Polymer-supported metal complex oxidation catalysts

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<u>Abstract</u> - Recent developments involving polymer-supported metal complexes
as catalysts in oxidation reactions, using dioxygen, hydrogen peroxide,
alkyl hydroperoxides, hypochlorite anion and iodosobenzene as oxidants are
reviewed.   Supported metallo-porphyrins are described for the reversible
binding of dioxygen, and in catalysis, along with the structurally closely
related metallo-phthalocyanines.   The important area of di-alkyl phenol
oxidative polymerization catalysed by polymer-supported copper (II)
complexes is reviewed along with more recent developments of supported
palladium (II) Wacker-type catalysts.   Novel Nafion supported rhodium
(III), chromium (III) and cerium (IV) complexes are described and their
potential for application in hostile chemical environments emphasised.
Alkene epoxidations using t-butyl hydroperoxide catalysed by polymer-
supported vanadium (V) and molybdenum (VI) species are dealt with in some
detail because of the industrial potential of these systems, and the
recent advances reported in the literature.   Finally polymer-supported
arsenic, selenium and tellurium based catalysts are described.   Though
not strictly metal complexes, these are very closely related to metal
complex catalysed hydrogen peroxide oxidations.

INTRODUCTION

The replacement of coal by crude oil as the feedstock for the petrochemical industry over
the last few decades has led to major changes in the types and importance of particular
industrial processes.   In simplistic terms the refining and cracking of oil yields alkenes,
particularly terminal alkenes, and the strategy for producing a wide range of crucial
organic chemical species is based substantially on the exploitation of such alkenes.   These
are converted by a whole series of catalytic reactions to the basic chemicals feedstock that
we often take for granted.   The most important transformations are hydrogenation to yield
alkanes, hydroformylation to yield aldehydes (and then alcohols), isomerization to yield
alternative alkenes, condensation to yield dimers, oligomers and polymers, hydrosilylation
to yield alkyl silanes, and finally oxidations to yield vinyl esters, epoxides, alcohols and
diols, aldehydes and ketones, and carboxylic acids.   Many of the catalytic systems used in
these transformations, or attractive (homogeneous) alternatives which might replace them,
have been supported on polymer matrices.   Intriguingly, however, a detailed review compiled
as late as 1977 (ref.1) described only about ten examples of polymer-supported metal complex
<u>oxidation catalyst</u> systems in the 364 references sited.   Since then an additional ten or so
examples have appeared each year in Chemical Abstracts, while examples of polymer-supported
hydrogenation, hydroformylation, isomerization, oligomerization and hydrosilylation
catalysts have run into thousands.

The relative lack of interest in the investigation and exploitation of polymer-supported
metal complex oxidation catalysts has arisen for two main reasons.   Firstly the science and
technology of selective homogeneous transition metal complex oxidation catalysts is itself
still in its infancy.   In many instances effective catalytic systems still require
discovery.   Reductive and isomerization catalysts are much further developed, and are
understood in some detail.   In contrast even some of the most selective and most successful
of known oxidation catalysts function by mechanisms which are still not clear.   Secondly
since polymers themselves are organic molecules there has always been an underlying
assumption that in general these would not yield long-lived practical supports.   There has
been a tacit 'understanding' that they themselves would be highly susceptible to the
oxidation reactions being carried out.   As we shall see this is proving not to be the case.
Indeed the area of polymer-supported metal complex oxidation catalysts remains an exciting
one, with a wealth of potential as yet untapped.

OXYGEN SOURCES

The most important oxygen sources at the moment are dioxygen, O_2, hydrogen peroxide, H_2O_2, alkyl hydroperoxides, ROOH (e.g. t-butyl hydroperoxide, tBHP, and cumene hydroperoxide, CHP), hypochlorite anion, ClO^-, and iodosobenzene, PhIO. Dioxygen is very attractive because of its low cost and availability from liquid air. It is also unreactive to most organic substrates without the presence of a 'catalyst' (which includes radical sources e.g. flames, sparks). Hydrogen peroxide is also cheap and is available from autoxidation of 2-ethylanthraquinol, H_2/palladium being used to recycle the quinone formed. It is, however, subject to facile and potentially violent decomposition in the presence of some metal ions, and can be highly reactive towards some organic substrates even in the absence of catalysts. Alkyl hydroperoxides are also relatively cheap and are available in large quantities via the autoxidation of hydrocarbons containing a tertiary carbon centre. They are stable species and do not oxidize organic substrates in the absence of a catalyst (see later). Hypochlorites are cheap and readily available as a by-product of chlorine and caustic alkali production. They can be, however, powerful oxidants even in the absence of catalysts. Finally iodosobenzene, this is expensive, although the costly iodo fragment might be recyclable. It is available from iodobenzene or by direct aromatic substitution using $(IO)_2 SO_4/H_2SO_4$. In addition it can be an oxidant in its own right without activation by a metal catalyst.

POLYMER-SUPPORTED METAL COMPLEX CATALYSTS

Historically the area has been approached by three scientific groups with essentially three different objectives in mind. The first is to produce polymer-supported systems which will bind dioxygen reversibly. Such systems might act simply as oxygen carriers or they might be directed specifically towards artificial life-support systems (ref. 2,3). The second is to produce polymeric mono-oxygenase enzyme models, which can function as mild and selective oxidation catalysts without the surrounding globular protein of the natural enzymes (ref. 4,5). The third is to develop polymer-supported analogues of existing metal complex based industrial oxidation catalysts, and indeed other homogeneous catalytic systems which are currently being researched in industry and academia (ref. 6,7). In reality of course these objectives overlap and the chemistry involved is often identical.

REVERSIBLE BINDING OF DIOXYGEN

Biological supply of dioxygen depends on the rapidly reversible complexation of molecular oxygen with hemoglobin and myoglobin. The dioxygen binding site is the Fe(II)-protoporphyrin IX (ferroheme) complex with the imidazole group of the globin protein, and the ferroheme complex is enclosed within the hydrophobic domain of globin. In principle therefore it might be possible to support metallo-porphyrins on a synthetic hydrophobic polymer and achieve similar reversible dioxygen binding. This area has been well researched (ref. 2,3). Polymer-supported porphyrins (1) have been achieved i) by using polymers containing N donor ligands (e.g. simple amino groups, lysine, histidine, imidazole and pyridine) capable of binding to the metallo-porphyrin in an axial position (1a), ii) by covalent attachment of the porphyrin ring, exploiting the vinyl group (1b) or the carboxylic acid group (1c); and iii) by aromatic substituents introduced at the bridging carbon positions on the porphyrin ring (1d) i.e. via tetraphenyl porphyrin derivatives. Both Fe and Co based systems have received much attention.
In hemoglobin dioxygen is bound axially opposite the axial imidazole group (which is a pre-requisite) and can either be removed reversibly, or move on into biological oxidation cycles (equation 1). With bare ferroheme, however, the oxygenated complex reacts rapidly with

$$(Im)Fe^{II}(P) + O_2 \rightleftharpoons (Im)(P)Fe-O_2 \longrightarrow (Im)Fe^{III}(P) + O_2^- \qquad (1)$$
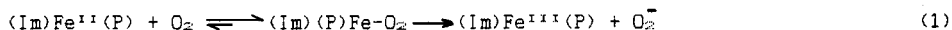
(P=porphyrin, Im=imidazole)

another ferroheme to produce a binuclear dioxygen-bridged complex. The latter is readily irreversibly oxidized to yield an inactive oxo-bridged binuclear complex (equation 2)

$$(Im)(P)Fe-O_2 \xrightarrow{\ (Im)Fe(P)\ } (Im)(P)Fe-O-O-Fe(P)(Im)$$

$$(Im)(P)Fe-O-Fe(P)(Im) \qquad (2)$$
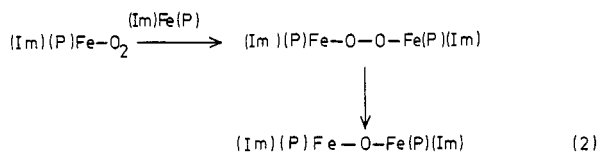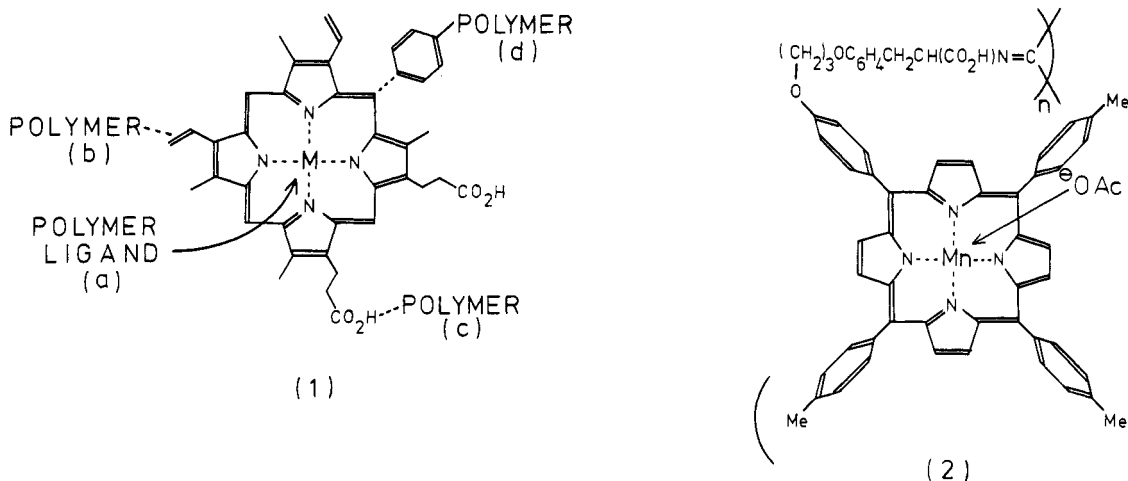
In addition to this, irreversible reactions involving the porphyrin ring can also occur. Supporting the porphyrin ring on a synthetic macromolecule can therefore provide the site isolation to inhibit binuclear complex formation, and simultaneously provide the required hydrophobic microenvironment.   Indeed oxygen reversibility has been maintained for up to 24 hours with some Co based systems, though clearly this is still far short of the hemoglobin performance.

Polymeric cobalt (II) Schiff-base complexes will also bind dioxygen reversibly (ref. 8), as indeed will related vanadium (II) and manganese (II) species (ref. 9).   In the former case the Schiff-base was attached in a pendant fashion to the polymer chain, while in the latter the Schiff-base formed an integral part of the main backbone.   The cobalt-containing species also proved to be an active catalyst for dialkylphenol autoxidation, while the manganese derivative catalysed cumene reaction with dioxygen to form a mixture of 2-phenyl-2-propanol and acetophenone.   The proportion of the latter increased with increasing temperature.

OXIDATIONS CATALYSED BY POLYMER-SUPPORTED METALLO-PORPHYRIN COMPLEXES

In principle dioxygen bound to a metallo-porphyrin might be exploitable in useful oxidation reactions.   Rollman (ref. 10) produced a bifunctional polymeric catalyst which contained both Co(II) tetraphenylporphyrin and a base to act as a proton acceptor.   This system readily catalysed the oxidation of thiols by molecular oxygen (equation 3).

$$2RSH + O_2 \longrightarrow R\text{-}S\text{-}S\text{-}R + H_2O \qquad\qquad (3)$$

However, the catalyst underwent rapid irreversible aging.   When similar supported species were exposed to a refinery hydrocarbon stream containing only 180 ppm of mercaptans rapid deactivation of the catalyst occurred, probably via free radical oxidation of the porphyrin rings themselves (ref. 11).

More recently Nolte and his coworkers have been trying to model mono-oxygenase enzymes using polymer-supported manganese (III) tetraphenylporphyrins (ref. 5,12).   Cytochrome P-450 models have been reported that epoxidize alkenes under relatively mild conditions (ref. 13). These utilize a synthetic metallo (III) porphyrin and an oxygen source such as hypochlorite or iodosylbenzene, or alternatively a combination of molecular oxygen and a reducing agent. The active species is probably an oxometallo (V) porphyrin and again dimerization to inactive oxo-bridged binuclear metallo (IV) porphyrins must be inhibited to achieve good turnover.   Nolte (ref. 5) has attached the manganese (III) tetraphenylporphyrin acetate (2) to a poly(isocyanide) $\geq$C=N-CH(CO$_2$H)CH$_2$C$_6$H$_4$OH)$_n$, via formation of a phenyl ether linkage. The porphyrin content of the polymeric catalyst was 1.5-4 weight %.   Cyclohexene was epoxidized using sodium hypochlorite as the mono-oxygen source in a methylene chloride/aqueous two phase system at 25°C with yields up to 80%.   Free N donor ligands such as pyridine enhanced the catalytic activity considerably, though imidazole completely blocked the epoxidation route.   In general the site-isolated polymeric catalyst showed higher activity than the free porphyrin analogue, presumably because of deactivation of the latter by dimerization.

The same group have immobilised a surface active manganese (III) tetraphenylporphyrin in a polymerized vesicle bilayer (ref. 12) to produce a microreactor.   The interior of the polyvesicle contained colloidal platinum.   The membrane contained an electron carrier, methylene blue, and the porphyrin catalyst with an axial ligand, N-methylimidazole.   The

external solution contained the alkene, 2,5-dihydrofuran or styrene. Both gaseous hydrogen and oxygen were supplied to the reactor. The furan substrate was converted into a mixture of 3,4-epoxy tetrahydrofuran and the ring-opened compounds <u>trans</u>-3,4-dihydroxytetrahydrofuran, while styrene yielded 1,2-dihydroxy-1-phenyl ethane only. The yield of oxygenated products after 24 hour at 25°C corresponded to catalyst turnover numbers of 30-200.

POLYMER-SUPPORTED PHTHALOCYANINE-BASED CATALYSTS

Phthalocyanines were develolped originally as pigments and indeed are still widely used as colourants. However, they are structurally closely related to the porphyrins, and indeed have the advantage that they are generally more stable. In the phthalocyanines (3) the bridging atom is nitrogen in place of carbon in the porphyrins, and the pyrrole residues displayed in a square planar symmetry are replaced by benzopyrrole moieties.
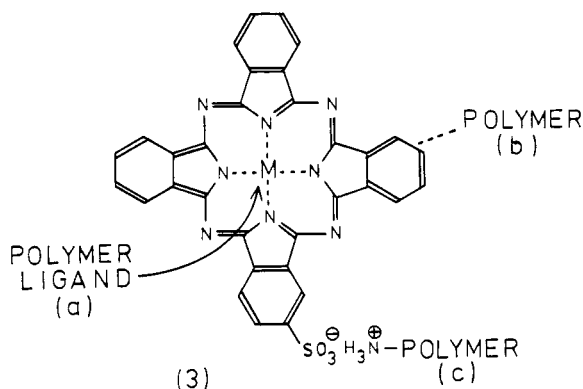
As with the porphyrins, metallo-phthalocyanine can be attached to a polymer support via an axial ligand (3a) or via a substituent on a phenyl group (3b) (ref. 3). Very commonly cobalt (II) phthalocyanine tetrasodium sulphonate has been bound by ionic forces to poly(vinylamine) (3c) (ref. 14-16). Again there is a great tendency for these complexes to dimerize, particularly in the presence of OH⁻ (ref. 17), and in this form, they are unable to bind and activate molecular oxygen. Site-isolation on a polymer inhibits this dimerization. In this form cobalt (II) phthalocyanines have proved very useful for catalysing the autoxidation of thiols (refs. 14-16). These reactions require the presence of a base, and free amino groups on the polymer backbone serve admirably in this respect, and no additional base is required. Hydrogen peroxide is generated as a co-product of thiol oxidation and its subsequent involvement in oxidation has been characterised (ref. 14). Scheme 1 summarises the reactions believed to be involved. Catalyst deactivation

Scheme 1
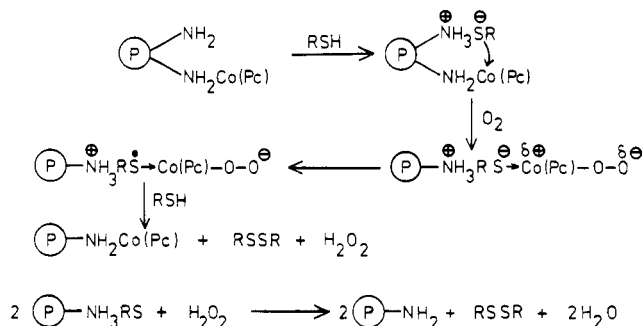
remains a problem (ref. 14) but the systems remain of industrial interest in terms of de-sulphurising hydrocarbon streams.

Very closely related to this is the autoxidation of aqueous thiosalt solutions. The milling and flotation of sulphide ores invariably generates aqueous waste streams containing partially oxidized sulphur oxanions (thiosulphate, tri- and tetrathionate). Poly (4-vinylpyridine) copper (II) complexes (ref. 18), and polythiosemicarbazide copper (II) complexes (ref. 19) have been examined as cheap autoxidation catalysts in an attempt to solve this problem, and these show some promise.

Polymer-supported metallo-phthalocyanines have also been reported to catalyse the epoxidation of cyclohexene using dioxygen as the oxidant (ref. 20). In this case nickel, vanadium, cobalt, iron and manganese complexes were attached to polystyrene resin beads (8 and 20% divinylbenzene) either by direct sulphonylation or via sulphonamide linkages. In general reactions were slow and only at elevated temperatures (70-80°C) were conversions significant. In addition a complex mixture of oxidation products was obtained. Analysis of the supported catalyst showed that a very large proportion of the metallo-phthalocyanine was concentrated near the external surface of beads, possibly in the form of aggregates.


PHENOL OXIDATIONS

The oxidation of thiols described above is just one example of a substrate with a relatively labile hydrogen atom. A generalised reaction for the oxidation of such species by dioxygen, catalysed by a polymer-supported metal complex is shown in equation 4. Ascorbic

$$2AH_2 + O_2 \xrightarrow{\text{(P)-metal complex}} 2A + 2H_2O \qquad (4)$$

acid and hydroquinone are readily autoxidized in this way (ref. 21).

Perhaps the most important and well researched example is the oxidative polymerization of 2,6-dimethyl phenol (Equation 5a). At slightly elevated temperatures copper (II)
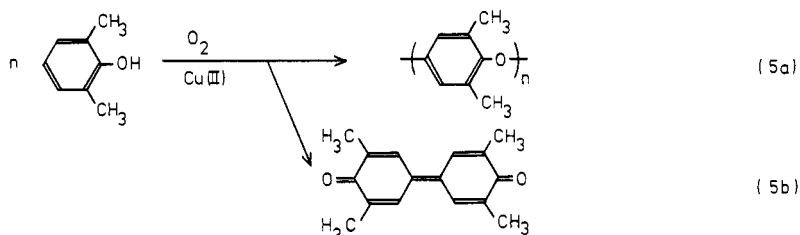
complexes with 1,2-diaminoethanes are the best catalysts for the production of high molecular weight poly-2,6-dimethyl-1,4-phenylene oxide (PPO) (ref. 22,23). This is an important industrial process and PPO is a very useful engineering plastic. The polymer is formed by C-O coupling of phenoxy radicals (Scheme 2), but C-C coupling is also possible yielding a substituted diphenoquinone (equation 5b and Scheme 2). Manipulation of the catalyst and conditions can alter the ratio of products. Below pH7 the diphenoquinone is favoured, whereas at pH8-10 PPO is formed preferentially. In the case of 2,6-di-t-butylphenol the corresponding quinone can be the sole product (ref. 24).

Scheme 2
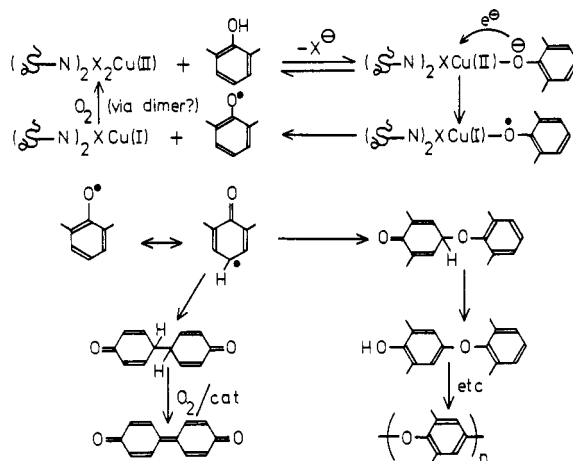
The production of water as a co-product reduces the lifetime of the Cu(II) catalyst, and it is well known that the immobilisation of amine Cu(II) complexes on hydrophobic polymers provides some microenvironmental protection (ref. 2). In addition polymeric catalysts show enhancement of the re-oxidation rate (Scheme 2), again due to the non-polar microenvironment. A considerable amount of careful and detailed work has been carried out by Tsuchida and his group (ref. 2), and more recently by Challa and his coworkers (ref. 24-29). Polyamines such as 4-vinyl pyridine copolymers (ref. 2,26) and imidazole containing

copolymers (ref. 27) are useful supports for Cu(II).   More recently copolymers carrying 4-aminopyridine groups have formed the basis of more active catalysts (ref. 28,29).   The details of the mechanisms(s) of catalysis are complex and indeed may vary from one polymer catalyst to another.   In some cases binuclear copper (II) species seem to be the active species (ref. 25), whereas in others, mono-nuclear analogues appear to the active moiety (ref. 28,29).   The reduced mono-nuclear Cu(I) complex is re-oxidized by dioxygen to re-form the catalyst, but this appears to require a pre-dimerization (ref. 28,29) for re-oxidation to occur rapidly.   A representative reaction sequence is shown in Scheme 2.

Soluble linear polymer ligands provide the basis for the best catalysts, whereas insoluble resins lead to diffusional problems.   Challa and his coworkers (ref. 26) have tried to overcome this problem by grafting a linear copolymer of styrene and 4-vinylpyridine onto the surface of non-porous silica spheres 12-40nm in diameter, in order to produce a 'heterogeneous' but readily accessible complex catalyst.   Use of this composite in a stirred flow reactor was demonstrated.

Recently oligomeric species with pendant urea and thiourea groups, $+CH_2CH_2N(CXNHPh)+_8$ have been used to complex copper (II).   These provided fast reaction rates and excellent coupling selectivities in the case of 2,6-dimethylphenol (ref. 30).   Telomers of 4-vinylpyridine with amphiphilic properties also form copper (II) complexes readily.   The hydrophobic environment of micelle-like structures formed by these also seem to be very favourable for catalysing the oxidative coupling of phenols (ref. 31).
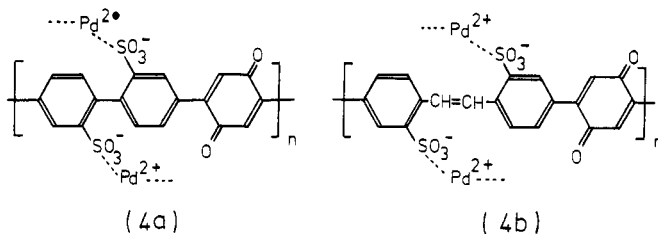
In the case of 4-methylcatechol as the substrate, poly(styrene-co-4-vinylpyridine) copper II complexes catalysed oxidative cleavage to yield the monomethyl ester of cis, cis-muconic acid in about 80% yield at room temperature (ref. 32) (Equation 6).   o-Phenylene diamine was similarly cleaved to yield cis, cis-mucononitrile.

(6)
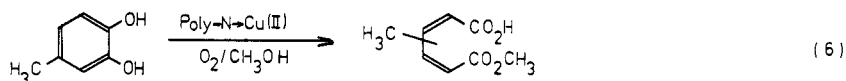
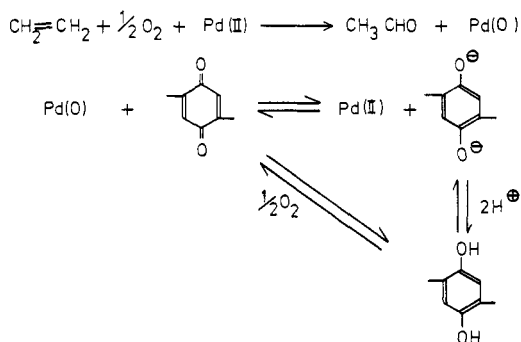## POLYMER-SUPPORTED PALLADIUM (II) BASED CATALYSTS

Palladium complexes form the basis of many hydrocarbon oxidation catalysts (ref. 33,34).   One of the most important industrial processes is the Wacker synthesis of acetaldehyde from ethylene using dioxygen and a palladium (II) catalyst.   Very closely related is the synthesis of vinyl acetate from ethylene and acetic acid using dioxygen in the presence of Pd(OAc)$_2$ (ref. 35).   Indeed PdCl$_2$ has been supported on a styrene-divinylbenzene copolymer resin containing $-CH_2N(CH_3)_2$ groups (ref. 36).   This catalyst is reported to yield vinyl acetate along with acetaldehyde and ethylene oxide, from a feed of ethylene, dioxygen and acetic acid.   Furthermore treatment of the polymeric complex with SnCl$_2$ produced a bimetallic species with higher selectivity and catalytic activity.

More recently an organic quinone polymer containing sulphonic acid groups has been used to support palladium (II), yielding a catalyst effective for the conversion of ethylene to acetaldehyde (ref. 37).   The polymer supports were prepared by coupling of bis-diazonium salts of diaryl disulphonic acids with quinone.   Ion exchange of the acidic protons firstly using Na , and then Pd(NH$_3$)$_4$$^{2+}$, followed by removal of ammonia under vacuum at 150°C, yielded the supported catalysts (4a,b).   In each case a crosslinked insoluble analogue
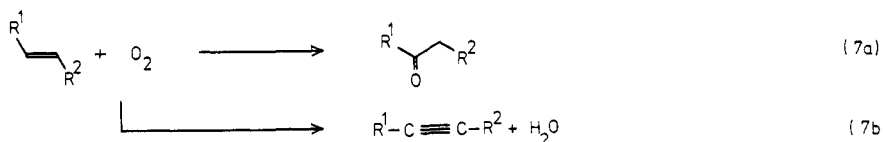

(4a)   (4b)

was also prepared.   Supported catalysts were dissolved or suspended in 1M HCl solution and ethylene and dioxygen passed through typically at 80°C.   Acetaldehyde was the only product, and no co-catalyst, e.g. copper (II) chloride, was required.   A conventional ion exchange resin loaded with Pd^{2+} was about an order of magnitude less active.   The quinone group is therefore active in the catalytic cycle possibly as shown in Scheme 3.
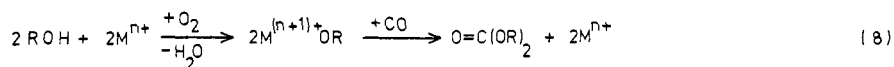
Scheme 3

$$CH_2 = CH_2 + \tfrac{1}{2}O_2 + Pd(II) \longrightarrow CH_3CHO + Pd(0)$$

A related Wacker-type supported catalyst has also been reported recently (ref. 38). The support in this case was an oligo-p-phenyleneterephthalamide (NHPhNHCOPhCO)$_n$ presumably chosen for its thermal stability. The supported catalyst was prepared by wet impregnation of the polymer with a water-acetic acid solution (9:1) of Pd(OAc)$_2$ at room temperature. After drying the temperature of the impregnate was raised to 950°C until all volatiles were removed. It is not clear therefore what the final molecular structure of the active catalyst really is. In a typical reaction air was bubbled through a suspension of the catalyst in a solution of alkene in ethanol/water or dioxane/water mixtures containing 70% aq. perchloric acid at 25-70°C. Alkenes examined were 1-pentene to 1-decene, and in addition 2-, 3- and 4-octene. Under the reaction conditions Wacker-type ketonization can occur (reaction 7a) or oxidative dehydrogenation to form alkynes (reaction 7b). Low levels of palladium catalyst in the dioxane/water mixture favoured ketone formation (often > 90%), whereas higher levels of palladium with the ethanol/water solvent favoured alkyne formation (often > 90%).

$$R^1 \diagdown \diagup R^2 + O_2 \longrightarrow R^1 \diagdown \underset{O}{\overset{}{C}} \diagup R^2 \qquad (7a)$$

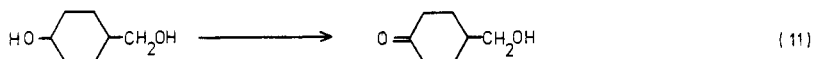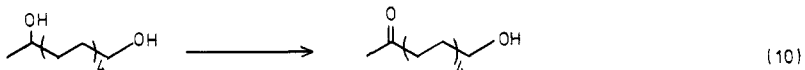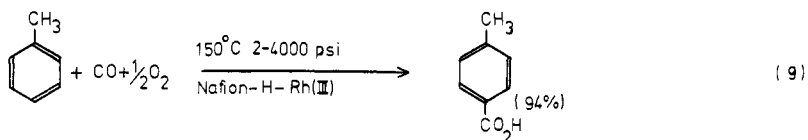$$\longrightarrow R^1 - C \equiv C - R^2 + H_2O \qquad (7b)$$

A successful oxidative carbonylation of alcohols has also been reported using a copper (I) catalyst supported on poly(4-vinyl pyridine) (ref. 39). A stream of dioxygen, carbon monoxide and methanol was fed under pressure over the catalyst to yield dimethyl carbonate. The reaction was performed in two ways: i) using successive cycles of dioxygen and carbon monoxide, or ii) using a continuous mixed feed of dioxygen and carbon monoxide. Amino alcohols, thio alcohols and amino thiols were also reported as substrates, and cyclic carbonates were formed from glycols. The mechanism involved a Cu(I)/Cu(II) redox process (equation 8) and no loss of activity was reported over 30 cycles. There appears to be no evidence of this work being pursued further.

$$2\,ROH + 2M^{n+} \xrightarrow[-H_2O]{+O_2} 2M^{(n+1)+}OR \xrightarrow{+CO} O = C(OR)_2 + 2M^{n+} \qquad (8)$$

NAFION-SUPPORTED TRANSITION METAL OXIDATION CATALYSTS

The development by Dupont of the Nafion range of polymers has led to the production of much more inert ion exchange membranes for use e.g. in chlor-alkali cells. Not surprisingly the acidic forms of Nafion are effectively solid superacids, and the use of these as catalysts has also received considerable attention (ref. 40). However, more recently it has been realised that the exchange or partial exchange of acidic protons for transition metal ions might offer even great opportunities in catalysis (ref. 41,42). Not only might the transition metal centre indulge in cooperative reactions involving superacidic protons, but also the overall inertness of the Nafion fluorocarbon structure might allow the use of reaction conditions generally too hostile for the use of more conventional polymer supports.

Currently terephthalic acid is manufactured by the cobalt-catalysed oxidation of p-xylene. Other potential routes which have been explored are the carbonylation of toluene: i) to yield p-tolualdehyde using HF/BF$_3$, amd ii) to yield toluic acid using a palladium catalyst with various oxidants. For these to be useful industrially high levels of para substitution are required. Using Nafion with protons partially exchanged for Rh(III) toluene can be converted to toluic acid with 94% para selectivity (ref. 41) (equation 9).

$$(9)$$

$$(10)$$

$$(11)$$

Both free superacid sites and Rh(III) are required. Rh(III) seems to act as an electrophilic reagent attacking the toluene nucleus para to the methyl group, and the free acid sites play a role either in accelerating CO insertion, or in the cleavage of the p-tolyl carboxylate from the Rh(III) centre.

Recently it has also been reported that Nafion exchanged with Cr(III) or Ce(IV) provides useful catalysts for the oxidation of alcohols using t-butylhydroperoxide (ref. 43). The exchange of protons was not quantitative but the residual content may well be inaccessible. The chromium based system yielded ketones cleanly (∿80%) from secondary alcohols, while primary alcohols gave a complex mixture of products. Typical reaction conditions were 80°C, 6 hours in aromatic solvents. In contrast the cerium based catalyst was very selective for secondary alcohols, which were converted to ketones in the presence of primary alcohol functions, which remained unaffected (equations 10,11). In this case NaBrO₃ was the oxidant used at 50°C for 3 hours in acetic acid. Use of the same catalyst with t-butyl hydroperoxide as the oxidant allowed oxidation of secondary alcohols to ketones selectively in the presence of olefinic moieties in the substrate.

ALKENE EPOXIDATION BY t-BUTYL HYDROPEROXIDE CATALYSED BY POLYMER-SUPPORTED METAL COMPLEXES

A strategically important petrochemical process is the conversion of alkenes to epoxides, and in particular ethylene and propylene. Currently ethylene is epoxidized in the gas phase using a silver catalyst on an inert aluminium oxide support (ref. 35). In contrast propylene is converted to its epoxide in a liquid process using alkyl hydroperoxides as the oxidant in the presence of a molybdenum or titanium catalyst. In the Halcon process a soluble molybdenum complex is used with t-butyl hydroperoxide (ref. 44), while Shell have patented a heterogeneous catalyst involving titanium (IV) on silica, and favour ethyl benzene hydroperoxide as the oxidant (ref. 45). Typically the reactions are run at ∿ 100°C in a suitable solvent. Almost certainly irrespective of the oxidation state of the metal catalyst initially, the highest available oxidation state is formed in situ as the active species.

Until relatively recently alkyl hydroperoxides have been regarded as highly reactive reagents not amenable to use in the laboratory. In reality this is far from the truth (ref. 6). Indeed these molecules present a number of very important advantages which mean that their use will grow increasingly both in the laboratory and in industrial processes. Firstly they are cheap and readily available on a large scale from the autoxidation of ter-hydrocarbons. They have a high intrinsic thermal stability, and are much less sensitive to spurious metal ion catalysed (violent) decomposition than are either hydrogen peroxide or peroxy acids. Only when anhydrous and without the presence of small amounts of solvent (i.e 100% pure) are they as sensitive as hydrogen peroxide. In terms of their oxidation behaviour they are extremely attractive because they are essentially inert to most organic molecules in the absence of a catalyst. This provides tremendous potential to develop particular catalysts to push the oxidation capability in pre-determined directions, in a highly selective fashion. Not surprisingly therefore there has been and continues to be a lot of activity directed tgowards developing potentially selective catalysts. From a practical point of view alkyl hydroperoxides are soluble in organic solvents (unlike hydrogen peroxide) and in water, and they can be used at neutral pH (unlike peroxy acids). With regards to use on a large scale they are less corrosive than peroxy acids and hydrogen peroxides. The co-product alcohol can be dehydrated, reduced and recycled, or in the case of t-butanol from t-butyl hydroperoxide, it can be used as a feed for methyl t-butyl ether production, or 2-phenyl ethanol from ethyl benzene hydroperoxide, it can be converted to styrene.

With regard to alkene epoxidation using alkyl hydroperoxides, transition metal species
capable of achieving and sustaining formally high oxidation states seem to be the best
catalysts, and indeed the effective ones assume, at least formally, a d^o electronic
configuration i.e. Mo(VI), W(VI), V(V) and Ti(IV).   In each case the highest oxidation
state can be achieved in situ in use (e.g. Mo(CO)$_6$ ———————➤Mo(VI)).   The catalyst must,
however, be a weak oxidant in its own right, to avoid non-selective oxidation of the
substrate, and indeed oxidative attack on the hydroperoxide Cr(VI) is poor in this respect
and the favoured order is Mo(VI) > W(VI) > V(V) > Ti(IV), except in the case of allylic alcohol
epoxidations where V(V) seems optimum.   In all cases the metal centre must be capable of
forming an oxo-metal bond i.e. -M=O, and it must possess Lewis acid properties to withdraw
electrons from the peroxidic oxygen of the alkyl hydroperoxide.   The favoured order in this
respect is CrO$_3$ > MoO$_3$ > WO$_3$ > TiO$_2$ > V$_2$O$_5$.

Considerable effort has been made to understand the mechanisms of these reactions in the
case of homogeneous catalysts, and the matter is not yet entirely settled.   What is clear
is that a heterolytic cleavage of the peroxo species is involved.   Metals such as iron and
cobalt having two comparably accessible oxidation states differing by a single unit, tend to
promote homolysis of the peroxy linkage.   These are not good epoxidation catalysts and tend
to initiate free radical reactions.   Earlier evidence with vanadium and molybdenum
suggested that the alkyl hydroperoxide becomes coordinated to the metal centre via its
distal oxygen atom and that attack by alkene follows, possibly preceded by coordination of
the alkene itself at the metal centre (reaction 12).   Many of these epoxidations are highly
stereospecific (ref. 6), and coordination of the alkene prior to attack on the peroxo

$$(12)$$

complex is an attractive proposition for explaining the high selectivity.   More recent
evidence has shown however that the alkyl hydroperoxide in fact becomes coordinated to the
metal centre via its peroxy oxygen atom.   Mimoun and his coworkers (ref. 46) then maintain
that the alkene becomes coordinated, followed by a rearrangement to form a five-membered
intermediate, which collapses to expel the epoxide (Scheme 4).   Ledon (ref. 47) and
Sharpless (ref. 48), however, maintain that alkene coordination does not occur, but
rather the alkene attacks the peroxo-metal species directly, with a concomitant concerted
rearrangement to form the epoxide, transiently bound to the metal (Scheme 4).   Irrespective
of these details however in both cases the oxo-metal bond remains in tact during the
process, and the metal alkoxide bond formed undergoes exchange with alkyl hydroperoxide to
reform the peroxo-metal species.

Scheme 4
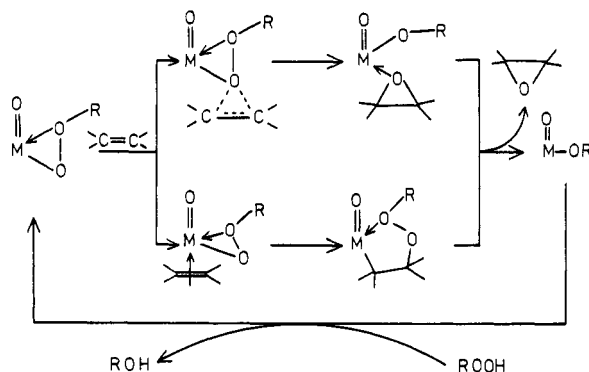
The earliest attempt to produce a polymer-supported analogue related to these catalysts
appears to be the work reported by Allen and Neogie (ref. 49), which must be regarded as
far in advance of its time.   They supported HWO$_4^-$ on Amberlite IRA-400 and used hydrogen
peroxide rather than alkyl hydroperoxide as the oxidant.   Maleic anhydride was the
substrate and molybdenum, vanadium, osmium and niobium were also examined.   It is not clear
what was achieved in a preparative sense.

Since this report there have a number of closely related studies involving the attachment of
oxo-metal complexes to ion exchange resins, including activity in the patent literature.
Linden and Farona supported oxo-vanadium (IV) species on a sulphonic acid type cation
exchange resin and successfully epoxidized both cyclic and acyclic alkenes using t-butyl
hydroperoxide (ref. 50).   It is not clear what the structure of the catalyst was, but
yields in excess of those produced using VO(acac)$_2$ were reported and the selectivity for
epoxide formation was ∾100%.   An anion exchange resin has also been used to support
[MO$_2$O$_4$(OX)$_2$(H$_2$O)$_2$]$^{2-}$ (where OX=oxalate) and the resultant catalyst used in the epoxidation

of cyclohexene with cumene hydroperoxide (ref. 51).   Resins containing -N(CH₃)₂ groups yielded more active catalysts than those with ⁺N(CH₃)₃ groups and it seems likely that in the former case the tertiary amine functions displaced water and/or the oxygen ligands to produce a more active complex.   It is not clear whether the binuclear structure survived.
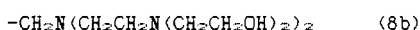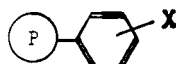
The remaining reports describing ion exchange resins as supports have used weakly acidic carboxy cation exchangers (ref. 52-55).   Addition of ammonium molybdate to resins such as Amberlite IRC-84 appears to generate a supported species with the molybdenum centre coordinated by resin carboxylate groups (5) (ref. 54,55).   Both propylene (ref. 54) and cyclohexene (ref. 55) have been successfully epoxidized using these catalysts with t-butyl hydroperoxide under relatively mild conditions   100°C (35 atmos pressure propylene).
μ_3- oxotrimetal hexacarboxylates, $[M_3O(O_2CEt)_6(H_2O)]^{n+}$, have also been ex changed onto weak cation exchange resins (ref. 53).   Of a wide range of metals examined only Mo, V and Co showed activity for the epoxidation of cyclohexene by cumene hydroperoxide, with predictably the Mo species performing best.   Some of the catalysts were also useful for catalysing the decomposition of the hydroperoxide itself to yield phenol and acetone.
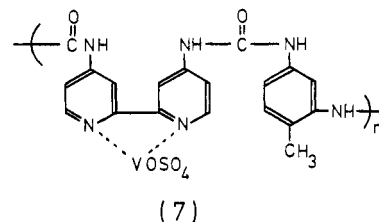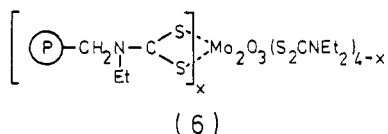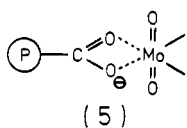
In the area of homogeneous epoxidation catalysts recent developments have involved the synthesis of structurally well-defined complexes involving specific chelating ligands (ref. 56), and polymer supports functionalised with chelating groups are also attracting attention.   Linden and Farona first described the use of polymers containing acetylacetonate, ethylenediamine and pyridine donor ligands to bind oxo-vanadium (IV) ions (ref. 57).   The resultant catalysts were active in the epoxidation of cyclohexene using t-butyl hydroperoxide.   Bhaduri and coworkers (ref. 58) examined in more detail a polystyrene resin-bound pentane-2,4-dione complex of oxo-vanadium (IV), again in the epoxidation of cyclohexene by t-butyl hydroperoxide.   The latter appeared to generate the active catalytic species, vanadium (V), in situ.   Yields of epoxide were very poor as perhaps expected for a vanadium catalyst with a simple alkene.   Substantial leaching of metal from the support was also detected, and no doubt accounted for the loss in activity observed.   This group subsequently produced a resin-supported dithiocarbamato-complex of molybdenum (V) (6) (ref. 59), a binuclear oxo-bridged species.   Treatment of this with t-butyl hydroperoxide again generated a Mo(VI) species, with substantial loss of metal from the resin if excess of hydroperoxide was used.   If however, the catalyst was activated with a controlled amount of hydroperoxide, subsequent epoxidation of cyclohexene could be achieved with a 70% conversion (based on hydroperoxide consumed).

Neckers and his coworkers have described the synthesis of vanadium catalysts supported on polyureas functionalised with bipyridine ligands (7) (ref. 60).   These catalyse the epoxidation of a number of alkenes at 80°C using 70% aqueous t-butyl hydroperoxide.   The presence of water predictably gave rise to some glycol formation and typical yields (%), epoxide/glycol, were 3-60/0-15%.   In general cyclic alkenes were more active than acyclic ones and the selectivity of epoxidation of substrates containing both endo- and exo- double bonds in the same molecule was examined.   Selectivities up to 98% were achieved.   The catalyst system was reported to be active after recycling five times, but no details were given.

Oxo-vanadium (V) and oxo- molybdenum (VI) catalysts supported on polystyrene resins carrying bis(phosphonomethyl) amino (8a), bis(2-hydroxyethyl) amino, (8b), and iminodiacetate (8c) functions have been reported by Suzuki and coworkers (ref. 61,62).   Two types of


X = -CH₂N(CH₂CH₂N(CH₂PO(OH)₂)₂)₂   (8a)

    -CH₂N(CH₂CH₂N(CH₂CH₂OH)₂)₂   (8b)

    -CH₂N(CH₂CO₂H)₂   (8c)

polystyrene resin have been utilised, a 2% crosslinked gel type material and a 10% crosslinked macroporous species (pore size ∼720A , surface area ∼ 7m²g⁻¹).   The polymer complexes (1-4mmol metal/g resin) were prepared by shaking each resin with aqueous solutions

of NaVO₃ or K₂MoO₄. Epoxidations were performed using 70% aqueous t-butyl hydroperoxide at 80°C. As anticipated the vanadium systems were the most effective in the case of allylic alcohol substrates, and all resin types gave high conversions (∿100%) and high regioselectivity (∿98%). The molybdenum based species were more effective in the case of cyclohexene with conversions up to∿90%. Selectivities however were poorer, up to∿60%, and again this is probably a reflection of the presence of water. The macroporous resin based catalysts showed much better kinetic properties, presumably as a result of better access to catalyst sites via the pore structure. Approximately 15-25% of vanadium was leached from the support over a sequence of five re-cycles though surprisingly the epoxide yield did not fall too much (98% → 93%). No metal loss nor reduction in activity was observed for the molybdenum catalysts after five runs, but no further details have been disclosed.

A closely related but less clearly defined supported molybdenum peroxide has been reported by Kurusu et al (ref. 63). Triethylenetetramine was attached to a chloromethylstyrene resin. This was then added to a solution of molybdenum peroxide formed by treatment of molybdenum metal with 30% hydrogen peroxide. The resin was isolated and dried. Epoxidations of various alkenes were then carried out in benzene at room temperature and 60°C using t-butyl hydroperoxide and the polymer catalyst. The yield for cyclohexene epoxide was 90% after 5 hours at 60°C. After four cycles of the same catalyst sample the yield dropped to∿70%, but it was improved to∿80% on the next cycle when the catalyst was 're-activated' first using 30% hydrogen peroxide.

Recently in our own laboratory we have also been examining polymer-supported vanadium and molybdenum complexes as epoxidation catalysts (ref. 64). Polystyrene and poly(glycidyl methacrylate) based resins functionalised with aminomethyl pyridine and pyridyl imidazole ligands provide the basis for highly selective copper chelating resins (ref. 65,66). In the case of the aminomethyl pyridine ligands (9a,b), vanadium (IV) and molybdenum (V) species are also readily complexed from solutions containing VO(acac)₂ and MoO₂(acac)₂ respectively. In the case of molybdenum the polymer becomes blue, probably as a result of the displacement of one acetylacetonate ligand by the pyridyl ligand, with simultaneous reduction of the metal to Mo(V) (often a blue-coloured species). Epoxidations of cyclohexene at 80°C using anhydrous t-butyl hydroperoxide are not accelerated by these resin catalysts, unless the latter are first activated by treatment with t-butyl hydroperoxide in the absence of alkene. During this pre-treatment the polymer-bound molybdenum complex becomes bright yellow, characteristic of Mo(VI), and the resulting species is a potent
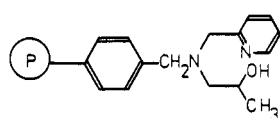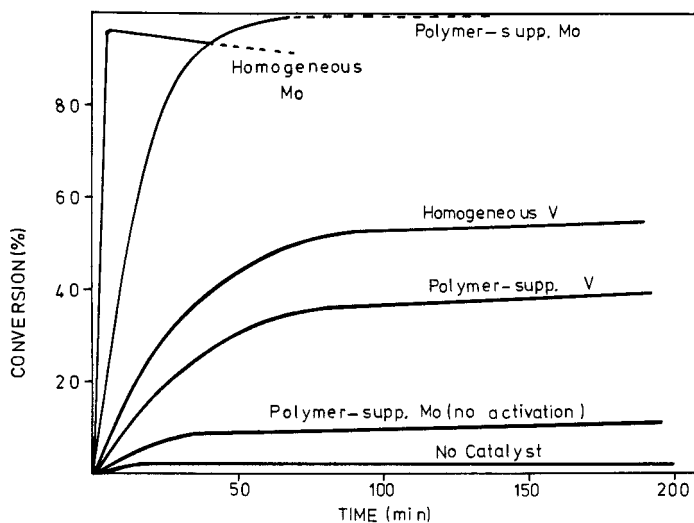

(9a)
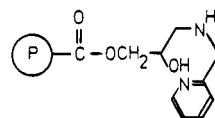
(9b)

Figure 1

catalyst, giving high conversions to epoxide with high selectivity in short times (Figure 1). No catalysis is observed without the activation step, even when large amounts of t-butyl hydroperoxide are added to reactions, and it seems that prior coordination of alkene inhibits formation of the active catalytic centre. The activation step is therefore a vital one, and the final activity of the polymer catalyst can be improved by using more severe activation conditions. During this process some metal is also lost from the support, up to ∿ 3% by weight depending on the conditions used, the ligand and the polymer type. Activated catalysts, however, appear to be very stable in favourable cases. Although the rate of epoxidation falls marginally on the first re-use, subsequent re-cycling nine times shows a stable activity. Some small levels of metal are lost during continuous re-use, but in the case of polystyrene based Mo catalysts the level of leaching tends
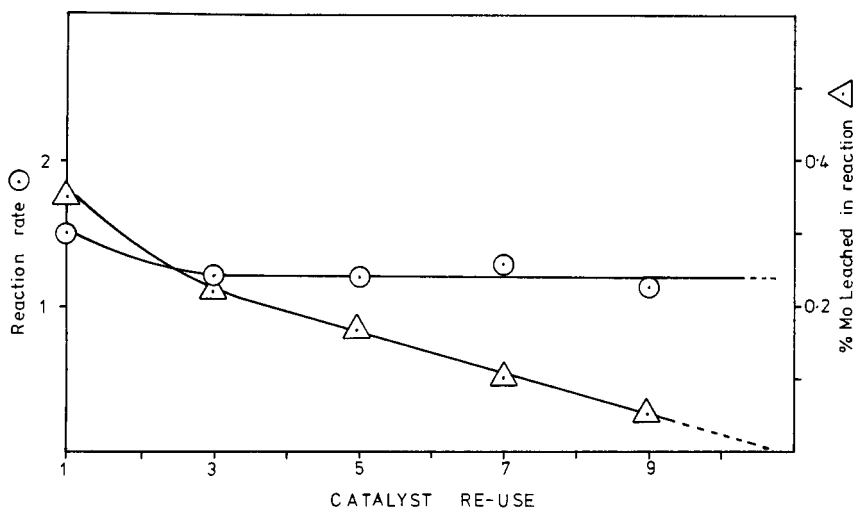
Figure 2

towards zero and the metallic species lost does not seem to be catalytically active.
(Figure 2). These systems hold out a realistic prospect for a long-lived polymer-supported
epoxidation catalyst.

POLYMER-SUPPORTED ARSENIC, SELENIUM AND TELLURIUM BASED OXIDATION CATALYSTS

Although falling outside the category of transition metal complex catalysts it would not be
appropriate to omit mention of important developments regarding polymer-supported
phenylarsonic acid, (ref. 67) phenylseleninic acid (ref. 68) and 'phenyltellurinic acid'
(ref. 69). The arsonated polymer is reported to catalyse olefin epoxidation using 30%
aqueous hydrogen peroxide. In comparison with its low molecular analogue secondary
hydrolysis was minimised, although regio- and stereoselectivities were sacrificed to some
extent. The reaction seems to involve the formation of peroxyarsonic acid groups (10).

(10)   (11)   (12)
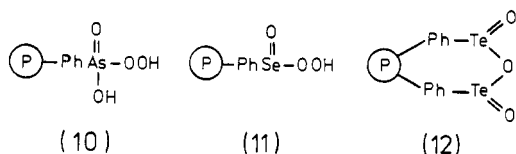
Polymer-supported phenylseleninic acid was also shown to be an effective catalyst for
converting olefins into trans diols, and ketones into esters using aqueous hydrogen peroxide
at room temperature. With t-butyl hydroperoxide as the oxidant benzylic alcohols were
converted to carbonyl species, and hydroxy aromatics to quinones. Again the corresponding
peroxy acid (11) seems to be involved. Perhaps most intriguing of all is the report that a
polystyrene bound tellurinic acid species catalysed the epoxidation of olefins using aqueous
hydrogen peroxide without producing diol side product. Phenyltellurinic acid is not
catalytically active under these conditions, and so some other active species must be formed
on the polymer. One possibility seems to be the corresponding acid anhydride (12) but this
is not yet clear.

FUTURE PROSPECTS

This review shows clearly that organic polymers can be used very effectively as supports for
metal complexes in a large number of oxidation reactions. In most instances the underlying
fear that the polymer would not survive the oxidative conditions has not been confirmed, and
indeed some systems hold out real potential for use as long-lived supports under industrial
conditions. Two trends reinforce the liklihood of much wider and useful application.
Firstly the ability to design and synthesise structurally well-characterised and stable
polymer-supported ligand species continues to grow. Secondly developments in, and
understanding of, selective oxidation catalysts capable of functioning under mild conditions
runs parallel with the sophistication of supports. The area is one which has not been well
exploited, and is therefore one which is ripe for further developments. The future
prospects look very good, and the science is currently poised for collaboration between
organo-metallic chemists and polymer chemists to yield major technical breakthroughs.

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