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Heterogeneous Catalysts for Liquid-Phase Oxidations: Philosophers' Stones or Trojan Horses?

ROGER A. SHELDON,*,[†] MARTIN WALLAU,[‡]
ISABEL W. C. E. ARENDS,[†] AND
ULF SCHUCHARDT*,[‡]

*Laboratory of Organic Chemistry and Catalysis,
Delft University of Technology, Julianalaan 136,
2628 BL Delft, The Netherlands, and Instituto de Química,
Universidade Estadual de Campinas, Caixa Postal 6154,
13083-970 Campinas-SP, Brazil*

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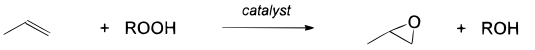
Introduction

In the early seventies one of us[1] was involved in the development of the heterogeneous Ti(IV)/SiO_2 catalyst which forms the basis of the Shell process for the epoxidation of propylene with ethylbenzene hydroperoxide (reaction 1).[2]

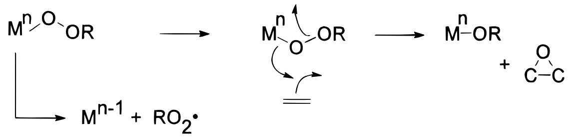


(1)

R = $PhCH(CH_3)$- or $(CH_3)_3C$-

catalyst: homogeneous Mo(VI) (ARCO)
heterogeneous Ti(IV) / SiO_2 (Shell)

Scheme 1



Halcon[3] and ARCO[4,5] workers had previously found, independently, that soluble compounds of early transition metals, e.g., Mo, W, Ti, and V, catalyze reaction 1. The mechanism of catalysis involves withdrawal of electrons from a coordinated alkylperoxo moiety, thereby increasing the electrophilic character of the peroxidic oxygens, i.e., the metal ion acts as a Lewis acid. Hence, effective catalysts are both a strong Lewis acid and a weak oxidant in their highest oxidation state. The latter criterion is necessary in order to minimize competing one-electron oxidation of the ROO ligand leading to homolytic decomposition of ROOH (see Scheme 1).

These criteria are best met by molybdenum(VI), and soluble molybdenum compounds exhibit the best combination of activity and selectivity.[6,7] Soluble titanium(IV) compounds, on the other hand, are rather mediocre catalysts for reaction 1. In contrast, Ti(IV)/SiO_2 exhibits selectivities comparable to homogeneous molybdenum and (for a heterogeneous catalyst) high activities.[8] The superior catalytic activity of Ti(IV)/SiO_2 was attributed to both an increase in Lewis acidity of the Ti(IV), owing to electron withdrawal by silanoxy ligands, and to site isolation of discrete Ti(IV) centers in the silica lattice preventing oligomerization to unreactive μ-oxo species (which readily occurs with soluble Ti(IV) compounds).

Furthermore, it was demonstrated that only the combination of titanium(IV) with silica affords a stable heterogeneous catalyst; all other combinations, e.g., Mo(VI), W(VI), V(V), etc., on silica, gave rapid leaching of the metal ion.

One property which soluble Ti(IV) compounds and Ti(IV)/SiO_2 share is a marked sensitivity toward deactivation by strongly coordinating ligands, especially water.[9] For this reason Ti(IV)/ SiO_2 is an ineffective catalyst for epoxidations with aqueous hydrogen peroxide. Hence the appearance in the mid-eighties of Enichem patents[10] describing the remarkable catalytic activity of titanium(IV) silicalite (generally known as TS-1) in, inter alia, the selective epoxidation of olefins under very mild conditions with 30% aqueous hydrogen peroxide (Figure 1) was greeted with some scepticism. Thus, two materials, Ti(IV)/SiO_2 and TS-1, having roughly the same elemental composition, i.e., 2% Ti in SiO_2, exhibited totally different catalytic properties.

Initial attempts by various groups to reproduce the Enichem results were largely unsuccessful. However, once it became clear that certain parameters in the synthesis

Roger A. Sheldon (1942) is a native of Nottingham (UK). He received a Ph.D. in chemistry from the University of Leicester (UK) in 1967. Following a postdoctoral sojourn with Jay Kochi he was with Shell Research, Amsterdam, from 1969 to 1980. From 1980 to 1990 he was R&D director of DSM-Andeno (Venlo, The Netherlands). In 1991 he was appointed Professor of Organic Chemistry at Delft University of Technology. His research interests are mainly concerned with the application of catalytic methods, in particular catalytic oxidations using homogeneous, heterogeneous and biocatalysts, in organic synthesis. He is the author/editor of several books on the subject of catalysis, notably "Metal Catalyzed Oxidations of Organic Compounds" which he coauthored with Jay Kochi.

Martin Wallau is Post-Doc at the State University of Campinas, Brazil. He received his Ph.D. from the University of Mainz, Germany. Following postdoctoral stays with J.L. Guth in Mulhouse, France, and W. Dünges in Mainz, he joined the group of U. Schuchardt.

Isabel W. C. E. Arends was born in the Netherlands in 1966 and studied chemistry at the University of Leiden (The Netherlands) where she received her Ph.D. in 1993 on the thermolysis of arene derivatives with coal-type hydrogen donors under the supervision of R. Louw and P. Mulder. Postdoctoral work followed with K. U. Ingold at the National Research Council in Canada on liquid phase oxidations catalyzed by iron-biomimetic complexes. She joined the group of R.A. Sheldon in 1995 and her research interests include metal-catalyzed selective oxidations, redox molecular sieves, and in particular catalytic oxidations with biomimetic vanadium systems.

Ulf Schuchardt is Professor of Inorganic Chemistry at the State University of Campinas, Brazil. He received his Ph.D. from the University of München, Germany. Following a postdoctoral stay at the Max-Planck-Institut für Kohlenforschung in Mülheim, Germany, he joined the Department of Inorganic Chemistry at the State University in Campinas.

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* R. A. Sheldon. Fax: 01-(31)-15-2781415. E-mail: r.a.sheldon@stm.tudelft.nl. U. Schuchardt. Fax: 01-(55)-19-239-3805. E-mail: ulf@iqm.unicamp.br.

[†] Delft University.

[‡] Universidad Estadual de Campinas.

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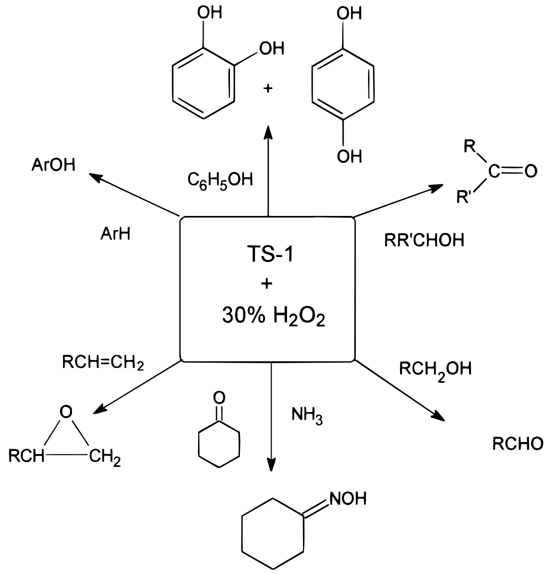


FIGURE 1. Oxidations catalyzed by TS-1.

of TS-1, e.g., the absence of traces of alkali metal ions in the tetrapropylammonium hydroxide template, are critical, its remarkable activity was confirmed.[11] Furthermore small catalyst particles are necessary to avoid diffusion limitations.[12]

It was subsequently shown, using various spectroscopic techniques,[11] that TS-1 contains titanium isomorphously substituted for silicon in the framework of silicalite-1, a hydrophobic molecular sieve possessing a three-dimensional system of intersecting elliptical pores with diameters of 5.3 × 5.5 and 5.1 × 5.5 Å[13] Its remarkable activity in oxidations with aqueous H_2O_2 is due to site isolation of Ti(IV) centers in the hydrophobic pores of silicalite which allows for the simultaneous adsorption of the hydrophobic substrate and the oxidant. This importance of fine-tuning of the hydrophobicity of the catalyst was clearly demonstrated by Klein and Maier[14] in the case of titanium-containing microporous glasses, where the activity increased with the hydrophobicity. The introduction of titanium into the silicalite framework increases its hydrophilicity, but the resulting material is still highly hydrophobic as measured by its hydrophobicity index, HI.[15−17] Thus Weitkamp et al.[16] measured the HI of a range of TS-1 samples and showed that it decreased linearly with titanium content for $n_{\mathrm{Si}}/n_{\mathrm{Ti}} > 40$, as was shown in a qualitative way also by others.[18,19]

Confinement of the active site in a cavity of molecular dimensions means that there is not enough room for the simultaneous presence of substrate and (several) solvent molecules in the active site, thus creating quasi vapor phase conditions conducive to fast reactions. Similar arguments were forwarded by Dewar[20] to explain the high activity of enzymes.

On reflection it occurred to us that TS-1 was perhaps the proverbial tip of an iceberg, i.e., the progenitor of a broad family of novel catalytic materials for use in selective liquid phase oxidations. Indeed, this subsequently proved to be the case, and we coined the generic term redox molecular sieve to describe such materials.[21,22]

Redox Molecular Sieves

Molecular sieves are commonly referred to as zeolites or zeotypes, which are crystalline oxides comprising corner sharing TO_4 tetrahedra (T = Si, Al, P, etc.) and consisting of a regular array of micropores of molecular dimensions (4−13 Å). In zeolites the centers of the TO_4 tetrahedra are occupied by silicon and aluminum atoms. The different valences of Si (tetravalent) and Al (trivalent) produce an overall negative charge for each incorporated aluminum atom. These negative charges can be balanced by protons (leading to Brønsted acids) or other cations. Substitution of the trivalent atoms in the zeolite framework by tetravalent atoms such as silicon or titanium produces (metallo)silicalites with an electrically neutral, hydrophobic framework. Aluminophosphates (AlPO's) possess a neutral, hydrophilic framework (P:Al = 1:1), and substitution of the pentavalent phosphorus by silicon produces silicoaluminophosphates SAPO's with a negatively charged framework. Incorporation of redox metals into molecular sieves (see Figure 2) affords potentially

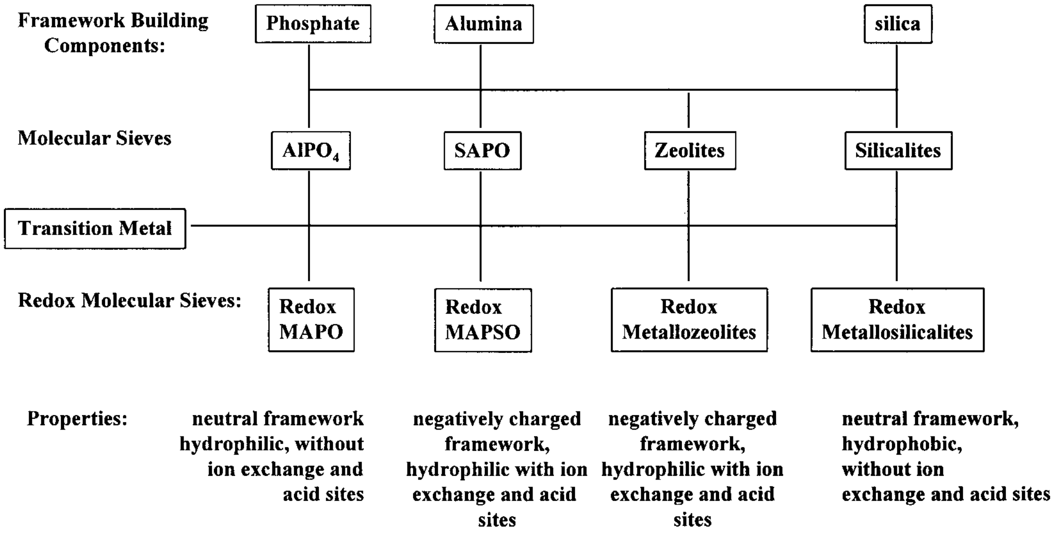


FIGURE 2. Types and properties of redox molecular sieves.

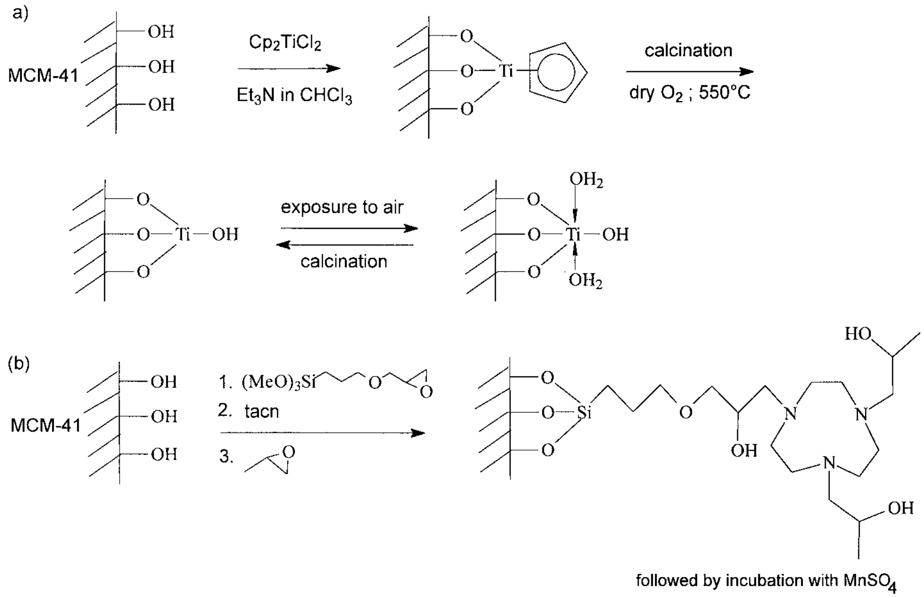


FIGURE 3. Grafting (a) and tethering (b) of metal complexes with molecular sieves.

interesting heterogeneous oxidation catalysts.[23] By a suitable choice of molecular sieve, one is able to influence which molecules have ready access to the active site on the basis of their size and/or hydrophobic/hydrophilic character. Such materials bear a distinct resemblance to redox enzymes in which the protein mantel plays an analogous role. It is perhaps not surprising, therefore, that they are sometimes referred to as “mineral enzymes”.

Synthesis of Redox Molecular Sieves

Molecular sieves are synthesized by so-called hydrothermal synthesis in which a sol−gel is produced from sources of the building blocks (e.g., $Si(OEt)_4$, Al_2O_3, H_3PO_4) and subsequently allowed to crystallize at elevated temperatures (generally 180−200 °C) and autogenous pressure in the presence of a structure directing agent (template), usually an amine or tetraalkylammonium salt. The as-synthesized material is subsequently calcined at ca. 500 °C to destructively remove the template. If a redox metal salt or complex is added during gel formation it can be incorporated into the framework of the molecular sieve. Alternatively, redox molecular sieves can be prepared by postsynthesis modification.[24−26] Framework aluminum atoms can be substituted, for example, by treatment with $TiCl_4$ in the vapor phase.[24] Borosilicates are more amenable to postsynthesis modification than the isomorphous zeolites since boron is readily abstracted from the framework under mild conditions,[27] followed by reoccupation of the formed silanol nests by Ti.[28]

A completely different postsynthesis approach consists of encapsulating a bulky metal−ligand complex, e.g., a metallophthallocyanine, within cages present in certain zeolites.[29−31] These so-called ship-in-a-bottle catalysts are prepared by first introducing the metal into the zeolite, after which the ligand is synthesized, in situ, to give a metal complex which is physically trapped within the zeolite lattice. Alternatively, metal complexes have been applied as templates during zeolite synthesis.[30]

The development of mesoporous molecular sieves such as MCM-41, which are amorphous silicates[32] containing a regular array of hexagonal ordered mesopores, extended the scope to much larger substrates and guest complexes. In this case metal complexes[33,34] can be grafted or tethered (via a spacer ligand) to the internal surface (see Figure 3).

Titanium-Substituted Molecular Sieves

A serious drawback of TS-1 is its restriction to substrate molecules with kinetic diameters[35] $\lesssim 5.5$ Å (see above). For example, 1-hexene is readily epoxidized with aqueous H_2O_2 at 50 °C whereas cyclohexene is essentially unreactive. Molecular graphics indicate that cyclohexene can just fit into the pores of TS-1 but that it is difficult to accommodate the transition state for oxygen transfer from a peroxotitanium(IV) species to the double bond. By the same token, TS-1 does not catalyze epoxidations with the more bulky *tert*-butyl hydroperoxide (TBHP); i.e., TS-1 exhibits complementary catalytic properties to the Ti(IV)/SiO_2 catalyst.

To circumvent this size restriction, many groups have incorporated titanium in larger molecular sieves.[11,23,36] For example, Corma and co-workers[37] synthesized titanium-substituted zeolite beta (pore diameter up to 7.6 Å) and showed that it catalyzed the oxidation of cyclohexene and 1-hexene, with aqueous H_2O_2 in methanol, at roughly the same rate. However, in contrast to reactions with TS-1, the main product was the glycol monomethyl ether, resulting from acid-catalyzed ring opening of the epoxide by the methanol solvent.

We subsequently showed that ring opening could be largely circumvented by neutralizing the Brønsted acid (aluminum) sites by ion exchange with an alkali metal

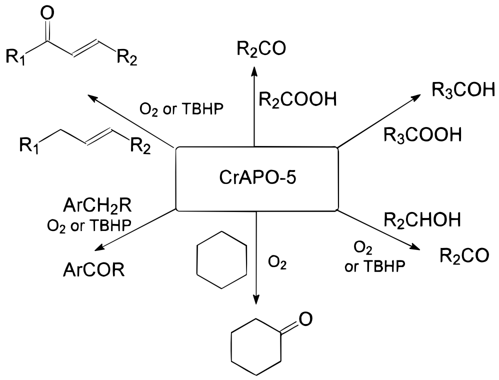


FIGURE 4. Oxidations catalyzed by CrAPO-5.

acetate and recalcination.[38] Similarly, 1-octene underwent selective epoxidation with TBHP in the presence of alkali metal exchanged titanium beta.[39]

Similarly, titanium-substituted MCM-41[40,41] and a titanium-grafted MCM-41 (see Figure 3)[33] were shown to catalyze the epoxidation of bulky olefins, such as pinene and norbornene, with TBHP. In the case of titanium-grafted on MCM-41, the importance of hydrophobicity in the system was demonstrated by the fact that use of a more hydrophobic alkyl hydroperoxide, 2-methyl-1-phenyl-2-propyl hydroperoxide, increased the reaction rate.[42]

Other Redox Metals

Following the success of titanium-substituted molecular sieves, a variety of metals have been incorporated into molecular sieve frameworks and the resulting materials tested as catalysts for liquid-phase oxidations.[23] For example, Sn(IV)[43] and Zr(IV)[44,45] substituted silicalite exhibited similar catalytic properties to TS-1, albeit with lower activities.[46,47] Vanadium-substituted silicalite and aluminophosphates have also been extensively investigated.[11,48,49]

We have carried out detailed investigations of chromium-substituted molecular sieves.[50,51] These were of particular interest because chromium(VI) reagents are widely used as stoichiometric oxidants in organic synthesis[52] or as homogeneous catalysts in the presence of alkyl hydroperoxides as terminal oxidant.[53] Moreover, chromium(VI) typically catalyzes oxidations via an oxometal mechanism, in which chromyl (CrO_2^{2+}) species are the active oxidants. Hence, chromium-substituted molecular sieves are expected to catalyze different oxidative transformations to titanium(IV) which involves a peroxometal mechanism.

Indeed, we found that CrS-1, CrAPO-5, and CrAPO-11 catalyze a variety of oxidations typical of oxometal oxidants, e.g., benzylic and allylic oxidations (Figure 4) using TBHP or O_2 as the terminal oxidant. A plausible mechanism for these transformations involves oxidation of the substrate by $Cr^{VI}{=}O$ followed by reoxidation of the resulting Cr^{IV} by TBHP, or, in the case of reactions with O_2, the hydroperoxide derived from (chromium-catalyzed) autoxidation of these substrates.

One of the first reactions which we studied was the decomposition of cyclohexyl hydroperoxide (CHHP) to a mixture of cyclohexanone and water. Both CrAPO-5 and CrS-1 were efficient catalysts for this reaction,[54] which is of importance in the manufacture of cyclohexanone by autoxidation of cyclohexane. CrAPO-5 gave cyclohexanone in 86% selectivity, together with 13% cyclohexanol, at 87% conversion in 5 h at 70 °C in cyclohexane. A plausible mechanism to explain the high selectivity to cyclohexanone is shown in Figure 5.

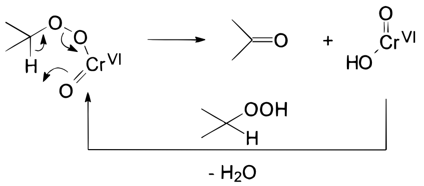


FIGURE 5. Chromium-catalyzed decomposition of alkyl hydroperoxides.

Cyclohexanol presumably results from cyclohexyloxy radicals formed in competing one-electron redox reactions of chromium with the hydroperoxide.[55] Thus, tertiary hydroperoxides, which cannot undergo the heterolytic decomposition shown in Figure 5, afforded the corresponding alcohols.

To confirm that the reaction takes place in the micropores of CrAPO-5, we performed experiments with the bulky tertiary hydroperoxide, triphenylmethyl hydroperoxide (TPMHP) which is too large to access the micropores.[54] We found that homogeneous $Cr(acac)_3$ and supported $CrO_2Cl_2/SiO_2{-}Al_2O_3$ were effective catalysts (75 and 72% decomposition in 2 h at 70 °C in dichloroethane). In contrast, CrAPO-5 gave only 1% decomposition of TPMHP which led us to conclude that the reaction occurred exclusively in the micropores and that no leaching of the chromium occurred. This subsequently proved to be a misinterpretation of the results (see below).

Philosophers' Stones or Trojan Horses? The Question of Leaching

Elsewhere we have referred to zeolites, and by implication redox molecular sieves, as the philosopher's stone of modern chemistry.[23] There is no doubt that they exhibit interesting activities and selectivities, but stability is also a *sine qua non* for industrial utility. A heterogeneous catalyst which simply releases its active species into solution—like Greek warriors from the Trojan horse—is likely to have limited practical utility. Hence, it is surprising that most papers pay scant attention to this aspect. In some cases[56] no recycling experiments are reported. Moreover, as we shall now show, even the conventional recycling of catalysts several times without significant loss of activity is by no means sufficient proof of heterogeneity.

One can envisage three different scenarios in the context of leaching:

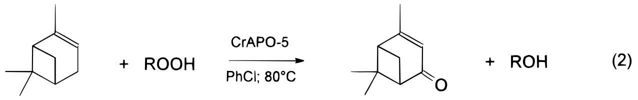
A. The metal leaches but is not an active homogeneous catalyst.

B. The metal leaches to form an active homogeneous catalyst.

C. The metal does not leach and the observed catalysis is truly heterogeneous in nature.

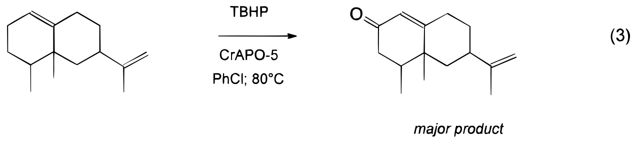
Since titanium(IV) is a poor homogeneous epoxidation catalyst,[57] the remarkable activity observed with TS-1, and to a lesser extent with other titanium-substituted molecular sieves, is clearly heterogeneous in nature. Hence, titanium falls into category A or C. Not being privy to the detailed information, we can only assume that extensive testing of TS-1 (and Ti(IV)/SiO_2) has demonstrated its stability toward leaching under operating conditions, i.e., that it falls into category C. We note, however, that this does not rule out a slow but practically insignificant leaching. Judgment on the many other titanium-substituted molecular sieves regarding whether they are category A or C has to be suspended in lieu of appropriate longevity tests. The same probably applies to analogous Zr(IV)-, Sn(IV)-, and Fe(III)-substituted molecular sieves.

Category B is the difficult one to assess; i.e., when a particular metal ion exhibits (high) catalytic activity in solution, what can be construed as rigorous proof of heterogeneity? A particularly poignant example is provided by chromium. Recently we returned to the question of leaching in a study of the allylic oxidation of α-pinene to verbenone with TBHP in the presence of chromium-substituted molecular sieves (reaction 2).[58]



To test for leaching we filtered the catalyst, e.g., CrAPO-5, after 30 min (ca. 25% pinene conversion) and allowed the filtrate to react further. Filtration was performed at the reaction temperature (80 °C) in order to avoid readsorption of solubilized chromium on cooling (this later proved to be important but for a different reason). Indeed, we found that after hot filtration the mother liquor (filtrate) reacted further at roughly the same rate as that observed when the catalyst was not filtered. In contrast, if the mixture was allowed to cool to ambient temperature prior to catalyst filtration, the procedure generally followed when testing for leaching, little further reaction was observed. On the basis of these results we concluded that chromium is leached from CrAPO-5 and that the observed catalysis is (predominantly) homogeneous in nature.

We subsequently compared the allylic oxidation of α-pinene with a bulky hydroperoxide: triphenylmethyl hydroperoxide (TPMHP) (reaction 2, R = Ph_3C) and a bulky olefin (valencene) with TBHP (reaction 3).



If the reaction took place in the micropores, one would expect to observe no reaction in both cases, since both TPMHP and valencene are too bulky to access the micropores of CrAPO-5. However, we observed facile conversion of valencene with TBHP but virtually no conversion of pinene with TPMHP. The most plausible explanation for these observations is that soluble chromium is responsible for the observed catalysis and that *it is leached by reaction with the hydroperoxide.* Support for this interpretation was obtained in experiments where CrAPO-5 was pretreated with TBHP, the mixture filtered, and pinene added to the mother liquor, which resulted in facile oxidation. In contrast, when the catalyst was pretreated with pinene and filtered, no reaction was observed when TBHP was added to the filtrate. Based on these results, the earlier observations of no decomposition of TPHMP in the presence of CrAPO-5 (see above) could be reinterpreted to mean exactly the opposite of our initial interpretation.

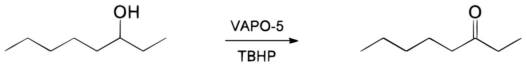
Having established that soluble chromium is responsible for the observed catalysis, the next question was: how much chromium is leached? By using a sensitive colorimetric test for chromium(VI), we were able to show that 0.3% of the 0.88% chromium (i.e., 0.0026% of the catalyst's weight) present in CrAPO-5 was leached during reaction, corresponding to a substrate/catalyst (S/C) ratio of 17 000 or 1−2 ppm Cr in the filtrate.[59] Analogous experiments with CrAPO-11 and samples of CrS-1 prepared by different procedures showed that the extent of chromium leaching varied between 0.3 and 34%, increasing markedly with decreasing crystallite size of the catalysts.

We furthermore showed that if the filtrate was allowed to cool to ambient temperature, the solubilized chromium was present only in the trivalent state. We subsequently carried out oxidations with soluble chromium(VI), $(py)_2Cr_2O_7$, and chromium(III), $Cr(acac)_3$, catalysts at various S/C ratios. When chromium was added as Cr(VI), the reaction always started instantaneously. This was also the case with Cr(III) at low S/C ratios (≤10), but induction periods of 5, 90, and 300 min were observed for S/C = 100, 1000, and 10.000, respectively. Combination of these results with the observation (see above) that on cooling the filtrate from the reaction temperature to ambient results in reduction of Cr(VI) to Cr(III) provides an explanation for the observed difference in the hot and cold filtration experiments. Apparently on cooling the reaction mixture, Cr(VI) continues to oxidize substrate but is not reoxidized by TBHP and, after filtration of the catalyst, only Cr(III) is present in the filtrate, at very low concentrations (S/C = 17 000 for 0.3% Cr). This results in a very long induction period which would lead to the erroneous conclusion that no leaching had occurred.

We subsequently compared the activity of a filtrate obtained from TBHP treatment of CrAPO-5, followed by hot filtration, with that of a solution containing $(py)_2Cr_2O_7$ in an amount corresponding to S/C = 17 000. The reaction profile was almost identical (the soluble Cr actually showed a slightly higher rate) which leads to the inevitable conclusion that *all of the observed activity* can be attributed to homogeneous Cr(VI) leached from the CrAPO-5 by reaction with TBHP.

We also call into question the common practice of comparing activities of putative heterogeneous catalysts with their homogeneous counterparts at (much) higher concentrations. When a similar level of activity is observed with the homogeneous catalyst only at significantly higher concentrations than could have been (were) leached, this is proffered as evidence in support of the catalysis being (predominantly) heterogeneous. However, this assumes a linear relationship between catalyst activity and catalyst concentration. In a comparison of a CrS-1 sample and CrAPO-5, which gave 34 and 0.3% leaching, respectively, we observed a much smaller difference in rate (in the oxidation of α-pinene with TBHP) than the expected factor of 100. Subsequent measurements of turnover numbers at 30% pinene conversion, with homogeneous chromium(VI) at S/C ratios varying from 10^2 to 10^5, revealed a nonlinear relationship between rate and catalyst concentration; the chromium was relatively more active at lower concentrations. This suggests that active monomeric chromium species are in equilibrium with less active dimers or oligomers in solution.

On the basis of our extensive studies, we conclude that chromium-substituted molecular sieves clearly belong to category B. What about other redox metal ions? van Hooff and co-workers[60] carried out a detailed investigation of VAPO-5 catalyzed oxidation of 3-octanol and epoxidation of 3-phenyl-2-propenol with TBHP (reactions 4 and 5). By filtering the reaction mixture at the reaction temperature and allowing the filtrate to react further, they were able to show that leached vanadium accounted for the observed catalysis.



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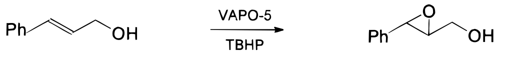


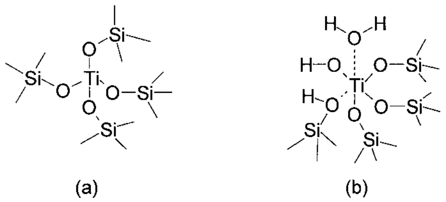
(5)

Similarly, the reported catalysis of oxidations with TBHP in the presence of vanadium silicalites, VS-1,[11] or VS-2[48] is almost certainly homogeneous in nature. A similar observation was made by Sayari and co-workers[61] for V−HMS molecular sieves during oxidation reactions with dilute H_2O_2. Indeed, we observed leaching of metal during oxidation reactions in all vanadium- and chromium-substituted molecular sieves that we have studied.[62−64] For example, we synthesized V− and Cr−MCM-41[64] and showed that, after pretreatment with a solution of the oxidant (H_2O_2), the filtrate had a similar activity to that observed without filtration. In contrast, with Ti−MCM-41 the filtrate was not active and no metal loss was detected.

Similarly, we have shown, by performing appropriate filtration experiments, that catalysis of epoxidations (with TBHP) by zeolite Y encapsulated vanadium−Schiff's base complexes is due to leached vanadium.[65]

Are Titanium Silicalites Unique?

Notwithstanding the plethora of studies devoted to redox molecular sieves,[23] the remarkable activity and stability of TS-1 have yet to be emulated. What is unique about TS-1? First, isomorphous substitution of titanium(IV) in tetrahedral framework positions appears to be essential. Perego et al.[66] reported that a maximum of 2.4 Ti atoms per unit cell (Si/Ti = 39) can be incorporated in the silicalite framework. Although other authors have claimed the preparation of TS-1 with higher Ti content, there are doubts regarding whether all of the Ti is in framework positions.[11]



(a) (b)

FIGURE 6. Ti in tetrahedral (a) and octahedral (site-defect) (b) positions of silicalite.

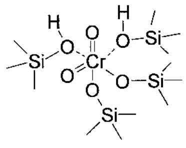


FIGURE 7. Cr attached to defect sites of silicalites.

Tetrahedral coordination of Ti(IV) in framework positions can be confirmed using, e.g., EXAFS, UV/vis spectroscopy, and other methods.[67,68] The presence of the 960-cm^{-1} peak in vibrational spectra of Ti sieves is not a good characteristic for isomorphous substitution of titanium; Smirnov[69] has calculated that this band can be assigned to a local Si−O vibration. We investigated TS-1 and Ti-beta samples with Si/Ti ratios < 40 and observed two different Ti species using UV/vis. One, characterized by a band at 212 nm,[70] could be assigned to tetrahedral Ti(IV) (Figure 6a) while the other, characterized by a band at 250 nm, was attributed to octahedral Ti(IV) in defect sites (Figure 6b) or to amorphous oligomeric Ti−O−Ti species.[70] Samples of TS-1 exhibiting the 250 nm band leached titanium when used as catalyst for cyclohexane oxidation with H_2O_2, probably due to complexation of titanium by carboxylic acids formed by overoxidation.

With chromium and vanadium the situation is more complicated. In the as-synthesized materials they are present as Cr(III) and V(IV), respectively. Both Cr(III) and V(IV) can isomorphously substitute for Si(IV) or Al(III) in the silicalite, AlPO or SAPO[71] framework, respectively. However, on calcination the chromium and vanadium are oxidized to Cr(VI) and V(V), respectively. Since chromium(VI) is presumed to always contain two extraframework Cr=O bonds, it can only be anchored to the framework at defect sites (see Figure 7). In this way chromium(VI) is attached to the surface by only two M−O bonds, and it is therefore perhaps not surprising that leaching is facile.

Thus, in a study of titanium(IV) silsesquioxanes, Abbenhuis et al.[57a] showed that at least three Ti−O−Si bonds are necessary for stability. This situation is extant in TS-1 where the mechanism of oxidation most likely involves conversion of a Ti−O−Si or Ti−O−H group to Ti−OOR (R = H, alkyl) which is still bonded to three silanoxy groups (Figure 8).[72] Similarly V^V=O ions appear to be

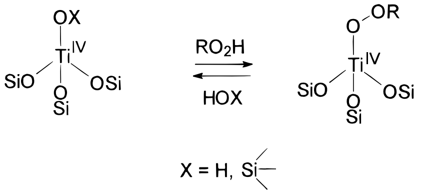


FIGURE 8. Activation of isomorphously substituted titanium.

attached to, e.g., the silicalite framework at defect sites[11] and is, hence, susceptible to leaching.

The synthesis of MoS-1 has recently been described.[56] By analogy with chromium this would be expected to consist of $Mo^{VI}O_2$ species attached to framework defect sites. The authors reported that the material was an active catalyst for the chemoselective oxidation of thioethers to the corresponding sulfoxides. However, no experiments were performed to establish the homogeneous or heterogeneous nature of the observed catalysis. Moreover, we note that oxidations of thioethers with H_2O_2 proceed readily under the prescribed conditions even in the complete absence of a catalyst.

Isomorphous substitution of tetrahedral Mn(II),[64] Co(II),[63,64,73] and Fe(III)[64,74] into various molecular sieves has been reported. After calcination manganese and iron are present in the trivalent state. The oxidation state of cobalt in CoAPO after calcination is still a matter of debate, however.[75−79] Evidence has been presented in favor of both Co(III)[75−77] and Co(II).[78,79] It is also worth noting that tetrahedral Co(III) is energetically highly unfavorable (all known Co(III) complexes are octahedral). Although Fe(III) is not further oxidized on calcination, we observed for Fe−ZSM-12[62] and Fe−MCM-41[64] that the crystals change their color from white to brown, indicating the formation of extraframework iron oxide. When the template molecules were removed by extraction, rather than calcination, e.g., with MnAPSO-37 and FeAPSO-37,[74] we observed no extraframework species and no metal leaching. Interestingly, however, the resulting materials were also completely inactive oxidation catalysts.

Conclusions and Prospects

Redox molecular sieves and grafted mesoporous materials, particularly titanium-substituted materials, undoubtedly have enormous catalytic potential in organic synthesis.[23] They catalyze a variety of synthetically useful oxidative transformations with environmentally and economically attractive oxidants. Their pore sizes and hydrophobic or hydrophilic properties endow them with special capabilities compared to analogous homogeneous catalysts. Moreover, they are readily recovered by simple filtration.

However, the initial euphoria based on the notion of a broad family of tailor-made heterogeneous catalysts for liquid-phase oxidations has been tempered by the realization that many of these materials are not stable toward leaching under oxidizing conditions in the liquid phase.

What have we learned from our studies? In the first place we have learned that the conventional practice of recycling a heterogeneous catalyst without observing any significant loss of activity is by no means proof of heterogeneity. CrAPO-5 could presumably have been recycled 10 or even a 100 times (corresponding to 3 or 30% leaching of available chromium) without any loss of activity (the Trojan horse could still keep releasing its Greek warriors). Rigorous proof of heterogeneity can be obtained only *by filtering the catalysts at the reaction temperature before completion of the reaction and testing the filtrate for activity*. Moreover, we emphasize that proof of heterogeneous catalysis is not necessarily proof that no leaching occurs. We venture to suggest that manuscripts claiming heterogeneous catalysis in the liquid phase should not be accepted for publication in the absence of rigorous proof of heterogeneity. This applies not only to redox molecular sieves, including encapsulated, grafted, and tethered redox metal complexes, but to all solid catalysts, e.g., the recently reported titanium- and vanadium-containing xerogels[80] and redox metal ions attached to organic polymers.[81] Only when the problem of catalyst stability has been solved will the potential of heterogeneous catalysts for liquid-phase oxidations be realized.

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