable solid catalysts with unique activities is via incorporation of redox

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metal ions or complexes into the framework or cavities of zeolites and related molecular sieves. These so-called redox molecular sieves [4], unlike conventional supported catalysts, possess a regular micro-environment with homogeneous internal structures consisting of uniform, well-defined cavities and channels of molecular dimensions. Confinement of the redox active site in such channels and/or cavities can endow the resulting catalyst with unique activity over and above that observed with conventional supported catalysts. Moreover, by choosing a molecular sieve with an appropriate pore size and hydrophobicity one is able to influence which molecules have ready access to the active site on the basis of size and/or hydrophobic/hydrophilic character. Hence, tailor-made catalysts can be designed which have a distinct resemblance to redox enzymes in which the protein mantel plays a similar role. It is perhaps not surprising, therefore, that such materials have been referred to as 'mineral enzymes' or 'zeozymes' [5]. Indeed, there is a marked parallel in recent developments in catalysis by enzymes and heterogeneous catalysis, from one of 'take what you get' to one of 'design what you need' [6,7].

Up until the late seventies attempts to develop redox molecular sieves were mainly limited to the introduction of redox molecular ions into zeolites via ion-exchange. A major disadvantage of this approach is the mobility of the metal ion which manifests itself in its facile leaching into solution. The situation changed dramatically with the discovery, by Enichem scientists in 1983 [8], of the unique activity of the framework-substituted titanium silicalite (TS-1) as a catalyst for selective oxidations with 30% aqueous hydrogen peroxide (see later). The success of TS-1 provoked a flourish of interest in the development and application in organic synthesis, of redox molecular sieves containing titanium (IV) or other metal ions [9–12].

A particular problem associated with the use of solid catalysts in the liquid phase, as opposed to the gas phase, is the predilection for leaching of the metal ion into solution. This generally involves solvolysis of M–O-surface bonds by reaction with water and/or polar solvents and solutes. Since the products of oxidation reactions are usually polar molecules one can safely assume that, in the absence of evidence to the contrary, leaching will be a problem. Obviously the synthetic utility of solid catalysts stands or falls with their stability towards leaching.

2. Elaboration of the concept

The basic concept we are concerned with, here is the confinement of a redox active centre in the constrained environment of a molecular sieve material, such as a zeolite. Such a confinement can be expected to endow the catalyst with unique activity as a result of strong electrostatic interactions between acidic and basic sites on the internal surface and the substrate or reaction intermediate. This is directly analogous to substrate interactions with acidic carboxyl and basic amino groups of amino acid residues in the active sites of (redox) enzymes. Moreover, the molecular sieve can impose an unusual (high energy) geometry at a metal site that enhances its catalytic properties. In bioinorganic chemistry this is referred to as the entactic state [13] and it is generally believed to play a major role in determining the activity of metallo-enzymes. For example, the entactic nature of copper (II) sites in the blue copper proteins, whereby copper (II) is forced to adopt a distorted tetrahedral structure, is thought to enhance its redox potential [14].

Two important variables in the de novo design of a redox molecular sieve with a particular metal centre are the nature of the molecular sieve (pore size, hydrophobicity) and the method of confinement. Zeolites and zeotypes are crystalline oxides comprising corner sharing TO_4 tetrahedra (T=Si, Al, P, etc.) and consisting of a regular pore system with diameters of molecular dimensions, hence the term molecular sieve. Zeolites refer to aluminosilicates (T=Si and Al) and zeotypes to molecular sieves having analogous structures but different elemental compositions, e.g. silicalites (T=Si), aluminophosphates (AlPOs; T=Al and P) and silica aluminophosphates (SAPOs; T=Si, Al and P). On the basis of their pore diameters, molecular sieves are categorized into small pore (<4 Å), medium pore (4–6 Å), large pore (6–8 Å), extra large pore (8–14 Å) and mesoporous (15–100 Å). The pore system may be one, two or three dimensional. From the viewpoint of catalysis a three dimensional pore system would appear to be advantageous because of better accessibility. Their well-defined pore systems combined with their capacity for small substrate-induced structural changes enable molecular sieves to organize and discriminate molecules with a precision of <1 Å [15], thus endowing them with shape selective properties [16], analogous to enzymes. By analogy with enzymes one would expect the optimum activity to be observed with the best fit, i.e. when the dimensions of the substrate are of the same order as those of the micropores. The recently discovered mesoporous (alumino) silicates [17,18], e.g. MCM-41, consist of a regular array of one dimensional pores with diameters in the range 15–100 Å and have properties intermediate between those of amorphous SiO_2 and Al_2O_3 and microporous sieves. This has considerably extended the size of molecules that can be adsorbed in molecular sieves and a vast array of new catalytic applications are envisaged [7,18]. Similarly, redox pillared clays [19] and redox aerogels [20] can be envisaged as special examples of mesoporous molecular sieve materials.

If we exclude ion exchange from our discussion we can distinguish three types of redox molecular sieves on the basis of the method of confinement:

a) Framework substitution;
b) encapsulation of metal complexes (ship-in-a-bottle method) and,
c) grafting or tethering of metal complexes to the internal surface

2.1. Framework substitution

Hydrothermal synthesis of molecular sieves involves allowing an aqueous gel, containing a source of the framework building elements (Al, Si and P) and a structure-directing agent (template; usually an amine or a tetraalkylammonium salt) to crystallize in an autoclave, under autogeneous pressure, at temperatures up to 200°C. When a source of a redox metal ion is added to the synthesis gel this can result in isomorphous substitution of Al, Si or P by the metal ion, whereby the latter occupies TO_4 tetrahedra. Isomorphous substitution is feasible when the $r_{\text{cation}}/r_{\text{oxygen}}$ ratio is between 0.225 and 0.414 [21]. We note, however, that the oxidation state of the metal and, hence, the structure and charge of the framework, can change substantially when the as-synthesized material is calcined to remove the template. For example, chromium-substituted molecular sieves generally contain Cr^{III} in the as-synthesized material which is transformed to Cr^{VI} on calcination. Since the latter contains two extra-framework Cr^{VI}=O bonds it can only be attached to a surface defect site rather than isomorphously substituted. Titanium and other redox active metals, e.g. V, Cr, Mn, Fe, Co, Cu, Zr and Sn have been reportedly incorporated in a variety of molecular sieve structures (silicates, zeolites, AlPOs and SAPOs) by hydrothermal synthesis [22]. However we note that in many cases true isomorphous substitution has not been verified. In fact, physical–chemical characterization is in most papers insufficient or insufficiently described. The consequence is that the reactivity of apparently similar but in fact very different materials is compared and discussed leading to erroneous conclusions. Moreover, the importance of crystal size on the catalytic activity of a catalyst, which was demonstrated to be crucial for TS-1 [23], is often not fully appreciated. Using standard characterization techniques such as XRD, IR, ^{29}Si-MAS-NMR and DREAS it was impossible to distinguish between active and less active TS-1 samples.

A more serious problem is the metal leaching from redox molecular sieves. Small amounts of metal leaching can have a significant effect on the observed catalytic results, making conclusions drawn from the physical–chemical characterizations invalid. In some cases, e.g. V and Cr, leached metal ions are probably responsible for all of the observed catalysis (see later), while for the other systems there is reasonable doubt about the heterogeneity. It should be emphasized in this context that experiments demonstrating that heterogeneous catalysts can be recovered and recycled without apparent loss of metal content or activity are not definitive proof of heterogeneity.

Alternatively, framework substitution can be achieved by post-synthesis modification of molecular sieves, e.g. via direct substitution of Al in zeolites by vapour phase treatment with $TiCl_4$ [24] or by the dealumination followed by reoccupation of the vacant silanol nests. Boron-containing molecular sieves are more amenable to post-synthesis modification than the isomorphous zeolites since boron is readily extracted from the framework under mild conditions [25]. Post-synthesis modification has the advantage that commercially available molecular sieves can be used as the starting material.

2.2. Encapsulated metal complexes

The ship-in-a-bottle method, as the name implies, involves assembling a metal complex in intrazeolite space such that the complex, once formed, is too large to diffuse out [26–28]. It has the advantage, compared to framework substitution, that there are, in principle, no restrictions with regard to the size of the metal ion. Moreover, because there is no covalent attachment to the surface a ship-in-a-bottle catalyst can be expected to more closely resemble its homogeneous counterpart, without having the disadvantages of the latter (see earlier). Three different approaches have been used to achieve encapsulation [26–28]:

a) Intrazeolite complexation (flexible ligand method);
b) Intrazeolite ligand synthesis;
c) Metal complexes as templates for zeolite synthesis.

In the first method the metal complex is introduced in the zeolite cavities, e.g. the supercages of faujasites (zeolites X and Y), by allowing the metal-exchanged zeolite to react with a ligand that is small enough to access the micropores. The metal complex, once formed, is too large to diffuse out. Examples include metal–bipyridyl complexes and metal–salen complexes. However, in the latter case there is virtually no difference in the kinetic diameter between the complex and the free ligand and metal–salen complexes are readily leached by protic solvents [26]a.

In the second method the ligand itself, constructed by intrazeolite synthesis, is too large to exit the supercages. Most examples involve faujasite-encapsulated metallo–phthalocyanines, first reported by Romanovsky and co-workers in 1977 [29]. The metal is first introduced into the zeolite, via ion-exchange or as a metal carbonyl or metallocene, followed by 1,2-dicyanobenzene, which reacts at elevated temperatures to form the metallophthalocyanine in the supercages. In order to fit into the faujasite supercages (13 Å) the phthalocyanine ligands are strongly deformed, reminiscent of the entactic state in enzymes (see earlier).

In the template method the zeolite is allowed to crystallize around the metal complex which is assumed to act as a structure directing agent, i.e. the bottle is built around the ship. This allows for the encapsulation of well-defined complexes without contamination by the free ligand or uncomplexed metal ions, which is a disadvantage of intrazeolite synthesis. The method is restricted however, to metal complexes, e.g. metallophthalocyanines, that are stable under the relatively harsh conditions of temperature and pH extant in hydrothermal synthesis. However, some doubt has been expressed regarding the structure-directing capability of a template, such as a metallophthalocyanine, that requires initial deformation [26]a.

2.3. Grafting or tethering of metal complexes

The grafting or tethering of a metal complex to the internal surface of a molecular sieve refers to the covalent attachment of organometallic or coordination complexes, either directly (grafting) or via a spacer ligand (tethering) [7]. These are well-proven techniques for the covalent attachment of organometallic complexes to a silica surface by reaction with pendant silanol (Si–OH) groups [30]. Hence, a logical extension is the grafting of the organometallic species to the internal surface of mesoporous molecular sieves such as MCM-41. The concept is exemplified by the synthesis of surface-grafted titanium (IV) and oxomanganese by reaction of MCM-41 with titanocene dichloride (Cp_2TiCl_2) [7,31] and $Mn_2(CO)_{10}$ [32], respectively, followed by calcination (see Fig. 1(a)).

An example of tethering of a co-ordination complex to the internal surface of MCM-41 is the recently described [33] heterogenization of a manganese triazacyclononane complex (Fig. 1(b)).

Similarly, Corma and co-workers [34] have described the tethering of chiral molybdenum complexes for use as asymmetric epoxidation catalysts, to the internal surface of mesoporous USY-zeolite (Fig. 2).

2.4. Choice of redox metal/oxidant: general considerations

The reactions discussed in the following sections all involve the use of H_2O_2, RO_2H or O_2 as the terminal oxidant. The type of oxidative transformation observed is largely determined by the metal catalyst used. Metal-catalyzed oxidations with H_2O_2 or RO_2H can involve homolytic pathways via free radical ($HO^{\bullet}$, $HO_2^{\bullet}$, $RO^{\bullet}$, $RO_2^{\bullet}$) intermediates and/or hetero-

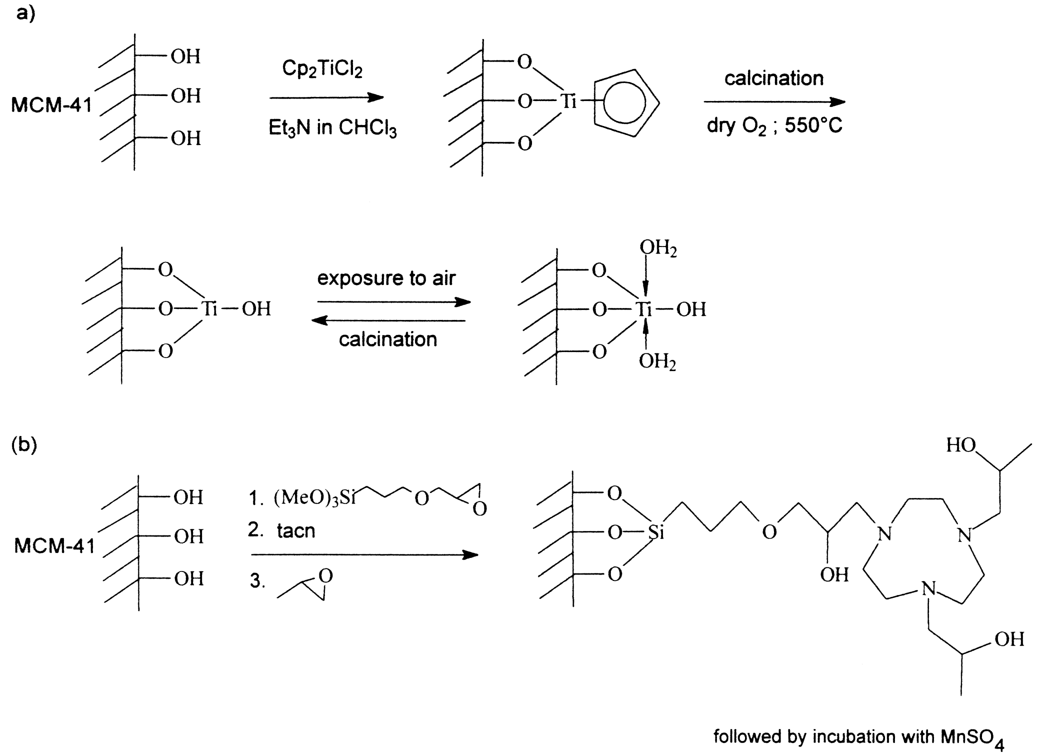


Fig. 1. Grafting of titanium (a) and triazacyclononane (tacn;b) to the internal surface of MCM-41.

lytic oxygen transfer processes (Fig. 3). The latter can proceed via oxometal or peroxometal species as the active oxidant [35].

Heterolytic peroxometal pathways are favoured when the metal in its highest oxidation state is both a Lewis acid and a weak oxidant, e.g. early transition metal ions with d^0 configurations such as Mo^{VI}, W^{VI} and Ti^{IV}. Catalysis is due to the Lewis acid character of the metal ion and its oxidation state does not change during the catalytic cycle. Strong (one-electron) oxidants, e.g. later and/or first row transition elements such as Cr^{VI}, Mn^{III}, Co^{III} and Fe^{III}, favour oxometal pathways and/or homolytic decomposition of RO_2H. Vanadium (V) is both a strong Lewis acid and a relatively strong (one-electron) oxidant and hence, exhibits all three types of activity.

Oxidations of hydrocarbons with O_2 are most likely to involve classical free radical autoxidation pathways with intermediate formation of RO_2H. The latter may subsequently undergo heterolytic oxygen transfer processes. Similarly, in oxidations with RO_2H (or H_2O_2) homolytic decomposition leads to the formation of $RO_2^{\bullet}$ ($HO_2^{\bullet}$) radicals which can afford O_2 via bimolecular termination (Russell mechanism). The latter can react further with alkyl radicals in an autoxidation mode.

In many cases homolytic and heterolytic pathways can afford the same products and results should be interpreted with caution. Certain elementary tests for homolytic pathways should be performed, e.g. inhibition by a radical scavenger indicates a free radical chain mechanism and loss of yield on flushing with an inert gas suggests the intermediacy of O_2 in reactions with RO_2H or H_2O_2. More sophisticated mechanistic probes have been used to test for the intermediate formation of alkoxy radicals in oxidations with RO_2H [36]. The relative rates of oxidation of secondary and tertiary C–H bonds are often used as an indication of the attacking species (e.g. for $HO^{\bullet}$ C^3/C^2 ca. 2–3) [37]. However, caution should be exercised as these ratios can be influenced by solvent, etc. Typical examples of reactions involving peroxometal pathways are olefin

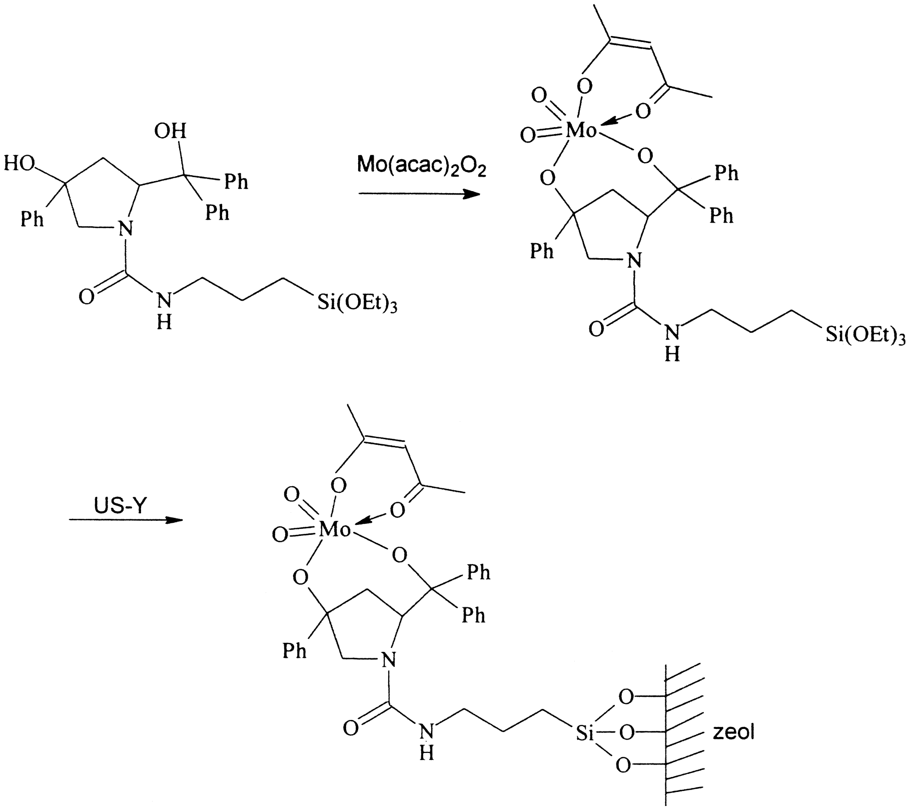


Fig. 2. Tethering of a chiral molybdenum (VI) complex to the internal surface of USY.

epoxidation, sulfoxidation and oxidation of nitrogen compounds. In contrast, allylic and benzylic oxidations and alkane oxidations are typical of oxometal or free radical autoxidation pathways, which are often difficult to distinguish. Alcohol oxidations may involve peroxometal or oxometal pathways. Thus, titanium-substituted molecular sieves operate via peroxometal pathways and catalyze e.g. the epoxidation of olefins. One would not choose them for allylic or benzylic oxidation. By the same token, the oxidation of alkanes with H_2O_2 in the presence of titanium or vanadium-substituted molecular sieves is unlikely to involve heterolytic oxygen transfer. The involvement of $HO^{\bullet}$ and/or $HO_2^{\bullet}$ radicals formed by the metal-mediated homolytic decomposition of H_2O_2 seems more likely as is the case, for example, for homogeneous vanadium systems [38]. On the other hand some authors [39] have proposed metalloperoxy radicals ($M–O–O^{\bullet}$) as the abstracting species. However, we suggest that, in the absence of convincing evidence to the contrary hydroxyl radicals resulting from homolytic decomposition of H_2O_2 are more likely candidates for the abstracting species.

3. Framework-substituted molecular sieves as oxidation catalysts

3.1. Titanium silicalite-1

The best example of a framework-substituted redox molecular sieve exhibiting novel activity is titanium (IV) silicalite-1 (TS-1) which catalyzes a variety of synthetically useful oxidations with 30% aqueous H_2O_2. Examples include olefin epoxidation [40], phenol hydroxylation [41] alcohol oxidations [42], sulfoxidations [43], the ammoximation of aldehydes and ketones with NH_3/H_2O_2 [44] and the oxidation of primary [45] and secondary amines [46] to oximes and hydroxylamines, respectively.

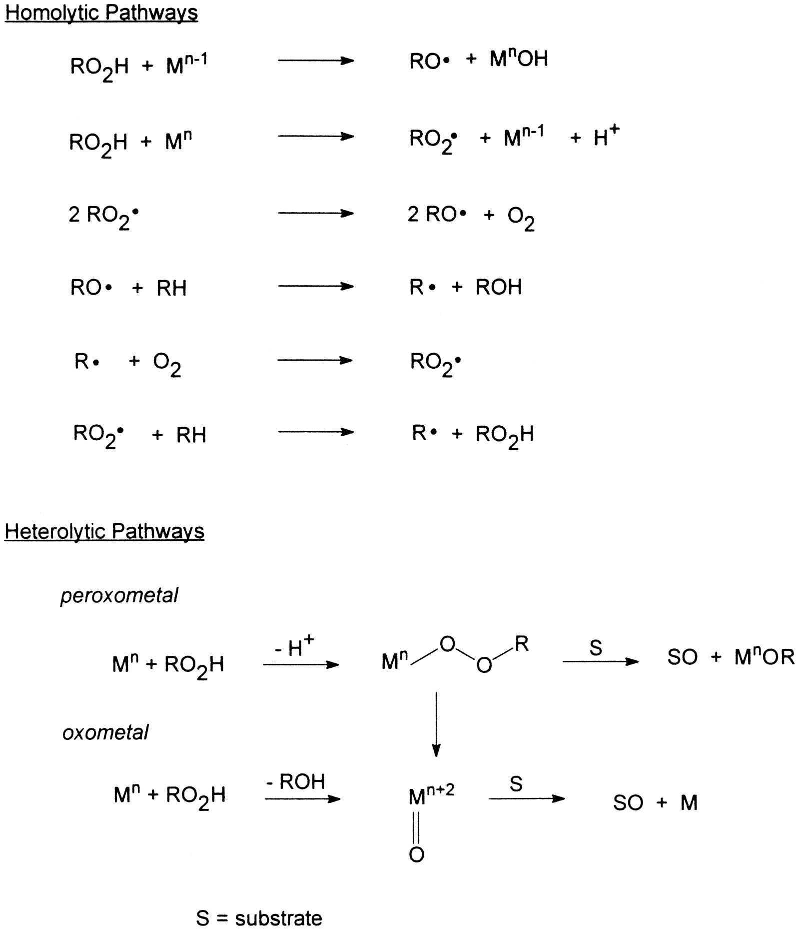


Fig. 3. Oxidation mechanisms.

The remarkable reactivity of TS-1 is believed to be largely due to the site-isolation of tetrahedral titanium (IV) in a hydrophobic environment. The hydrophobic character of the silicalite provides for the selective adsorption of apolar substrates and relatively apolar H_2O_2 from the aqueous reaction mixtures. The titanium (IV) acts as a Lewis acid thereby decreasing the electron density in the coordinated hydroperoxide and promoting nucleophilic attack of the olefin on the O–O bond. The electrophilicity of this species is assumed to be further increased by the co-ordination of alcohol solvent to the titanium hydroperoxo species forming a five membered peracid-type species, in which oxygen transfer is facilitated (Fig. 4).

The observed reactivity trend in alcoholic solvents is methanol>ethanol>tert-butanol which is consistent with the coordination of the alcohol becoming increasingly difficult with increasing steric bulk. The rates of epoxidation of olefins with TS-1 [40] depend strongly on the structure of the olefin and differ markedly from those observed in homogeneous solution. Owing to the steric restrictions of the TS-1 pore (6 Å) only linear olefins are smoothly epoxidized while cyclo-

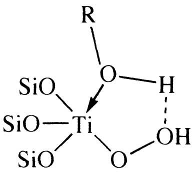


Fig. 4. Structure of the active oxidant formed with H_2O_2 and alcohols on the internal surface of TS-1.

hexene is completely unreactive. Similarly, 1-butene and 1-pentene react much faster than isobutene and 2-methyl-1-butene. Thus, reactivity is determined by steric rather than electronic properties of the olefin and even relatively electron poor olefins such as allyl chloride are smoothly epoxidized. TS-1 also catalyzes the hydroxylation of phenol to a 1 : 1 mixture of hydroquinone and catechol [41]. H_2O_2 conversion is quantitative and high selectivities on H_2O_2 and phenol are observed. Other aromatic compounds also undergo hydroxylation, e.g. benzene, toluene, anisole and chlorobenzene albeit with significantly lower activities and selectivities [47]. Ammonia is oxidized by H_2O_2, in the presence of TS-1, to afford hydroxylamine [44]. The latter reacts with ketones in the bulk solution to give oximes thus providing an attractive route for the ammoximation of ketones [48]. The oxidation of alkanes to secondary alcohols and ketones is also possible with the TS-1/H_2O_2 system [49,50]. The general trend in linear alkane oxidation is that the 2-position is more reactive than the 3-position and conversions for cycloalkanes are much lower than for *n*-alkanes due to the steric constraints. As noted earlier alkane oxidation most likely involves homolytic mechanisms with possible involvement of $HO^{\bullet}$ radicals.

A more recent development comprises the in-situ formation of H_2O_2 from H_2 and O_2 using TS-1 modified with Pt or Pd, e.g. in the oxidation of alkanes [51]. The use of Pt and Pd is based on the known capacity of Pd supported on carbon for catalyzing the production of H_2O_2 by combination of O_2 and H_2 in an acidic medium [52]. TS-1 modified by the impregnation with Pt or Pd was active in the oxidation of *n*-hexane with an O_2/H_2 mixture via in-situ formation of H_2O_2 (Fig. 5).

Interestingly, TS-1 loaded with 0.2% Pd gave a higher yield (13%) of oxygenated products than TS-1 with 0.8% Pd (4% yield). The best result (21% yield) was obtained with a catalyst in which Pt was introduced during hydrothermal synthesis which probably provides for high dispersion of Pt. Owing to the acidic conditions used in this method of the in situ H_2O_2 formation, catalytic oxidation of phenol afforded halophenols instead of hydroquinone and catechol presumably via the oxidation of the added HCl and HBr. Similarly, this modified TS-1 catalyst is also not useful for epoxidation owing to the acid-catalyzed ring opening of the epoxide to the corresponding glycol and/or halohydrin.

For the epoxidations of olefins with the in-situ generated H_2O_2 another method has been used by the Enichem workers [51]. They showed that TS-1 was an effective catalyst for the epoxidation of propylene with H_2O_2 generated in-situ by the autoxidation of a dihydro-anthraquinone (Fig. 6). The anthraquinone is hydrogenated in a separate step over a Pd/C catalyst to afford a two-step process for the epoxidation of propylene with H_2/O_2.

Owing to the bulky nature of the dihydroanthraquinone and anthraquinone they cannot enter the pores and consequently do not influence the catalytic properties of TS-1. Because of the complexity of the reaction mixture the solvent should at the same time be chemically inert, exhibit a high solubility for the (dihydro)anthraquinone and be favourable for the epoxidation step. A single solvent cannot meet all of these requirements. Hence, a solvent mixture was used, typically consisting of methanol, an aromatic hydrocarbon and an aliphatic ketone, alcohol or ester. In this way 78% yield of propene oxide was obtained based on the amount of anthraquinone added.

3.2. Other titanium-substituted molecular sieves

A disadvantage of TS-1 is its limited pore size which restricts its utility to the oxidation of substrates with a kinetic diameter <6 Å. This prompted several research groups to synthesize Ti molecular sieves with

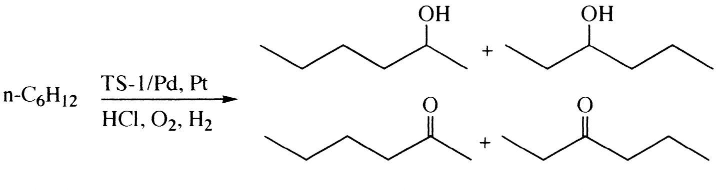


Fig. 5. Oxidation of *n*-hexane over TS-1 modified with Pd or Pt and in-situ formation of H_2O_2.

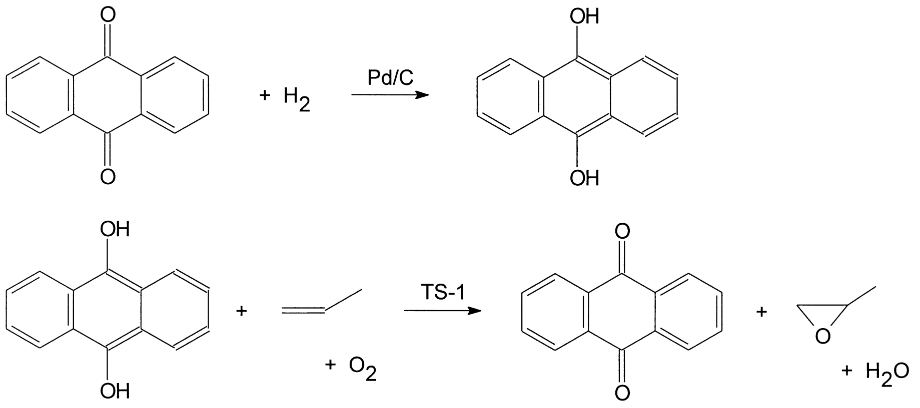


Fig. 6. Epoxidation of propylene over TS-1, with in-situ formation of H_2O_2 and anthraquinone as the co-oxidant.

larger pores such as Ti-β [53], TAPSO-5 [54] and Ti-MCM-41 [55]. Larger substrates can be oxidized with H_2O_2 using these catalysts, e.g. cyclododecene is epoxidized using Ti-β [56] and 2,6-di-tert-butyl-phenol is oxidized to the corresponding quinone with Ti-MCM-41 [55]. However, owing to the Brönsted acidity of Ti-β and TAPSO-5 the major products of olefin oxidation were glycols and glycol ethers resulting from acid catalyzed hydrolysis of the epoxide. This could be suppressed by using Ti-β in which Brönsted acid sites were neutralized by ion-exchange with alkali or earth alkaline metal ions [57]. Aluminum free Ti-β has also been used as an epoxidation catalyst with H_2O_2 [58]. Some ring opening was observed, however, which was assumed to be due to the titanium producing a Brönsted acid site in combination with the alcoholic solvent. This acidic character could be reduced by using weakly basic solvents such as acetonitrile [57,58].

Since Ti-MCM-41 is a potentially useful catalyst for the oxidation of bulky substrates its thermal and chemical stability was investigated [59]. Although the material showed high thermal stability, chemical stability under the conditions of a liquid phase oxidation was low; the MCM-41 structure collapsed and titanium was leached from the framework.

Generally pore restrictions preclude the use of TBHP in oxidations of organic compounds using TS-1 presumably because of severe steric constraints in the transition state for oxygen transfer. By using large pore molecular sieves this restriction can be overcome and Ti-β [57b], [61], titanium mesoporous silicates (HMS) [60] and Ti-MCM-41 [61] are active catalysts for oxidations with TBHP.

The Brönsted acidity in a titanium substituted zeolite can also be an asset to the catalytic activity, for example in the conversion of linalool to cyclic ethers [61] (Fig. 7). The bifunctional (Ti-β or Ti-MCM-41) catalyst first epoxidizes the electron rich double bond at a titanium site, followed by the acid catalyzed rearrangement at an aluminum site. The observed conversion of linalool to cyclic hydroxy ethers closely resembles that catalyzed by epoxidase enzymes in vivo.

3.3. *Zirconium and tin containing molecular sieves*

The success of TS-1 also stimulated investigations of redox molecular sieves containing other metals, e.g. Zr and Sn, with properties similar to titanium. For example, ZrS-1 [62] and SnS-1 [63] have been prepared and their catalytic activity compared to TS-1. In the case of SnS-1 very similar conversions were obtained in the hydroxylation of phenol with H_2O_2 compared to TS-1, while ZrS-1 was considerably less active in the hydroxylation of benzene compared to TS-1. As with TS-1, these results prompted researchers to investigate larger pore Sn-substituted molecular sieves. Sn-MCM-41 [64], for example, catalyzed the hydroxylation of the bulky substrate 1-naphthol with H_2O_2. This catalyst was also active in the oxidation of 2-methyl naphthalene or toluene with tert-butyl hydroperoxide (TBHP).

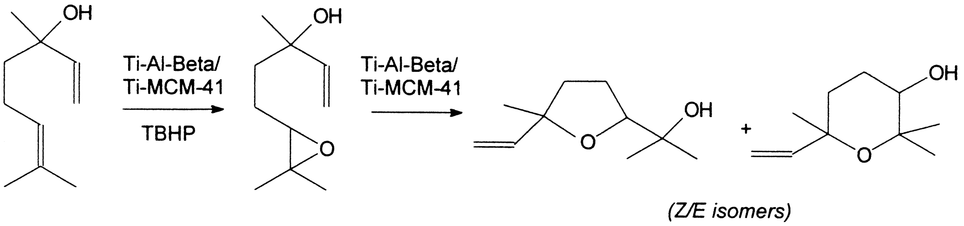


Fig. 7. The conversion of linalool to cyclic ethers over Ti–Al-β.

3.4. Vanadium containing molecular sieves

Vanadium can, depending on the substrate used, react via an oxometal or a peroxometal pathway. For reactions involving a peroxometal pathway only H_2O_2 can be applied with small pore molecular sieves while both H_2O_2 and TBHP can be applied with large pore molecular sieves. When reactions follow a oxometal pathway both oxidants can in principle be applied with either small or large pore molecular sieves (see also chromium molecular sieves).

In the case of vanadium substituted molecular sieves the reported results are contradictory regarding stability and activity. For example, during the VS-1 catalyzed oxidation of toluene with H_2O_2 up to 92% of the vanadium was leached into solution [65]. Nevertheless, the authors still proposed that the heterogeneous catalysis was taking place! Similarly in the VS-1 catalyzed oxidation of *para*-chlorotoluene [66] vanadium was shown to be leached by analysis of the vanadium content of the catalyst before and after reaction and by analysis of the reaction solution. However when the catalyst was filtered from the reaction solution the filtrate did not react further. We note, however, that in order to give a meaningful result the catalyst should be filtered at the reaction temperature and not, as is usually the case, be first allowed to cool to ambient temperature as this may result in the re-adsorption of metal ions from the solution. Filtration of V-HMS during the oxidation of 2,6-di-tert-butylphenol with H_2O_2 afforded a filtrate which exhibited catalytic activity [67]. Similarly the activity of VAPO-5 in oxidations with TBHP was shown to be due to the leaching of the vanadium. The stability of vanadium in VAPO-5 in the presence of H_2O_2 was also shown to be low [68]. In an experiment where VAPO-5 was refluxed in 30% H_2O_2 ca. 40% of the original VAPO-5 vanadium was leached into the solution. VAPO-5 catalyzed epoxidations and benzylic oxidations with TBHP were postulated to occur solely inside the pores of VAPO-5 [69]. This was based on epoxidation experiments carried out in the presence of triethylamine, which can access the pores of AlPO-5 structure and triphenylamine, which is too bulky to enter the pores. No epoxidation was observed in the presence of triethylamine due to the facile competing oxidation of the triethylamine. In the presence of triphenylamine, on the other hand, smooth epoxidation was observed. However, the authors overlooked the enormous difference in the nucleophilicity of triethylamine and triphenylamine which is probably responsible for the observed lack of reactivity of the latter. Thus, careful analysis of the reaction solution for leached vanadium and filtration experiments [70], clearly showed that these reactions are catalyzed by small amounts of leached vanadium.

3.5. Chromium containing molecular sieves

Another metal which reacts via oxometal pathways and is a useful catalyst for allylic and benzylic oxidations, is chromium. As noted earlier, because the active oxidant in oxometal pathways does not contain the alkylperoxo group, oxidations with e.g. TBHP are not subject to the same steric constraints as in peroxometal pathways. Thus, CrS-1 was shown to be an active and recyclable catalyst for the oxidation of benzyl alcohol and ethylbenzene with TBHP to benzaldehyde/benzoic acid and acetophenone respectively [71]. Similarly, CrAPO-5 was shown to be an active and recyclable catalyst for a variety of oxidative transformations with either TBHP or O_2 as oxidant [72]. In initial experiments carried out by us these catalysts appeared to be stable toward chromium leaching as the chromium content of the catalyst before and after the reaction remained, within experi-

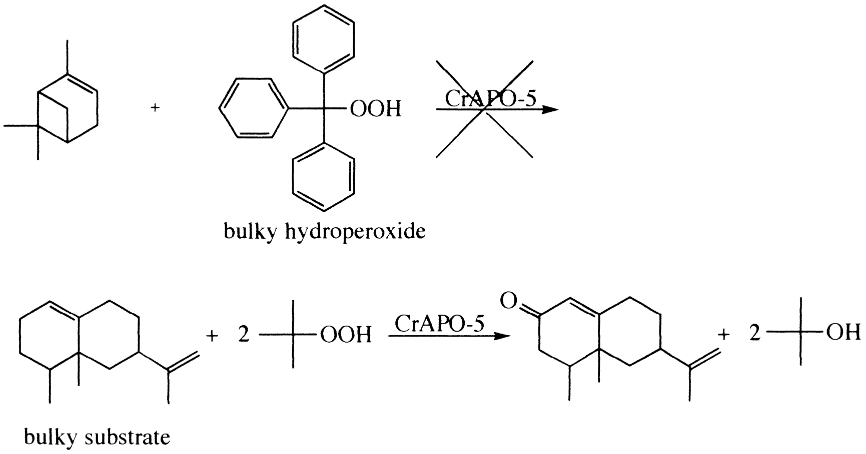


Fig. 8. Oxidation of a bulky substrate (valencene) with a small hydroperoxide (TBHP) and oxidation of a small substrate (α-pinene) with a bulky hydroperoxide (triphenylmethylhydroperoxide) over chromium containing molecular sieves.

mental error, constant and after filtration of the catalyst from the reaction solution the filtrate did not exhibit appreciable reactivity, which was also observed by other researchers [73]. However, when filtration was performed at the reaction temperature the filtrate continued to react at roughly the same rate [74]. Moreover, we showed that the oxidation with TBHP of substrates, which are too bulky (valencene) to fit in the micropores, was catalyzed by CrAPO-5, while with small substrates and bulky hydroperoxides (triphenylmethylhydroperoxide) no catalysis was observed. (Fig. 8). This result was rationalized by assuming that the leaching of chromium occurs by extraction with TBHP.

This was confirmed by an experiment in which CrAPO-5 was incubated with TBHP. After filtration of the catalyst substrate was added and the reaction started.The reverse experiment where CrAPO-5 was first incubated with substrate, filtered and then hydroperoxide added did not show any reaction. Careful spectroscopic determination of chromium in filtrates, obtained from filtration at the reaction temperature, further showed that the amount of leaching depends on the crystal-size of the catalysts [75]. Small crystallites can lose more than 30% of the chromium while large crystallites lose less than 0.5% of the chromium. Hence, we conclude that experiments demonstrating that heterogeneous catalysts can be recovered and recycled without any apparent loss of active metal or activity are certainly not the definite proof of heterogeneity. As with Ti, Zr and Sn, chromium-substituted mesoporous materials have been synthesized and used in catalytic oxidation. However, bearing in mind the results obtained with CrAPO-5 and CrS-1, we consider it highly unlikely that Cr-MCM-41 [76], Cr-MCM-48 [77] and Cr-HMS [78] are truly heterogeneous catalysts. A general conclusion which can be drawn regarding the framework-substituted redox molecular sieves is that notwithstanding the large number of new materials that have been synthesized and characterized since the advent of TS-1 none of these materials appear to be able to compete with the outstanding activity, stability and recyclability of TS-1.

4. Zeolite encapsulated metal complexes as oxidation catalysts

4.1. Zeolite encapsulated iron complexes

Pioneering studies of oxidations catalyzed by zeolite-encapsulated iron phthalocyanines (FePc) were performed by Herron [79,80]. He studied the oxidation of alkanes with iodosylbenzene catalyzed by FePc encapsulated in zeolites NaX and NaY. Although rather interesting (shape) selectivities were observed, reminiscent of heme-containing enzymes, activities were poor (ca. 6 turnovers) which was attributed to pore blockage by iodoxybenzene. Jacobs and co-workers re-initiated these studies using TBHP as the oxidant [12]. They found that FePc-Y, containing 1 FePc per 77 supercages, gave turnovers as high as 6000, in the oxidation of *n*-octane with TBHP in a single run at ambient conditions [81]. Admittedly this activity could only be attained at a low TOF of 12 h^{-1} (the TBHP should be added slowly to minimize degradation) and for high substrate/catalyst ratios. In a more recent study, FePc-Y catalysts containing 1 FePc complex per 7 supercages were synthesized and shown to give roughly the same TOF of 10.2 h^{-1} for oxidation of cyclohexane to cyclohexanol and cyclohexanone [82]. Turnover numbers could be further increased by introducing electron-withdrawing nitro groups on the phthalocyanine ring [83]. These activities are significantly higher than those obtained with homogeneous FePc complexes (25 turnovers vs. 6000 under comparable conditions) [81]. Apart from protecting the ligands against oxidative degradation, site isolation of the active Fe-centers prohibits dimer formation which is a major cause of the deactivation for catalysis by homogeneous complexes. Besides activities, also peroxide efficiencies are considerably higher in the case of zeolite encapsulated FePc [82]. The presence of free iron ions in the zeolite leads to nonselective peroxide decomposition and synthesis methods have been optimized to minimize this effect: use of ferrocene as metal source was found to be essential [81]. Sorption effects due to the hydrophilic zeolite were reflected in the product distribution. In the oxidation of cyclohexane, subsequent oxidation of cyclohexanol is stimulated by the enrichment of the alcohol in the active site, leading to high ketone to alcohol ratios [81,82]. In general the catalyst activity could be restored by the soxhlet extraction which liberates the channels that were blocked by the adsorption of polar products. A further technological improvement to this system was achieved by embedding the zeolite in a hydrophobic polydimethylsiloxane (PDMS) membrane (Fig. 9), which was interposed between the immiscible substrate and oxidant phases. In this way, the membrane acted as a solvent, adjusting the relative concentrations of hydrophobic substrate (cyclohexane) and hydrophilic oxidant (aqueous TBHP) and a TOF of 198 h^{-1} could be reached [84].

Balkus and co-workers synthesized a NaX encapsulated ruthenium perfluorophthalocyanine complex ($RuF_{16}Pc$-X), containing 1 Ru per 125 NaX supercages [85] by the template method (see earlier) and showed it to be an active catalyst for the room temperature oxidation of cyclohexane with TBHP (Table 1). The catalyst showed no sign of deactivation, in contrast to the iron analogue. Summarizing, encapsulation of the metallo–phthalocyanine complexes appears to increase the oxidative stability of the ligand.

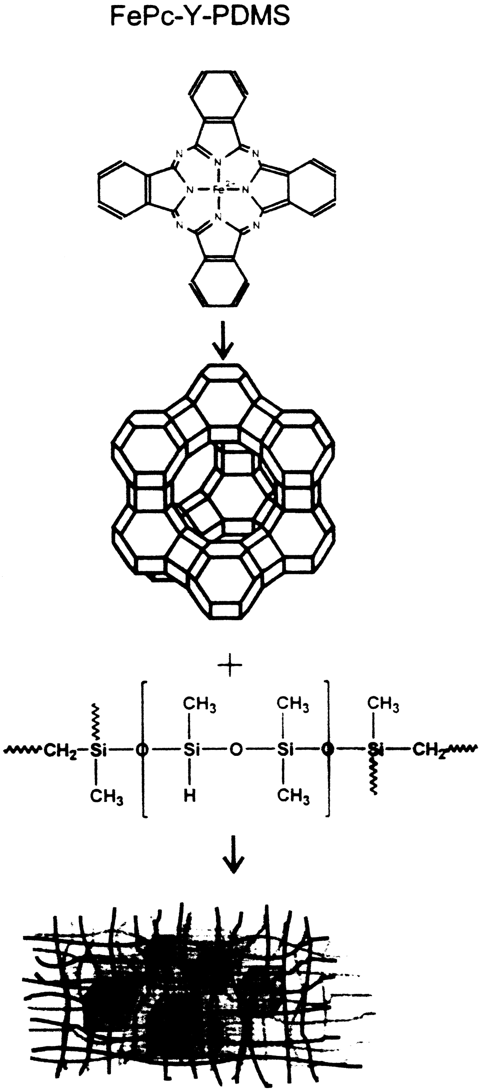


Fig. 9. Assembly of iron phthalocyanine, encapsulated in zeolite Y (FePc-Y), within a polydimethylsiloxane membrane [adapted from [84]].

Table 1
Ru-phthalocyanine-catalyzed oxidation of cyclohexane with TBHP [85]

Catalyst	Time (h)	Conv. (%)	Selectivity		TBHP Efficiency (%)	TOF (h^{-1})
			Ketone	Alcohol		
RuPc	5	47	72	27	30	7.5
$RuF_{16}Pc$	24	83	78	22	48	15
$RuF_{16}Pc$-X	192	86	98	1	97	125

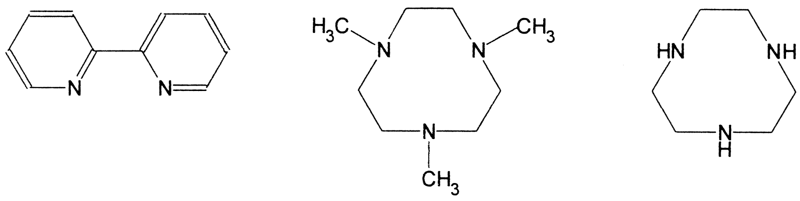

bipy tmtacn tacn

Fig. 10. Structures of ligands; bipy, tmtacn, tacn.

Recently, Fe-picolinate and 2-pyridinecarboxamide type complexes, encapsulated in NaY, were reported to be active for the partial oxidation of alkanes with H_2O_2 and TBHP [86]. These complexes are interesting examples of biomimetic complexes for the iron-oxo active site in methane monooxygenase.

4.2. Zeolite encapsulated manganese complexes

Another advantage of the encapsulated complex concept compared to the framework substitution is that it is amenable to tailoring of the catalytic activity of the metal ion by varying the structure of the coordinated ligands. This is illustrated by the use of faujasite-entrapped Mn-bipyridyl, tacn and tmtacn complexes (see Fig. 10) in the catalytic epoxidation of alkenes with H_2O_2. Uncomplexed manganese ions in zeolite Y exhibit mainly catalase activity – the tendency to decompose H_2O_2 – while complexed manganese ions can catalyze the selective epoxidation of alkenes without competing processes such as self-oxidation or catalase activity. Results obtained for the epoxidation of cyclohexene are summarized in Table 2 [87–90]. The initially formed epoxide undergoes acid-catalyzed ring-opening to the diol followed by further oxidation to the di-acid (Fig. 11). When NaX is used instead of NaY as the host material, the strength of the acid sites is reduced and epoxide

Table 2
Cyclohexene epoxidation catalyzed by encapsulated Mn-complexes and H_2O_2 [80,89]

	H_2O_2/ substrate	Conv.(%)	TON epoxy	Sel. epoxy	Sel. diol	Sel. diacid
$Mn(bipy)_2$-Y	2	62	11	6	79	–
$Mn(bipy)_2$-Y	10	100		–	–	80
$Mn(bipy)_2$-X	1.3	41	76	62	32	–
Mn(tacn)-Y[a]	1	–	–	–	–	–
Mn(tmtacn)-Y[a]	1	25	30	95	5	–

Reaction conditions; temp. 298 K; acetone as solvent; H_2O_2 added gradually; tacn=triazacyclononane, tmtacn=trimethyltriazacyclononane. Reaction ends when H_2O_2 is consumed. Time frames are 18 h, 40 h, 4 h, 12 h and 12 h respectively.

[a] Temperature was lowered to 273 K, which gave a significant improvement in epoxide yield.

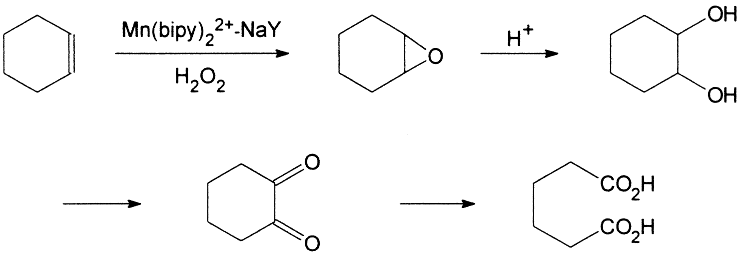


Fig. 11. Conversion of cyclohexene to the di-acid over $Mn(bipy)_2^{2+}$ – NaY

hydrolysis can be limited [87]. Typical turnover frequencies in these systems are in the order of 6–18 h^{-1}. The ligand effects observed are analogous to those for homogeneous complexes. For example, methylation of the amine groups leads, also in case of homogeneous Mn(tacn) complexes, to less decomposition of H_2O_2 [89–91]. Interestingly, in contrast to the homogeneous oxidations, no products of allylic oxidation were observed with Mn(tmtacn)-Y [89–91].

Although epoxidation of alkenes by Mn-entrapped complexes was also performed in methanol solutions, the activities mentioned above were all obtained in acetone solutions. Apparently an adduct with acetone and H_2O_2 is formed, which slowly releases H_2O_2. Thus, acetone is not merely a solvent but also a reactant. Interestingly, in the Mn(tmtacn)-Y system an ESR signal characteristic of the μ-oxo dimer was observed, which coincided with the end of the induction period [90]. The homogeneous Mn(tmtacn) complexes are known to be dimeric and it seems that the zeolite encapsulated complexes are also dimers.

The concept of encapsulated complexes is especially applicable to the design of heterogenized chiral complexes. Recently a chiral bulky Mn–salen complex (salen= (S,S)–*N*, *N*′-bis (3-tert-butyl-5-methylsalicylidene)-cyclohexadiamine), assembled in zeolite EMT, was reported to give enantioselective oxidation of alkenes with NaOCl as the oxidant. The observed enantioselectivities were identical to those obtained with the homogeneous complex and leaching tests were performed to demonstrate the heterogeneity of the reaction [92].

4.3. Zeolite encapsulated vanadium complexes

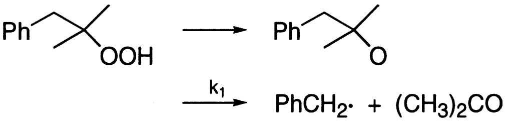
The preceding examples involve metals which are known to react via M-oxo intermediates. Examples of the encapsulated complexes that react via a peroxometal mechanism are few. VO $(bipy)_2$-Y (vanadyl-bis-2,2′-bipyridine-Y) ([93] and VO (salen)-Y (vanadyl-*N*,*N*′ (bis)salicylideneimine-Y) [94] were reported to give slow room temperature epoxidation of cyclohexene with TBHP at ambient temperature. We found that VO (HPS)-Y (vanadyl-*N*-(2-hydroxyphenyl)salicylideneimine-Y) gave selective epoxidation of cyclooctene and (−) carveol with TBHP at 70°C [95]. However leaching of the vanadium took place.

Leaching of metal ions from the molecular sieve is a general problem and not all systems reported in the literature have been appropriately evaluated in that respect. According to Jacobs, cationic complexes are considerably more robust towards leaching than neutral complexes such as Schiff base complexes, due to the retention by the anionic lattice [12]. For example, although zeolite Y-occluded metal Schiff base complexes are stable in dichloromethane they are washed out by ethanol. Apparently, the thermodynamically favourable adsorption of ethanol in zeolite Y is a strong enough driving force to cause dissociation and, hence, leaching of the metal–salen complexes from the zeolite cages. In this context it is noteworthy that polar aprotic molecules, e.g. alcohols, carboxylic acids are produced in many oxidative processes and hence, can be expected to leach, for example, metal–salen complexes.

5. Zeolite-grafted and tethered complexes as oxidation catalysts

As noted earlier the concept of immobilizing a redox active centre in intrazeolite space has been extended to the construction of grafted or tethered organometallic or coordination complexes to the internal surface [7]. This approach creates new possibilities for the preparation of novel catalysts containing structurally well-defined active centres. Moreover, as noted by Thomas [7] the tethered complexes in particular contain a readily accessible active site which is 'free to flutter in the molecular breeze during the process of catalytic conversion'.

Thomas and co-workers [31] prepared a heterogeneous titanium (IV) catalyst by grafting $(Cp)_2TiCl_2$ to the internal surface of MCM-41 followed by the calcination to remove the organic ligands (see Section 2.3). The resulting material was shown to catalyze the selective epoxidation of cyclohexene and pinene with TBHP [31]. More recently, it was shown [96] that the grafted titanium catalyst, designated as Ti→MCM-41 (Si/Ti $=1{:}0.041$) was ten times as active per Ti^{IV} ion as the analogous titanium-substituted MCM-41, prepared by hydrothermal synthesis and designated as Ti→MCM-41 (Si/Ti $=1:0.058$). In the same study 2-methyl-1-phenyl-2-propyl hydroperoxide (MPPH) was used as a mechanistic probe. Homolytic cleavage of the O–O bond of MPPH affords an alkoxy radical which undergoes extremely rapid β-scission ($k_1 \approx 2\times10^8\ s^{-1}$) to give a benzyl radical (reaction 2). The fact that smooth epoxidation of cyclohexene was observed with MPPH in the presence of the titanium catalysts confirmed the heterolytic nature of the reaction.



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Oxomanganese species grafted onto the inner walls of MCM-41 were shown to be effective catalysts for the total combustion of propylene [32]. It would be of interest to test the activity of this catalyst in liquid phase oxidations under milder conditions. A MCM-41 tethered manganese TACN complex, prepared by Jacobs and co-workers [33] via glycidylation of the internal surface of MCM-41 (see Section 2.3), was shown to catalyze the epoxidation of cyclohexene and styrene with 35% H_2O_2 in acetone, acetonitrile, or methanol as solvent. Manganese complexes of TACN had been previously shown to be capable of catalyzing olefin epoxidation with aqueous H_2O_2 in homogeneous solution [89,91,97].

The tethering of chiral molybdenum (VI) complexes to the internal surface of a mesoporous USY-zeolite (Section 2.3) afforded a catalyst for the asymmetric epoxidation of allylic alcohols with TBHP [34]. The activity and regioselectivity was comparable to that observed with the analogous homogeneous catalysts in the epoxidation of nerol and geraniol. Interestingly, the enantioselectivities increased significantly from homogeneous to heterogenized catalysts suggesting that the constrained environment of the zeolite promotes preferential oxygen transfer to the pro-S face of the double bond. Thus, the zeolite-tethered complex shown in Fig. 2 gave enantioselectivities of 47% and 64% with geraniol and nerol, respectively, compared to 28% and 10% with the corresponding homogeneous complexes. Although these are only moderate enantioselectivities their results appear to demonstrate the positive influence of the constrained environment on chiral recognition. The zeolite-tethered complex was recycled five times with only a slight decrease in epoxide yield. This observation, taken together with the different enantioselectivities, suggests that the zeolite-tethered complex acts (mainly) as a heterogeneous catalyst but there remains a need for rigorous proof of heterogeneity.

6. Extension of the concept: other examples of constrained environments

As mentioned earlier redox pillared clays [19] and redox aerogels [20] also constitute examples of oxidation catalysts in constrained environments.

6.1. Redox pillared clays

Clays are colloidal layered hydrous aluminosilicates. The most well-known clay is montmorillonite which is an example of a smectite clay. In smectites the layers are assembled from octahedral AlO_6 sheets sandwiched between two tetrahedral SiO_4 sheets in which oxygen atoms on the apices of the tetrahedra are shared with the octahedra (see Fig. 12).

In montmorillonite, the layer charge originates from the substitution of octahedral Al^{III} by Mg^{II}. The positive charge deficiency is balanced by exchangeable cations, e.g. Na^+, K^+, which are distributed in both the interlamellar space and on the external surface. The layers are held together by relatively weak

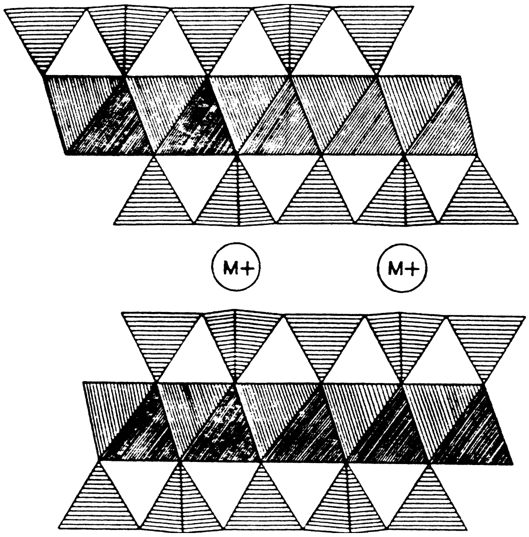
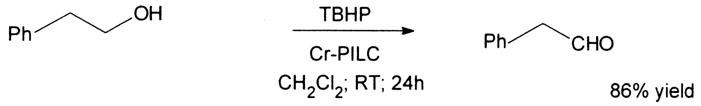


Fig. 12. Interlamellar space in redox pillared clays [adapted from [28]].

dipolar and Van der Waals forces and the interlamellar distance depends on the number of intercalated cations and water molecules. For dry Na-montmorillonite the interlamellar distance is about 12 Å which contracts to ca. 9 Å on calcination at 500°C. In hydrated montmorillonite the interlamellar space increases to 20–50 Å, i.e. distances comparable with mesoporous sieves.

Pillared clays (PILCs) are prepared by exchanging the interlamellar cations by bulky, thermally stable ions which act as molecular pillars and prevent collapse of the interlamellar region on dehydration. Pillaring with (oxo)transition metal ions, such as titanium (IV), vanadium (V) and chromium (VI) affords microporous materials with redox properties, i.e. redox pillared clays. However, we note that these materials suffer from several disadvantages compared to redox zeolites. For example, they do not have the same uniformity of structure and, because they are one-dimensional, pore blockage can be a problem. Moreover, since the pillars are 'oxide' aggregrates they do not contain site-isolated, monomeric metal species.

Chromium-pillared montmorillonite (CrPILC) [98] has been reported to catalyze the oxidation of alcohols [99] and benzylic oxidations [100] with TBHP as oxidant, e.g. reactions 3–6.



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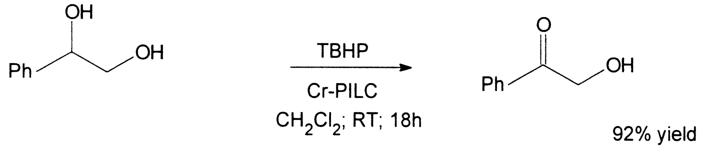

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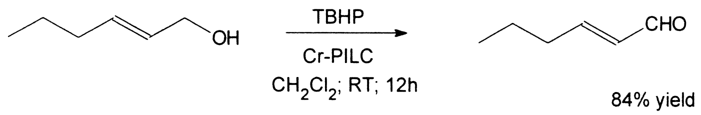

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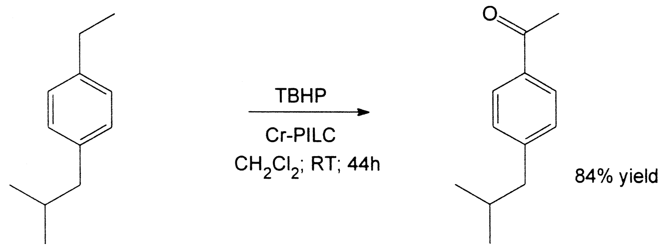

(6)

The chemoselectivities observed in alcohol oxidations- secondary over primary and selective oxidation of allylic alcohol moieties is the same as that observed with chromium-substituted molecular sieves. However, bearing in mind the results obtained with the latter (see Section 3) and in the absence of rigorous evidence to the contrary, we assume that activity can probably be ascribed to leached chromium. Nevertheless, the selective oxidation of the benzylic hydrogens in the ethyl group of *p*-isobutylethylbenzene (reaction 6) is remarkable and worthy of further investigation.

Similarly vanadium-pillared montmorillonite (VPILC) was reported to catalyze the regioselective epoxidation of allylic alcohols [101] and the selective oxidation of benzylic alcohols [102] with TBHP. Here again, based on the experience gleaned from the studies of analogous reactions with vanadium-substituted molecular sieves, we consider it highly likely that the observed activity is due to the leached vanadium.

Analogous to the zeolite-encapsulated complexes described earlier, clay-intercalated metal complexes have been synthesized [28]. Most studies have involved the intercalation of metalloporphyrins and metallophthalocyanines. In contrast with the zeolite-encapsulated complexes the intercalated complexes are not physically entrapped and can be readily leached. Hence, the best results have been obtained with metal complexes of the tetracationic ligands, tetra (4-pyridyl)porphyrin and tetra (4-*N*-methylpyridyl)porphyrin [28,103], which are tightly bound by ionic interactions. Despite their obvious potential, little has been published on their synthetic utility as oxidation catalysts [28,103].

6.2. *Redox aerogels*

Controlled hydrolysis of silicon alkoxides by the solution-sol–gel (SSG) technique followed by low-temperature drying by extraction with supercritical CO_2 affords highly porous aerogels with pore size distributions in the 20–70 nm range [20]. By adding a transition metal alkoxide to the sol–gel mixture redox active sites can be incorporated in the aerogel structure (c.f. hydrothermal synthesis of redox molecular sieves). For example, Baiker and co-workers [104] have prepared titania–silica aerogels using this technique and shown them to be highly active catalysts for the epoxidation of bulky olefins with TBHP [105]. An advantage of this method is that much higher amounts of titanium (ca. 20%) can be incorporated compared to titanium-substituted molecular sieves (ca. 2%). However, they do not possess the uniform micro- or mesopores characteristic of the zeolitic materials. It was subsequently shown that the titanium aerogel catalyst is considerably more active per gram than the Shell Ti^{IV}/SiO_2 catalysts and Ti–BEA, Ti–MCM-41 or Ti-grafted MCM-41 in the epoxidation of cyclohexene [106].

A heterogeneous titanium catalyst was prepared by the sol–gel condensation of Cp_2TiCl_2 with $Si(OEt)_4$ [107] analogous to the synthesis of the titanium-grafted MCM-41 described earlier. However, the gel was dried by the conventional calcination at 250°C which affords a so-called xerogel lacking the high porosity of the aerogel structure. This material was shown [106] to have a much lower epoxidation activity than the titanium aerogel. More recently, the same group has reported the synthesis of the hydrophobic titania–silica xerogels with high surface areas and pore size distribution maxima (7 Å) in the range of large pore zeolites [108]. They were shown to catalyze epoxidations with TBHP or even aqueous H_2O_2.

Recently, a new class of hybrid organic–inorganic materials has been synthesized by the copolycondensation of Si $(OEt)_4$ with an iron porphyrin containing a pendant trifluoroalkyl functionality [109]. The resulting sol–gel comprises the iron porphyrin tethered at four sites to the silica superstructure (Fig. 13). The materials are described generically as 'metalloporphyrinosilicas'.

The iron porphyrinosilica catalyzed the oxidation of alkanes and the epoxidation of cyclooctene with PhIO or TBHP. This technique would appear to open up the possibilities for the synthesis of a range of interesting oxidation catalysts including chiral variations on this theme. Furthermore, we note that the materials were dried conventionally (80°C; 24 h) and application of supercritical drying (see above) could result in further improvement of their activity.

7. Conclusions and perspectives

Hopefully this review has shown that many interesting developments are emerging in the design of recyclable oxidation catalysts containing the active centre in constrained environments. Several different approaches are followed to achieve the goal of an active, selective and stable catalyst. Each approach appears to have inherent limitations. With the excep-

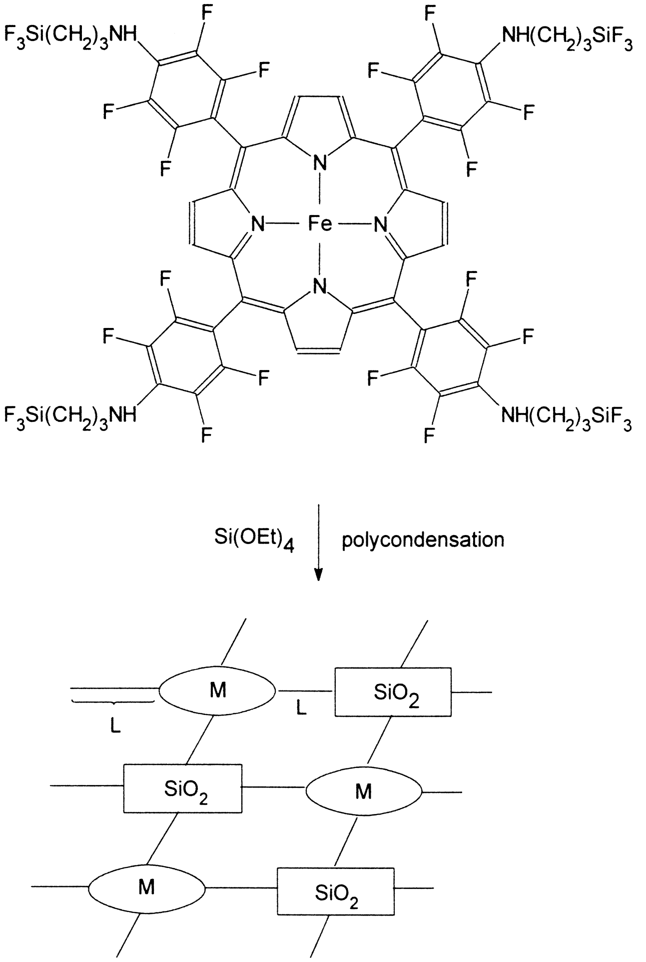

Fig. 13. Assembly of metalloporphyrinosilicas [108].

tion of TS-1 and perhaps some other titanium-substituted molecular sieves, framework substitution does not appear to give catalysts which are stable towards leaching under oxidizing conditions. The same limitation probably applies to zeolite-grafted complexes, redox pillared clays and redox aerogels. Encapsulated complexes would appear to be more stable towards leaching if the complex is stable towards dissociation and/or oxidative destruction of the ligands. However, these catalysts appear to exhibit low activities due to diffusion limitations. Zeolite-tethered complexes and the related hybrid catalysts prepared by the sol–gel method appear promising but a more rigorous investigation of their stability towards leaching is urgently needed. Indeed, there is a pressing need for more comparisons of the activities (TOFs) and stabilities of the different types of catalysts in the same oxidative transformation under identical conditions.

Assuming that the problems of activity and stability can be solved, this will lead to the development of a range of synthetically useful catalysts for selective oxidations, including asymmetric oxidations, with clean oxidants. This in turn will fill an urgent need for atom-efficient, environmentally attractive processes in the fine chemicals industry.

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