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Recent Progress in the Heterogenization of Complexes for Single-Site Epoxidation Catalysis

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Epoxides are of central importance in organic synthesis since they provide access to a series of different 1,2-difunctionalized intermediates starting from cheap olefins. Olefin epoxidation is catalyzed by a whole bunch of transition metal elements in high oxidation states, the most important are molybdenum, tungsten, rhenium and manganese. Organic peroxides, hydrogen peroxide bleach and even dioxygen have been used as the source of the oxygen atom that is transferred to the olefin. The present microreview summarizes the recent developments in terms of catalyst heterogenization for olefin epoxidation. Such strategies are requested for green synthesis protocols and are of special interest for expensive catalysts derived, e. g. from rhenium or complex chiral ligands.

Introduction

Zeolites are the paradigms for porous heterogeneous materials. They have found significant applications especially for the environmentally benign production of chemicals.[1] On the other hand, the micropores in zeolites can make mass transport become important and are thus responsible for limitations of the overall reaction rate. This often limits their performance in liquid-phase synthesis of fine chemicals and pharmaceuticals.[2] Thus the discovery of surfactant-templated mesoporous solids by Mobil researchers is considered as one of the most exciting discoveries in the field of material synthesis in the last decades.[3] The ability of surfactants to template well-defined structures by self-assembly has thereafter directed the design and synthesis of

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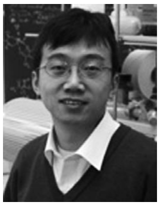

Mingjun Jia was born in 1971 in Daqing (China) and received his PhD at Jilin University, Changchun (China) in 1999. He then joined the group of Dr. Vicente Cortés Corberán as a post-doctoral fellow at the Institute of Catalysis and Petrochemistry, CSIC (Spain). In 2001 he moved, granted by a research fellowship of the Alexander von Humboldt-Foundation to the group of Prof. W. R. Thiel at the TU Chemnitz (Germany). Since 2003 he is professor of physical chemistry at the Jilin University, Changchun (China). His current research interests mainly focus on the synthesis and catalytic applications of a variety of transition-metal-functionalized zeolites, mesoporous aluminophosphates and carbon materials, as well as inorganic-organic hybrid materials.

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various inorganic materials with nanosized pore dimensions.[4] Today, a very large number of mesoporous materials of varying pore size, composition and morphology are accessible using anionic, cationic, neutral surfactants and polymers under different reaction conditions.[5]

Such mesoporous materials can be converted into organic-inorganic hybrid nanocomposites by surface modifications. During the last years, organic-inorganic hybrid mesoporous materials constitute an emerging area in the field of materials science and have shown their impact in a wide range of heterogeneous catalytic reactions.[6] They possess high mechanical, thermal and structural stability provided by the inorganic components while the organic groups can be readily modified for specific applications. In general, surface modifications are performed either by co-condensation or grafting. The first route involves the one-step co-condensation of tetraalkoxysilanes [$Si(OR)_4$, R = Et, Me] and one or more organoalkoxysilanes [$X–Si(OR)_3$, R = Et, Me]. The main advantages of this method are relied to the homogeneous distribution of the organic group X over the pore channels and the single-step preparation procedure. However, the resulting structural ordering and the chemical stability are dependent on the amount and nature of $X–Si(OR)_3$.[7]

On the other hand, grafting refers to a post synthesis modification of the inner surface of a pre-fabricated mesoporous support, where the organic functional groups are introduced as terminal groups, usually after surfactant removal.[5] Mesoporous silicas possess surface silanol groups (Si–OH) in high concentration which act as convenient anchoring points for organic groups. The advantages of the post synthesis grafting method can be summarized as follows, (a) the structure of the resultant mesoporous materials is ordered after the grafting reactions, (b) the functional groups can be chosen according to the requirements, (c) the obtained materials show enhanced hydrothermal stability and (d) their hydrophilic–hydrophobic properties can be tailored by the choice of the organoalkoxysilanes.

An alternative and fascinating strategy in the synthesis of mesoporous organic-inorganic hybrid materials is the replacement of one or more siloxane groups by organic linkers to form periodic mesoporous organosilicas (PMOs). The usage of organosilanes of the type $(RO)_3Si-X–Si(OR)_3$ generates stable materials by condensation to a three dimensional network that contains organic groups in the framework.[8] PMOs are unique in terms of their inherent hydrophobic nature, high hydrothermal stability, tuneable pore size, high surface area, and crystalline pore channels (e. g., phenylene-silica PMO).

Under moderate reaction conditions, homogeneous catalysts often provide better results in terms of activity and selectivity compared to heterogeneous catalysts while the latter can be reused by simple methods of recovering from the reaction mixture or allow the operation of continuous processes. Therefore "heterogenization" or "fixing" homogeneous catalysts on organic-inorganic hybrid mesoporous materials opens up one way to combine the benefits of both heterogeneous and homogeneous catalysis.[9]

Heterogenization of homogeneous catalysts on supports can be achieved by either formation of a covalent bond between the support and the catalyst, by adsorption or ion-pair formation or by encapsulation or entrapment.[10] Generally, the support material has to be thermally, chemically and mechanically stable during the reaction process and the active sites have to be well dispersed over the whole surface and easily accessible. This requires the support to possess a reasonably high surface area and an appropriate pore size,[11] which is fulfilled for mesoporous materials. If the functional groups or the catalytically active sites are attached firmly to the solid support and the reaction mechanism does not include any ligand dissociation step, catalyst leaching should be avoidable.[12]

In the very beginning of catalyst heterogenization, often polymers were used as support, which allows grafting by the formation of stable C–C or C–element bonds. If soluble polymers are used, the active sites are distributed homogeneously through out the reaction solution with a catalyst architecture similar to the homogeneous catalyst[13] but catalyst recovery is difficult. Therefore insoluble polymer supports are preferred. For those cases, swelling of the polymer has to be taken into account,[14] which is no problem for inorganic oxides.

Due to the lack of ordered pore channels, amorphous silica gels are not able to provide the size/shape specificity properties. Hence the immobilization of single-site catalysts on mesoporous high surface area organic-inorganic hybrid supports by heterogenization is particularly beneficial since it allows facile recovery of the catalyst after reactions and often avoids catalyst deactivation. However, heterogenized molecular catalysts may show different substrate scopes or stereo selectivities compared to their homogeneous counterparts according to the pore geometry of the support. This is of particular importance for asymmetric reactions.[15]

Olefin epoxidation is of importance for a series of industrial processes, epoxides are for instance precursors in the synthesis of epoxy resins, plasticizers, perfumes, surfactants, etc.[16] In this article, we will highlight recent developments in the synthesis and application of heterogenized transition metal catalysts for liquid phase olefin epoxidation and will mainly focus on group VI and VII transition metals since these groups cover the main applications of single-site catalysts. Special attention is given to the heterogenization of single-site catalysts based on molybdenum and tungsten, although other elements are discussed too, and to the usage of ecologically benign "green" solvents. It however has to be mentioned here, that there are also examples of highly active heterogeneous epoxidation catalysts containing for example group IV or V elements, such as TS1, which are out of the focus of this review article.

The first examples of liquid phase catalytic oxygen transfer dates back to 1936. So-called Milas reagents were formed by reaction of transition metal oxides with H_2O_2 in *tert*-butanol solution giving soluble inorganic peracids. With certain metal oxides such as MoO_3 or WO_3 selective epoxide formation was observed.[17] There is large interest to substitute pollutant oxidants by more environmentally friendly ones. Due to the high active-oxygen content and the by-products water/alcohol,[18] hydrogen peroxide and organic peroxides are often the oxidants of choice.[19] For molecular oxygen the radical nature of the oxygen transfer reaction restricts its applicability.

Two main problems are generally encountered when H_2O_2 is used as the oxidant. Both are related to the formation of water during the reaction.[20] For heterogeneous/heterogenized catalysts ligand-metal units in the active sites or the linkage between the support and the active site may irreversibly be hydrolyzed or water may obstruct the active sites of the catalyst, resulting in a decreased activity of the catalyst.

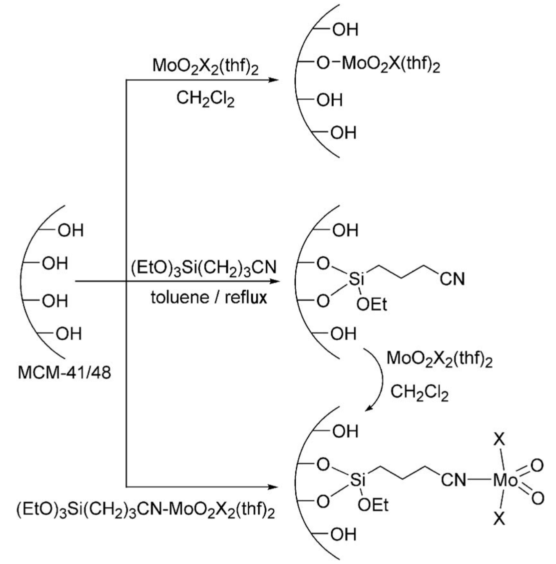
Molybdenum

While mesoporous materials possess unique textural and morphological features, they show limited catalytic activity themselves. The incorporation of heteroatoms or catalytically active organic sites into the inert framework of mesoporous materials is an important and simple way to modify these materials. In this context the activity of titanium substituted mesoporous materials (Ti-MCM-41/48, Ti-SBA-15, Ti-HMS, etc) in different oxidation reactions must be mentioned.[21] In contrast to Ti^{IV}, octahedral coordinated Mo^{VI} sites, known as catalytically active centres for olefin epoxidation cannot easily be incorporated into the tetrahedral positions of porous silicas (zeolites/mesoporous materials).[22] Therefore the heterogenization of molybdenum-based organometallic or coordination compounds on the surface of mesoporous materials becomes a promising alternative.

The Halcon–Arco process,[23] applied to the liquid-phase epoxidation of propylene with organic hydroperoxides, initiated extensive research on molybdenum-catalyzed homogeneous alkene epoxidation reactions. In particular, homogeneous Mo^{VI} complexes of the type $[MoO(O_2)(L-L)]$ and $[MoX_2(O)_2(L-L)]$ (X = Cl, Br, Me), $(\eta^5-C_5R_5)MoO_2Cl$ turned out to be efficient catalysts in the presence of TBHP (TBHP = *t*BuOOH).[24] Turnover frequencies (TOF) of up to 21.000 $mol\,mol_{Mo}^{-1}\,h^{-1}$ were noted for $(\eta^5-C_5R_5)$-MoO_2Cl complexes which even surpass the well known CH_3ReO_3/H_2O_2 system.[25]

Earlier attempts focused on the immobilization of soluble Mo^{VI} catalysts on polymer supports by anion or cation exchange and by using chelating ion exchange resins.[26] Sherrington et al. pioneered the development of aminated polystyrene, polymethacrylate, polybenzimidazole and polysiloxane resins for the immobilization of Mo^{VI} epoxidation catalysts. Among them, polybenzimidazole and polysiloxane based polymers showed the best performance in terms of activity and stability/reusability.[27] However, the inherent drawbacks of such polymer supported catalysts like the swelling of polymers, thermo-oxidative as well as mechanical instability directed the attention towards inorganic supports.

Heterogenization of molybdenum catalysts can be realized either by the direct grafting of molybdenum complexes or by using a linker between the catalyst and the support material.[28] Gonçalves et al. for instance described the heterogenization of MoO_2X_2 type complexes in the ordered channels of hexagonal MCM-41 and cubic MCM-48 by the direct grafting (impregnation) and by the spacer ligand $(OEt)_3Si(CH_2)_3CN$ (Scheme 1).[29]

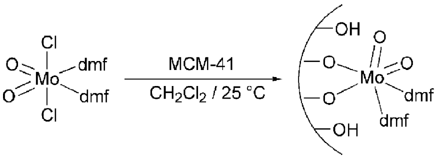


Scheme 1. Heterogenization of $MoO_2Cl_2(thf)_2$ on mesoporous MCM-41/48 solids with and without linker units.

The homogeneous and the heterogenized complexes were tested at 55 °C as catalysts for the epoxidation of cyclooctene with TBHP as the oxidant. MCM-$MoO_2Cl(THF)_2$ showed a conversion of 31% after 2 h with 100% epoxide selectivity but MCM-$MoO_2Br(THF)_2$ just showed 17% of conversion (56% selectivity). Both systems behave similar to their homogeneous counterparts. The kinetic profiles for the cyclooctene epoxidation catalyzed by homogeneous and heterogenized $MoO_2Cl_2NC(CH_2)_3Si(OEt)_3$ are similar showing that the reaction follows the same mechanism in both cases. Hot filtration studies however proved that a part of the catalytic activity resulted from leached molybdenum species in the reaction solution probably due to weak ligand–metal interactions.

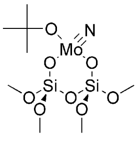
The same group also investigated the grafting of $MoO_2X_2(thf)_2$ (X = Cl, Br) on mesoporous MCM-41 in presence and absence of a base.[30] Mo *k*-edge EXAFS data indicated the presence of isolated surface fixed monomeric molybdenum species with a loading of 1 wt.-%. Similar grafting reactions conducted in presence of Et_3N gave higher Mo loadings (4 wt.-%) leading to dinuclear Mo(V1) species with two Mo centres bearing two Mo=O groups and one or two linking oxo bridges. The catalysts were evaluated in the liquid phase epoxidation of olefins and alcohols with TBHP. The catalyst grafted in the presence of NEt_3 gave poorer activities than the samples prepared without (TOFs: 5 vs. 38 $mol\,mol_{Mo}^{-1}\,h^{-1}$) and showed active site leaching. 1,2-Cyclooctanediol was formed after the epoxidation of cyclooctene. The authors attributed the different behaviour to the different molybdenum species formed on the support surface in the presence and the absence of NEt_3.

By opting a molecular designed dispersion method, Gonçalves et al. recently showed that $MoO_2Cl_2(dmf)_2$ is an efficient precursor for the deposition of oxidomolybdenum species on mesoporous MCM-41 (Scheme 2). A low surface concentration of molybdenum (0.17 Mo/nm^2) guaranteed that the active sites exist as isolated, monometallic $Mo^{VI}O_2$ species, which was corroborated by EXAFS measurements.[31] The catalytic performance was evaluated for the epoxidation of cyclooctene, 1-octene, *trans*-2-octene, *R*-(+)-limonene, norbornene, α-pinene and styrene with TBHP as the oxidant. The MCM-41 grafted complex exhibited high activity in the epoxidation of cyclooctene at 25 °C (TOF: 306 $mol\,mol_{Mo}^{-1}\,h^{-1}$) and its kinetic profile was similar to that exhibited by the homogeneous complex. Alkenes such as cyclooctene, *trans*-2-octene, norbornene showed >80% of conversion with 100% of selectivity towards the epoxide after 6 h. The more demanding *R*-(+)-limonene showed moderate conversions (ca. 78%) while α-pinene and styrene showed <20% of conversion and their epoxide selectivity remains at 30% after 6 h. Stability tests confirmed that the reaction is mainly heterogeneous in nature. Besides the stability and recyclability of this system in epoxidation reactions were superior than the earlier mentioned $MoO_2Cl_2(thf)_2$ catalysts grafted on MCM-41.[29]



Scheme 2. Direct grafting of $MoO_2Cl_2(dmf)_2$ on mesoporous MCM-41 without linker units.

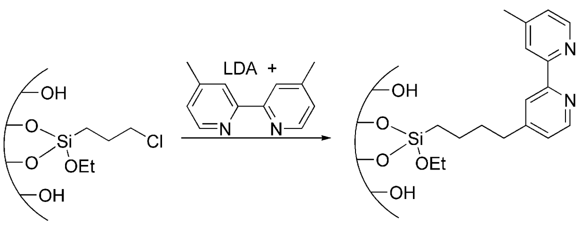
Surface coordination chemistry provides a uniform distribution of active sites on the surface of solid supports in a relatively facile and concise manner.[28] Using this method, Basset et al. reported molybdenum anchored on MCM-41 by treatment with (N≡)Mo(O*t*Bu)$_3$ (Scheme 3). In situ IR spectroscopy studies confirmed the displacement of *tert*-butoxy ligands for siloxyl groups from the silica surface and also showed that the hexagonal channels of MCM-41 enhance the formation of multigrafted species.[32] The catalyst gave a high initial rate (24.9 $mmol\,mmol^{-1}\,min^{-1}$) for the epoxidation of cyclohexene with TBHP, which was attributed to isolated molybdenum sites arising from the controlled grafting process. Leaching studies however showed a continuous decrease of catalytic activity and a loss of ca. 15 mol-% of molybdenum during each catalytic cycle.



Scheme 3. Heterogenized (N≡)Mo(O*t*Bu)$_3$ on mesoporous MCM-41 silica.

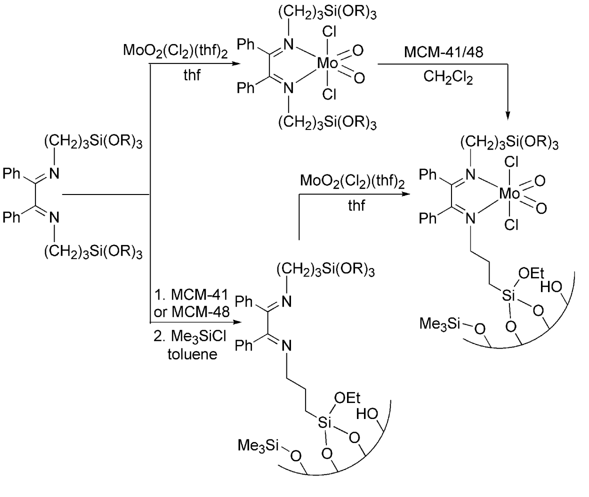
Meantime Bregeault et al., reported Mo^{VI} complexes supported on mesoporous Si-MCM-41/SBA-15 and silica by reacting Mo^{VI} peroxo species with TEOS, pure SiO_2 or precipitated silica in an acidic and peroxidic medium (peroxo route).[33] Spectroscopic data proved that the peroxo routes lead to supported molybdenum oxide zones in restricted size due to the porous structure of the silica supports with the presence of mononuclear oxidoperoxo species. Catalytic studies on the epoxidation of cyclooctene with anhydrous TBHP showed high conversions (> 90% in 3 h at 40 °C). Sterically more demanding (+)-(*R*)-limonene was epoxidized with good regioselectivity for the monoepoxides, too.

Gonçalves et al. described the grafting of 4,4′-dimethyl-2,2′-bipyridyl groups on mesoporous MCM-41, which is of importance not only for epoxidation catalysis. The chelate ligand 2,2′-bipyridyl is well known to bind to a variety of catalytically active transition metal complexes, among them oxidomolybdenum(VI) species.[34] 4,4′-Dimethyl-2,2′-bipyridine was deprotonated at one of the methyl groups by treatment with LDA (LDA = lithium diisopropylamide) and then reacted with surface-grafted ω-chloropropanyl units (Scheme 4). Spectroscopic data revealed that instead of the favoured system MoO_2Cl_2(N-N), unidentate bridged entities of the type O_2Mo-X-MoO_2 with a metal-metal distance of 3.28 Å were obtained. Catalytic results showed a high initial reaction rate for cyclooctene epoxidation followed by a sudden drop in activity due to the competitive inhibition by the by-product *tert*-butyl alcohol. Besides, catalyst reuse studies showed a drastic decrease in activity/selectivity. For instance, the initial activity in the first run (40 $mmol\,g^{-1}\,h^{-1}$) decreased to <1 $mmol\,g^{-1}\,h^{-1}$ in the second run due to pronounced leaching of molybdenum. Thus the observed activity was attributed to the presence of leached species. The authors concluded that the leached molybdenum species derive from the immobilized dimeric species, which were weakly bound to the lattice.



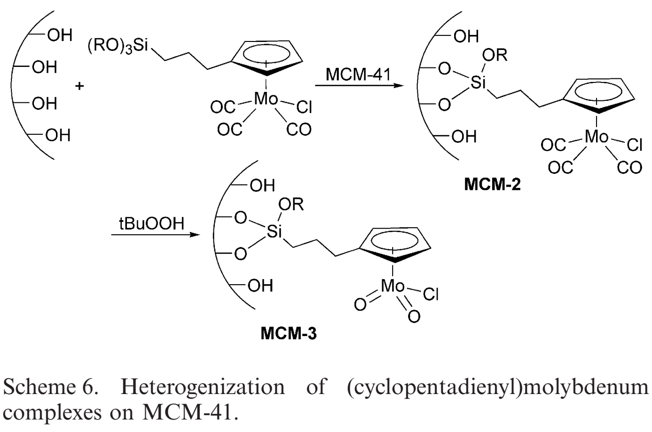
Scheme 4. Heterogenized bipyridyl groups on mesoporous MCM-41.

Dioxidomolybdenum(VI) complexes of the type [MoO_2Cl_2(L-L)] bearing a bidentate 1,4-diazabutadiene ligand of the type $(OEt)_3Si–(CH_2)_3N=C(Ph)–C(Ph)=NR$ immobilized on mesoporous MCM-41/48 were also reported by Gonçalves et al.[35] These catalysts showed high activities/selectivities in the cyclooctene epoxidation, comparable to the data of the analogous homogeneous molybdenum complex. Alternatively, these catalysts were obtained by a stepwise approach via grafting of the ligand followed by immobilizing the oxidomolybdenum species and silylating residual Si–OH groups (Scheme 5). Both catalysts exhibited similar activities. However the epoxide selectivity obtained for the latter method was lower than for the first one which was attributed to traces of HCl remaining after the surface silylation which enhance the epoxide cleavage. The catalysts were also found to be active in the epoxidation of other olefins. The activity decreased in the order cyclooctene > cyclododecene > α-pinene.



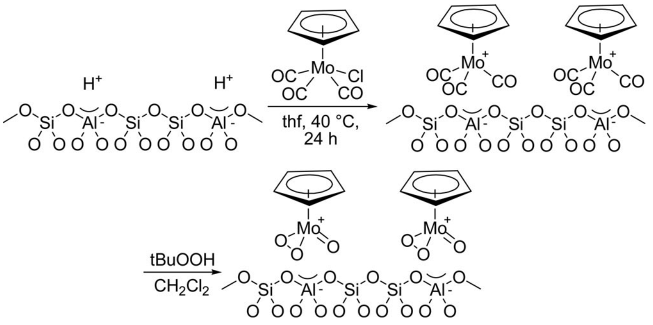
Scheme 5. Heterogenized dioxidomolybdenum(VI) complexes containing the bidentate 1,4-diazabutadiene ligand immobilized on mesoporous MCM-41/48.

The incorporation of cyclopentadienyl molybdenum complexes in mesoporous materials was reported by Gonçalves et al. Cyclopentadienyloxidomolybdenum complexes (η^5-$C_5H_4RMoO_2Cl$), being isoelectronic to MoO_2X_2(L-L) were generated on MCM-41 by the oxidative decarbonylation of covalently tethered η^5-$C_5H_4RMo(CO)_3Cl$ (Scheme 6).[36] The modified MCM-2 and MCM-3 as well as the homogeneous catalyst were tested in the liquid phase cyclooctene epoxidation with TBHP at 55 °C. Interestingly, MCM-2 and MCM-3 exhibited similar initial activities (12–13 $\mathrm{mol\,mol_{Mo}^{-1}\,h^{-1}}$) which proves that the in-situ oxidative decarbonylation of MCM-2 by TBHP is fast and produces MCM-3. The catalysts were also active in the epoxidation of cyclododecene and *trans*-2-octene (ca. 35–60% of conversion) whereas 1-octene exhibited negligible activity (<1%). However, both the catalysts showed an induction period in the second and third run which the authors attributed to the formation of inactive peroxo complexes of the type [$Cp^*MoO(O_2)Cl$].



Scheme 6. Heterogenization of (cyclopentadienyl)molybdenum complexes on MCM-41.

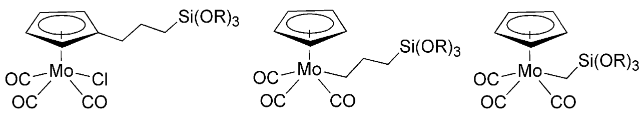
As reported by Kühn et al. η^5-$CpMo(CO)_3Cl$ can be grafted on H-β and H-Y zeolites by exchange of chloride ligand.[37] By spectroscopic methods, the heterogenization of the molybdenum complexes inside the pore channels of the zeolites could be confirmed, the formation of molybdenum oxide clusters could be excluded. To transfer the molybdenum species from Mo^{II} to Mo^{VI}, the material was treated with TBHP. The disappearance of the CO bands was followed by FT-IR, new absorptions at 918 and 966 cm^{-1} appeared confirming the formation of oxido and peroxo species (Scheme 7). The heterogenized catalysts showed 98–100% cyclooctene conversion with 80–100% selectivity after 24 h under a catalyst:oxidant:substrate ratio of 1:700:350 and 1:300:150 for the molybdenum complex heterogenized on H-β and H-Y zeolites. However, compared to the homogeneous system, the catalysts encapsulated in the zeolite showed decreased TOFs, indicating that a diffusion limitation exists due to the small zeolite pore channels.



Scheme 7. Immobilization of cyclopentadienylmolybdenum complexes on solid zeolites.

Therefore, Kühn et al. grafted $CpMo(CO)_3Cl$ on mesoporous Si-MCM-41/48 and Al-MCM-41/48 materials by the reaction of the chloro ligand with the surface hydroxy groups of the mesoporous solids.[38] As already mentioned, $CpMoO_2Cl$ is known as a highly efficient homogeneous catalyst for olefin epoxidation with TBHP. The corresponding $CpMo(CO)_3Cl$ complex shows similar activities, since this complex is readily oxidized to give $CpMoO_2Cl$ in the presence of TBHP. Furthermore, it is less sensitive towards oxygen and moisture than $CpMoO_2Cl$. Grafting on the aluminium-containing mesoporous material resulted in higher molybdenum loadings than grafting on neat silica. These "surface organometallic catalysts" utilized in the epoxidation of cyclooctene yielded cyclooctene epoxide as the sole product with TOFs exceeding 4000 h^{-1}, similar to the homogeneous counterpart. This demonstrates the absence of diffusion limitations inside the mesopore channels. Leaching experiments proved that the activity results from truly heterogenized catalysts, the catalysts were recyclable for four runs. The higher activity of the Al-MCM-41/48 supports was dedicated to an enhanced Lewis acidity compared to the neat silica material.

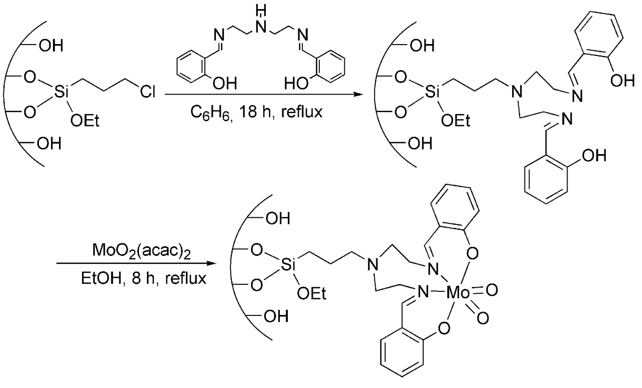
Tricarbonylcyclopentadienylmolybdenum complexes containing siloxane groups either attached at the cyclopentadiene ligand or directly at the molybdenum centre, grafted on MCM-41/48 were also reported as active and robust catalysts (TOF: 2900–10200, selectivity: 73–100%) for cyclooctene epoxidation with TBHP.[39] Alternatively, an in-situ synthesis of surface fixed $CpMoR(CO)_3$ by the first treating the support with $(OR)_3Si(CH_2)_3Cl/(OR)_3SiCH_2Cl$ followed by reaction with $Na^+[CpMo(CO)_3]^-$ was presented. Structural characterization proved the retention of the *meso*-structural ordering after the organic modification whereas FT-IR data of the heterogenized molybdenum complexes before and after treatment with TBHP confirmed the oxidative conversion of the Mo–CO groups into the catalytically active Mo=O species. The authors concluded that the direct grafting of the metal complexes is more efficient in terms of Mo loading and catalytic activity (95–100% conversion) than the two-step grafting method (65–68% conversion). In particular, the material having the longer hydrocarbon bridge between the Mo centre and the surface Si–O groups reduces the influence of electron donor abilities of the surface on the Lewis acidity of catalytic centres and showed high catalytic activity (Scheme 8). The catalyst, however, displayed decreased activity during recycling which was attributed to the formation of coke and to chemisorption of organic molecules on the surface.



Scheme 8. Siloxane-functionalized organometallic molybdenum precursors used for grafting reactions.

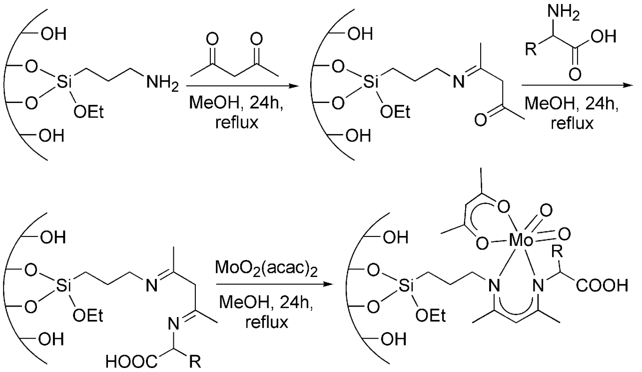
Maiti et al. opened up a different approach to heterogenize single-site molybdenum catalysts. They reported the immobilization of oxidodiperoxo(8-quinolinol)molybdenum(VI) complexes in MCM-41 without the usage of a linker.[40] Two different compounds were screened: the neutral complex $MoO(O_2)_2(QOH)_2$ (QOH = 8-quinolinol) and an anionic oxidodiperoxo-8-quinolinolatomolybdate(VI) system. The immobilized catalysts showed excellent catalytic activities and recycling abilities (six times), much better than their homogeneous counterparts. Here $H_2O_2/NaHCO_3$ was used as the oxidizing agent. Epoxystyrene was formed with >95% of conversion and >75% of epoxide selectivity after 20 h (TON > 1500). The authors noted that the heterogeneous catalysts were equally effective in the epoxidation of other olefins such as 1-octene, 9-decen-1-ol and norbornene. The oxidizing agent generates peroxymonocarbonate (HCO_4^-), which is more nucleophilic than H_2O_2 and thus speeds up the reaction.

Masteri-Farahani et al. reported the condensation of *N*,*N*′-bis(3-salicylidenaminopropyl)amine (salpr) with chloropropyl modified MCM-41 to obtain a salpr modified mesoporous material.[41] The salpr/MCM-41 material was then reacted with $MoO_2(acac)_2$ to produce MoO_2(salpr)/MCM-41 as shown in Scheme 9. The obtained materials catalyze the epoxidation of 1-hexene, 1-octene, cyclohexene and cyclooctene with TBHP to yield 95–99% selectivity for the corresponding epoxides. Cyclohexene and cyclooctene give higher activities (TOF: 16–59 mol mol^{-1} h^{-1}) than linear olefins. The observed catalytic activity arises from truly heterogeneous reaction.



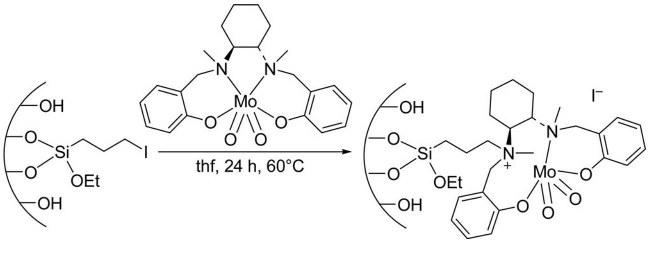
Scheme 9. Heterogenization of Mo(salpr) complexes on MCM-41.

The same group also reported the condensation of acetylacetone with aminopropyl groups grafted on MCM-41 giving Schiff bases, which were further reacted with amino acids to form heterogenized *N*,*N*′-bidentate ligands.[42] Complexation of these Schiff-base ligands with $MoO_2(acac)_2$ resulted in heterogenized epoxidation catalysts (Scheme 10). Kinetic studies with TBHP as the oxygen source showed decreasing activities in the order cyclooctene > cyclohexene > 1-hexene > 1-octene and the catalytic activities varied with the nature of the groups R. Bulky R groups, such as $–CH_2C_6H_5$ or $–CH_2CH(CH_3)_2$ for instance, gave higher conversions than smaller ones. The stability of the catalyst was examined by hot filtration studies and the reuse of the recovered catalyst confirmed the heterogeneous nature of the molybdenum based catalysts.



Scheme 10. Heterogenization of *N*,*N*′ bidentate Schiff-base ligands on mesoporous MCM-41.

Asymmetric catalysis is a powerful method to produce a single enantiomer of a chiral compound. Enantioselective epoxidation of unfunctionalized olefins is known to be a difficult task. Kühn et al. reported the heterogenization of achiral and chiral dioxidomolybdenum(VI) complexes bearing hydrosalen ligands on MCM-41/48.[43] One of the amino units of the complex was treated with iodosilane modified MCM-41/48 to yield the desired catalyst (Scheme 11). Recycling experiments proved that leaching is negligible for this system. The conversion as well as the asymmetric induction was better for *cis*-configured than for the *trans*-configured substrates. For instance, ca. 21% *ee* and 36–46% of conversion were noted for *trans*-β-methylstyrene while *cis*-β-methylsytrene gave ca. 31% *ee* and 27–55% of conversion at room temperatures. A series of other chiral heterogenized hybrid catalysts designed for asymmetric olefin epoxidation are beyond the scope of this system.[16] The activation barrier for the oxygen transfer is quite high, preventing the epoxidation reaction to be carried out at low temperatures, which should give a better transfer of the stereo information.

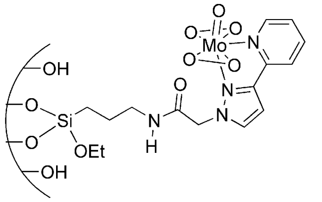


Scheme 11. Heterogenization of chiral dioxidomolybdenum(VI) complexes on MCM-41/48.

During the last years our group was engaged to elucidate the mechanism of the olefin epoxidation with seven-coordinated oxidodiperoxomolybdenum complexes $MoO(O_2)_2$(L–L) (L-L = pyrazolylpyridine ligand).[44] Detailed NMR experiments, quantum chemical calculations and kinetic studies revealed that the catalytic cycle includes a partial dissociation of the chelate ligand from the molybdenum centre wherein the complexes do not transfer oxygen from one of the η^2-O_2 ligands or by precoordination of the olefin to molybdenum as postulated in literature. Instead they activate the oxidising agent ROOH. Based on these results we were able to draw a new mechanism wherein the oxidising agent coordinates to the Mo^{VI} centre undergoes a proton transfer to one of the peroxo ligands and is activated for oxygen transfer by η^2 coordination.[45] Since the complete dissociation of the ligand is energetically unfavourable in non-polar solvents these catalysts rely as good candidates for the heterogenization on various solid supports.

In most of the above cited literature reports it is noted that the activity of catalyst gets decreased from the first to the second run and thereafter remains more or less constant. This is typical for an undesired (partial) adsorption/entrapment of the active species on the support, being leached during the first run. To overcome this, pre-formed silyl-functionalized catalysts can be used for grafting. Of course the overall stability of the heterogenized catalyst also depends on strength of the metal ligand interaction.

Opting a post synthesis grafting method, we reported the synthesis of an organic-inorganic hybrid catalyst by covalent anchoring of the oxidodiperoxomolybdenum complexes (L–L)$MoO(O_2)_2$ {L-L = (3-triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide} (Scheme 12) on neat Si-MCM-41 and an aluminium-doped Al-MCM-41.[46] Structural and spectroscopic characterization techniques confirmed that the structure of both the mesoporous material and heterogenized complex was preserved after the grafting reaction. The hybrid materials were tested as catalysts for the cyclooctene epoxidation with *t*BuOOH at 61 °C. The data proved that these catalysts are highly active and selective (100% conversion and epoxide selectivity). Gonçalves et al. recently also noted that molybdenum complexes bearing substituted pyrazolylpyridine ligands are approximately one order of magnitude more active than similar compound derived from 2,2′-bipyridine.[47]



Scheme 12. Oxidodiperoxomolybdenum complex grafted on MCM-41.

Interestingly, the Al-MCM-41 support gave higher activity than the corresponding neat silica materials, which we address to the higher Lewis acidity of Al-MCM-41. This may influence the activation of *t*BuOOH for the proton transfer or directly the catalytically active site by interaction with the oxido or the peroxo ligands. The catalytic properties (activity and recyclability) of the supported materials were improved by silylation with Me_3SiCl to remove residual surface Si-OH groups. They are active centres for the adsorption of polar organic compounds present in the reaction mixture such as *t*BuOOH, *t*BuOH, epoxide. Silylation makes the supports surface hydrophobic and improves its stability against moisture and mechanical stress.

As mentioned in introduction, the post synthesis grafting method is easy to perform but the distribution of organic groups is not uniform inside the pore channels. To overcome this problem, we developed an organic-inorganic hybrid mesoporous MCM-41 material by co-condensation of TEOS and the silylated chelate ligand in the presence of CTAB as template.[48] The epoxidation catalyst was obtained by introducing $MoO(O_2)_2$ into this hybrid material and used for the liquid phase epoxidation of cyclooctene with *t*BuOOH. This novel hybrid catalyst synthesized by a co-condensation process showed excellent activity (TOF = 71–102), selectivity (100%) and stability. The high stability of this catalyst was attributed to the strong covalent linkage between the organic ligand and the inorganic mesoporous materials and to the strong binding between the $MoO(O_2)_2$ unit and the chelating ligand.

Noting the excellent catalytic activity of the heterogenized oxidodiperoxomolybdenum catalysts we evaluated some hybrid organic-inorganic materials containing the chelate ligand. They were synthesized by a sol-gel co-polymerization with TEOS in the absence of the template CTAB.[49] Usually, an acid or base catalyst is required for the sol-gel polymerization of TEOS with $RSi(OR')_3$. Due to the presence of basic pyridine and/or pyrazole groups in the ligand it also catalyzes the co-condensation process to form the hybrid material SG-1. Other hybrid materials (SG-2 and SG-3) were obtained by using $Et\text{-}NH_2$ or a HCl + $EtNH_2$ mixture as the catalyst. SG-1 displayed isotherms typical for mesoporous materials (surface area: $138\ m^2 g^{-1}$) while SG-2 and SG-3 possess only low surface areas of $< 5\ m^2 g^{-1}$ and $43\ m^2 g^{-1}$, respectively. The epoxidation catalysts were subsequently obtained by treatment of the supports with $MoO(O_2)_2(dmf)_2$. They were tested for the epoxidation of cyclooctene with *t*BuOOH at 61 °C. Kinetic profiles showed that Mo-SG-3 catalysts gives higher reaction rates than Mo-SG-1 although the molybdenum content is almost similar. As expected, the activity of Mo-SG-2 is low due to the low loading of molybdenum sites arising from the low BET surface area of SG-2. Leaching tests showed a complete different behaviour of the three catalysts: Mo-SG-1 is truly heterogeneous, Mo-SG-2 is partly homogeneous and Mo-SG-3 is almost completely homogeneous, which means that in this case the oxidodiperoxomolybdenum species are solely adsorbed on the silica surface of the support and get leached with *t*BuOOH. Schuchardt et al. found a similar behaviour for $MoO_2(acac)_2$ on silica.[50]

Since the linkage of a catalyst to an organic support relies on strong C–C, C–N or C–O bonds, it is less sensitive against cleavage than a Si–O–Si linkage to a silica support. We therefore investigated a polystyrene resin functionalized with oxidodiperoxopyrazolpyridinemolybdenum(VI) units for the epoxidation of cyclooctene.[51] While the homogeneous analogue is quite reactive (TOF: $703\ mol\,mol^{-1} h^{-1}$ for cyclooctene epoxidation with *t*BuOOH), the polymer bound system only shows poor activity (TOF: $33\ mol\,mol^{-1} h^{-1}$), which we attributed to the hindered diffusion of the substrates and products in the cavities of the polymer support.

From the results discussed above it is clear, that removing residual Si–OH groups on the support by silylation will enhance the stability of the material and facilitate the regeneration. This prompted us to investigate the heterogenization of oxidodiperoxomolybdenum catalysts on hydrophobic "periodic mesoporous organosilicas" (PMOs). Catalysts of the type $(L\text{-}L)MoO(O_2)_2$ were tethered on hydrophobic PMOs derived from phenylene (BMo) and ethylene (EMo) bridged silsesquioxane precursors.[52] The PMO catalysts were tested for the cyclooctene epoxidation at 60 °C in the presence of 1 mol-% of catalyst with different solvents ($CHCl_3$, $C_6H_5CH_3$, CH_3CN) and oxidizing agents (70% *t*BuOOH in H_2O, H_2O_2). The yields were solvent and oxidant dependent: a combination of $CHCl_3$ and *t*BuOOH gave the best conversions with nearly 100% selectivity for epoxycyclooctane. Interestingly, under identical reaction conditions, BMo/H_2O_2 converts cyclooctene to about 60% yield after 6 h, while EMo gives only 30% and MMo shows an almost negligible conversion of 6%. This effect, which is observed less pronounced for 70% *t*BuOOH in H_2O too, is assigned to the differences in hydrophobicity of the materials. The unique hydrophobic pores of the BMo material facilitate the adsorption of olefins close to the active sites and/or reduce the adsorption of the more polar epoxide and the by products (*t*BuOH or H_2O). Recycling studies further supported the truly heterogeneous nature of the supported catalysts.

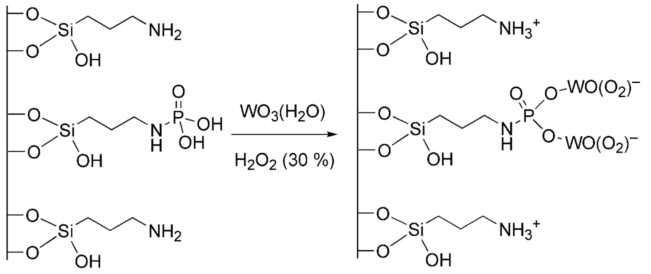
The catalyst system shown in Scheme 12 can also be combined with iron oxide nanoparticles. This allows the simple and efficient separation of the catalyst from the reaction mixture by application of an external magnetic field. For this purpose we used magnetic nanoparticles of approximately 10 nm diameter which were subsequently coated with a dense silica layer of 50 nm thickness. For the grafting on the surface we again used the {(3-triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide} ligand.[53] A series of olefins were tested as substrate for this system all giving high yields of the corresponding epoxide. The catalyst is reusable for at least six times with just a minimum loss of activity.

Tungsten

As molybdenum, tungsten also displays high activities in homogeneous epoxidation reactions, the reaction mechanisms can be considered to be mainly similar, activity differences of structural identical complexes should arise from the different Lewis-acidities of the two elements. However, it must be mentioned, that for heterogenized tungsten catalysts, leaching of the active sites is frequently observed. Even though, a series of quite active and stable heterogeneous tungsten based epoxidation catalysts have recently been reported. These publications include tungsten oxide-containing mesoporous materials, heterogenized polyoxotungstates and tungsten complexes, as well as tungstate-exchanged layered double hydroxides.

Strukul et al. reported a series of mesoporous mixed tungsten/silica oxides prepared by sol-gel methods under basic conditions,[54] which turned out to be active for the selective epoxidation of allylic alcohols with hydrogen peroxide. The excellent catalytic properties of these materials can be related to the preparation method allowing the formation of amorphous WO_3 entities, which are well dispersed and tightly bound to the silica matrix. Koo et al. obtained nanosized WO_3 particles supported on mesoporous MCM-48 which are highly efficient and selective heterogeneous catalysts for olefin epoxidation, the oxidation of sulfides and the Baeyer–Villiger oxidation of cyclic ketones with hydrogen peroxide or peracetic acids. Their catalytic activities depend on the nature of the supports and the particle size of WO_3.[55] Gao et al. found that mesoporous WO_3/MCF materials show good activity and recyclability in the epoxidation of cycloocta-1,5-diene again with hydrogen peroxide, which is mainly attributed to the presence of isolated tungsten species anchored on the support through W–O–Si covalent bonds.[56]

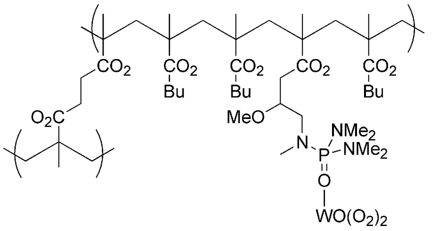
By selecting different supports (resins or mesoporous silica) and linkers, a variety of heterogenezied polyoxotungstates or tungsten complexes were prepared and tested as catalysts for epoxidation reactions. Jacobs et al. for instance, introduced different tungsten based catalysts into either macroreticular resins or siliceous materials via ion-exchange or covalent immobilization (Scheme 13).[57] These catalysts are capable to epoxidize a broad variety of olefins with H_2O_2 in a heterogeneous way, tungsten leaching could be limited to less than 2% of the total amount of tungsten.



Scheme 13. Anionic oxidodiperoxotungsten complexes grafted on functionalized silica.

By using a similar approach, Liu et al. reported that the tungsten peroxo compound $HPO_4\{W(O)(O_2)_2\}_2$ could be introduced onto the surface of a mesoporous HMS material by reacting the functionalized support HMS–$(CH_2)_3NH(PO_3H_2)$ with $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$.[58] Subsequently palladium ions were exchanged into the channels of the HMS support to form the final catalyst, which was active in the epoxidation of propylene in methanol using O_2 as an oxidant to produce propylene oxide in 83% selectivity and with 34% conversion. The active components, palladium and tungsten, did not leach into the reaction medium, and the catalyst could be reused.

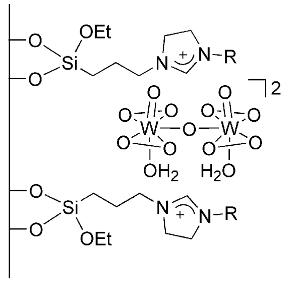
Gelbard et al. reported that aminophosphorylated polymethacrylate is a remarkable polymeric ligand for coordination to peroxotungstic species (Scheme 14). The resulting hybrid material is a highly active and stable heterogeneous catalyst for the epoxidation of cyclohexene with hydrogen peroxide.[59]



Scheme 14. Oxidodiperoxotungsten complex grafted on a functionalized polymethacrylate support.

Recoverable and reusable dendritic polyoxotungstate complexes, wherein the tungsten species are linked to the dendrimeric supports by ionic interaction, were synthesized by Astruc et al. These systems have been characterized by AFM (AFM = atomic force microscopy) and were used for the catalytic epoxidation of cyclohexene with hydrogen peroxide.[60]

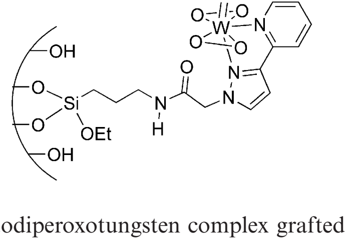
Mizuno et al. immobilized the dinuclear peroxotungstate anion $[\{WO(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$ by anion exchange on a silica support modified by an dihydroimidazolium based ionic liquid (Scheme 15) leading to a heterogeneous system for the epoxidation of a variety of commercially interesting alkenes.[61] High epoxide yields were obtained using 0.2 equiv. of 30% H_2O_2 in acetonitrile at 60 °C. Furthermore, this catalyst can easily be recovered by filtration and reused at least three times without loss of catalytic activity and selectivity. In a subsequent work by the same group, an analogous strategy was used to immobilize the polyoxometalate anion $[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$ on a silica support.[62] The resultant catalyst is capable to heterogeneously oxidize a broad range of olefins and sulfides with high selectivity at room temperature.



Scheme 15. Anionic dimeric oxidodiperoxotungsten complexes grafted on a IL-functionalized support.

Tilley et al. prepared a heterogeneous hybrid catalysts by grafting the tri(alkoxy)siloxy complexes $MO[OSi(OtBu)_3]_4$ (M=Mo, W) on mesoporous SBA-15 silica via displacement of one of the $-OSi(OtBu)_3$ ligands by a siloxy group from the silica surface.[63] The catalytic activities of these catalysts are generally low, but depending on the active sites and the oxidizing agent, they show pronounced differences in the selectivity during the oxidation of cyclohexene: with *t*BuOOH as the oxidizing agent, the tungsten and the molybdenum complex lead to the epoxide with almost perfect selectivity. Using hydrogen peroxide leads to the additional formation of cyclohexenone/cyclohexenol, especially for the molybdenum catalyst.

We recently started to transfer our experiences in oxidodiperoxomolybdenum chemistry to the analogous tungsten system. Following the route described in ref.[46] a hybrid mesoporous SBA-15 catalyst containing an oxidodiperoxotungsten complex of the type $WO(O_2)_2$ L (L = pyrazolylpyridine) could be synthesized by a post-grafting process (Scheme 16).[64] This catalyst shows good activity and recoverability for the epoxidation of cyclooctene with H_2O_2



Scheme 16. Oxidodiperoxotungsten complex grafted on SBA-15.

as the oxidant under mild conditions. No apparent leaching of the active tungsten species could be detected under optimized reaction conditions.

Similarly Masteri-Farahani et al. could synthesize heterogenized dioxidotungsten catalyst of the type WO_2-(salpr)/MCM-41 by repeating the process published for molybdenum[41] with an appropriate tungsten precursor.[65] However, here *t*BuOOH is used as the oxidizing agent as for molybdenum. The authors do not comment on the activation of hydrogen peroxide with the tungsten system.

A series of differently functionalized silica supports bearing cationic groups such as $–NH_3^+$, $–NEt_3^+$, $–NC_5H_5^+$, and $–PPh_3^+$ were used for the heterogenization of $[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]^{2-}$ by Fraissard et al.[66] The influence of different surface lipophilicities on the catalytic activities in the epoxidation of cyclooctene and (*R*)-limonene with H_2O_2 in *t*BuOH was followed. Catalysts with low densities of organic functions and hydrophilic surfaces were easily deactivated. End-capping improved their stability but decreased their activity. Catalysts with dense coverage of onium groups and the active site in a hydrophobic chloropropyl environment gave high activity and excellent recycling stability.

Tungsten hexacarbonyl immobilized on cross-linked polystyrene was reported as a catalyst precursor for olefin epoxidation by Tangestaninejad et al.[67] It turned out, that in this case, hydrogen peroxide in acetonitrile solution gave the best results. The catalyst could be reused up to ten times for the epoxidation of cyclooctene.

Jacobs et al. reported that tungstate-exchanged (Ni,Al) layered double hydroxides can be used as active heterogeneous catalyst for mild oxidative bromination and bromide-assisted olefin epoxidation with H_2O_2.[68] They found that bromide-assisted epoxidation is characterized by much higher turnover frequencies than classical tungsten-catalyzed epoxidations.

In a recent work reported by De Vos et al. a tungstate-exchanged layered double hydroxide of the Takovite type, was applied as a heterogeneous catalyst in the bromide-assisted epoxidation of terpenic olefins using H_2O_2 as environmentally benign oxidant.[69] The bromide-assisted oxidation shows very interesting chemo-selectivity for various substrates with unique regio- and stereoselectivity often opposite to that of many traditional methods. Moreover, this tungstate-exchanged takovite catalyst was found to be stable under reaction conditions and recyclable.

Manganese

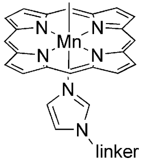
There are four main types of manganese-based catalysts for olefin epoxidation differing in the coordination environment. Manganeseporphyrin complexes have probably made the longest career in this field. Thus a whole series of such system has been functionalized for anchoring on solid supports.

Moghadam et al. recently reported the biomimetic epoxidation of alkenes catalyzed by tetrakis(*p*-aminophenyl)porphyrinatomanganese(III) chloride grafted covalently on functionalized multi-wall carbon nanotubes (MWCNT).[70] They used $NaIO_4$ as the oxidant and could reuse the catalyst for several times without significant loss of catalytic activity. Surface –COOH groups were activated and reacted with the amine function of the porphyrin ligand resulting in stable amide bonds, which did not undergo hydrolysis under the given reaction conditions.

A different approach was chosen by van Koten et al. who used "click" chemistry to graft the manganese complex of tetrakis(4-[(trimethylsilyl)ethynyl]phenyl)porphyrin on azide-functionalized SiO_2.[71] The resulting material was investigated for its activity in the catalytic olefin epoxidation with various oxidants (iodosylbenzene, *tert*-butylperoxide). The authors found that the heterogenized system was less active than its homogeneous congener (TOFs: 82 h^{-1} vs. 230 h^{-1}) and even lost activity when being recycled, which was not assigned to a degradation of the catalyst itself but to a chemical and mechanical degradation of the silica support.

Instead of using covalent bonds for anchoring the porphyrin to the support, Rahiman et al. grafted a cationic [*meso*-tetrakis(4-trimethylammoniophenyl)porphyrinato]-manganese(III) species on Al-MCM-41 and V-MCM-41 by ionic interactions and applied this material for the epoxidation of cyclohexene and styrene with PhIO as oxygen source.[72] Pronounced effects of the support have been observed, which were explained with the different acidities of the supports. Increasing the Al or V content of the support allows to increase the porphyrin loading and thus the catalytic activity of the heterogeneous systems. However, in this case the catalytic activity of theses systems also decreases after recycling, which is attributed to catalyst leaching and/or decomposition of the porphyrin complex. Moghadam et al. chose a similar approach and introduced quaternized tetra(4-pyridyl)porphyrinatomanganese(III) for ionic grafting.[73]

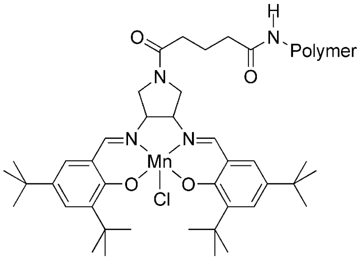
A further way to graft manganese(III) porphyrin complexes on solid supports is given by the coordination of surface bound ligands to the sixth co-ordination site of the manganese centre (Scheme 17). This feature was used to anchor these catalysts onto imidazole modified silica and polystyrene.[74] The resulting catalysts were described as stable and recyclable.



Scheme 17. Manganese porphyrin complexes grafted by using imidazole-functionalized supports.

The most important type of manganese-derived epoxidation catalysts was developed by Jacobsen et al. in the 1990s.[75] It allows the enantioselective epoxidation of aromatic olefins with a series of different oxygen donors (Na-

OCl, hydrogen peroxide, *N*-methylmorpholine *N*-oxide, PhIO, etc.). It is therefore not surprising, that a series of papers on the heterogenization of such systems was published during the last decade. Therein a whole bunch of methods is described, starting from heterogenization on polymers.[76] This approach was successfully used by Song et al., who coupled a chiral salen ligand to the NovaSyn® TG amino resin LL (Scheme 18) and achieved excellent enantioselectivity of up to 95% and yields of epoxides of up to 96% with NaOCl/PPNO as the oxidant [PPNO = (4-phenylpyridine *N*-oxide)].[77] However, the polymer-bound catalyst underwent partial decomposition under the epoxidation conditions.



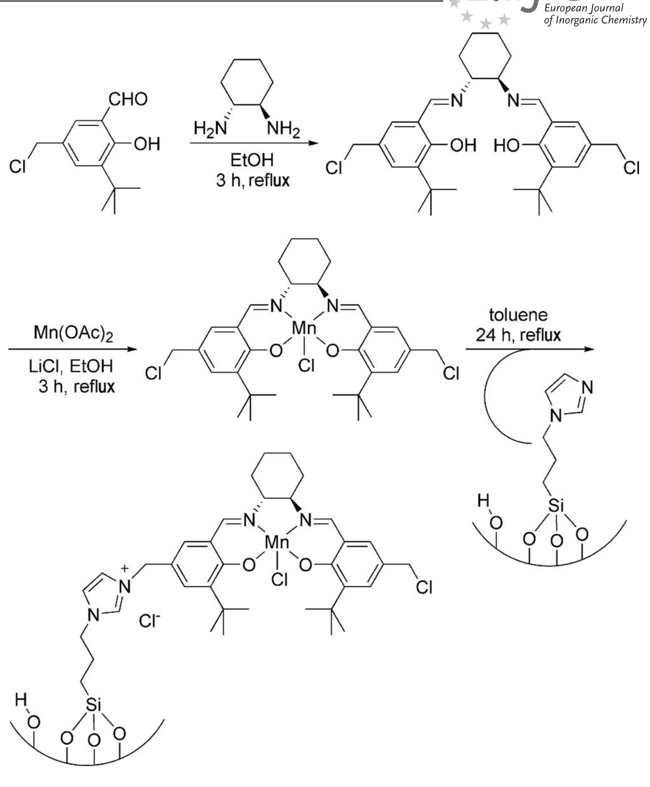
Scheme 18. A chiral manganese salen complex coupled to an amine-functionalized resin.

Liu et al. were able to heterogenize Jacobsen's catalyst on MCM-41 starting from 3-*tert*-butyl-5-chloromethyl-2-hydroxybenzaldehyde, which gave by condensation with enantiomerically pure *trans*-1,2-diaminocyclohexane a twofold chloromethyl-functionalized salen system.[78] After the introduction of the manganese(III) site, the catalyst was coupled with imidazole-functionalized MCM-41 and SBA-15 supports (Scheme 19). The catalyst was evaluated for the asymmetric epoxidation of unfunctionalized olefins with *meta*-chloroperoxybenzoic acid as the oxidant, wherein it showed high conversions of the substrates and substrate dependent medium to high enantioselectivities. They could be recycled five times without loss of activity.

A similar approach was used by Jasra et al., who succeeded in coupling a monofunctionalized salene system to aminopropyl-functionalized MCM-41 (50 Å) and SBA-15 (75 Å).[79] The catalyst immobilized in SBA-15, possessing the larger pore diameter was found to be more active. In general, the heterogenized catalysts turned out to be more stable than their homogeneous counterparts and sometimes gave higher enantioselectivities.

Li et al. heterogenized a chiral manganese salen catalyst on silica, MCM-41 and SBA-15 by exchanging the chloro ligand at the manganese site against a silica bound phenyl sulfonic group.[80] For *cis*-methylstyrene as the substrate, the heterogenized catalysts gave mainly the *cis*-configured product in contrast to the homogeneous system. It also exhibited stereo inductions for the *cis*-product, being remarkably higher than those of the homogeneous system. However, for the minor *trans*-configured product, an opposite behaviour was found.

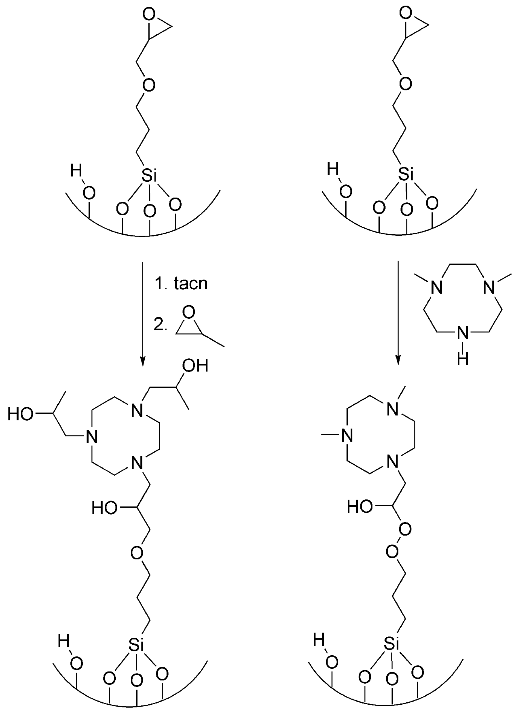
These are just a few examples of heterogenized chiral Jacobsen type manganese salen catalysts with inorganic supports. A whole series of related system had been published in the literature during the last years.[81] In general, one can consider, that the activity and the stereo inductions of such systems are high and that catalyst degradation plays a minor role as compared to homogeneous Jacobsen type catalyst.



Scheme 19. Covalent grafting of a manganese salen catalyst to imidazole-functionalized MCM-41 and SBA-15.

In the 1990s a series of publications on the usage of novel manganese complexes for oxidation reactions and bleaching appeared in the literature.[82] Common to these catalysts are ligands derived from facially co-ordinating 1,4,7-triazacyclononane (tacn) system. In 1996 Bein and DeVos succeeded to encapsulate a manganese 1,4,7-trimethyl-tacn complex in a NaY zeolite.[83] They found clean epoxidation of styrene and cyclohexene with hydrogen peroxide as the oxygen source and acetone as the solvent. Compared to the reactivity of this catalyst in solution, a dramatically reduced tendency to decompose hydrogen peroxide was observed, which was explained with the site isolation of the catalyst embedded inside the cavities of the zeolite. These findings induced further investigations mainly devoted to the group of De Vos and Jacobs, who were able to heterogenize manganese tacn catalysts via a glycidol linker on silica surfaces by applying two different methods (Scheme 20).[84]

For the *N*-methyl-functionalized system (see Scheme 20, right) they found that the yields based on the peroxide consumption were around 50%, and the yield based on the substrate (styrene) was at 82% in acetone as the solvent. This catalyst exhibited high turnover frequencies, much higher than those of analogous systems in which the ligand bears 2-hydroxyalkyl side chains (see Scheme 20, left).

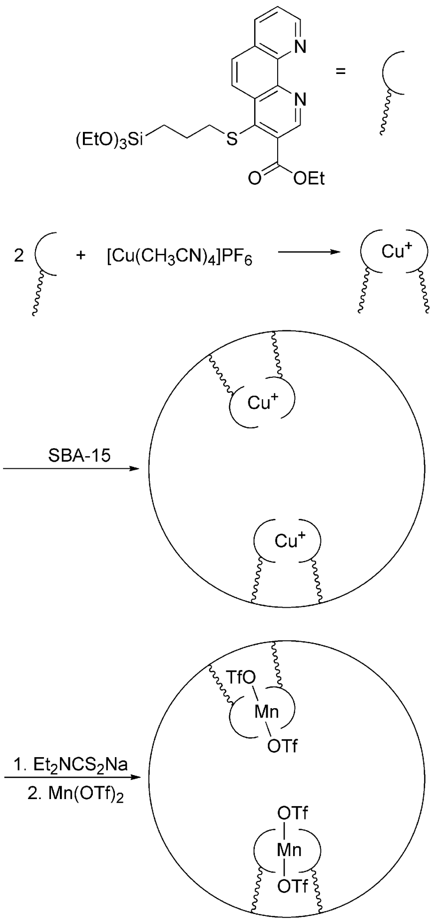


Scheme 20. Covalent grafting of tacn ligands on silica surfaces by using a glycidol linker.

While a homogeneous manganese *N*,*N*′-dimethyl-tacn catalyst was inactive in the epoxidation of 1-hexene, the heterogenized system was able to convert this weakly activated olefin to 1,2-epoxyhexane. This again supports the idea that binuclear pathways for hydrogen peroxide decomposition are unimportant for heterogenized manganese tacn catalysts.

De Vos and Jacobs also investigated the epoxidation activities of bis(bipyridyl)manganese complexes encapsulated in the supercages of zeolites with hydrogen peroxide as the oxygen source and found a strongly reduced catalase activity (H_2O_2 decomposition) compared to the corresponding homogeneous system.[85] In 2006 Stack et al. took up these results again and investigated complexes of the type $[Mn(phen)_2](X)_2$ (X = weakly coordinating anion, phen = 1,10-phenanthroline). They found these systems to be highly active, homogeneous epoxidation catalysts with peracetic acids as the oxygen source.[86] They catalyze the epoxidation of unfunctionalized olefins as well as of α,β-unsaturated ketones and esters. However, in this homogeneous reaction still low catalyst loadings are required for high conversions, electron rich tri- and tetrasubstituted olefins are gradually degraded and *cis* olefins are partially isomerized to the *trans* epoxides.[87] These disadvantages can clearly be overcome by covalently grafting such manganese catalysts onto high-surface area, mesoporous SBA-15 silica by application of a metal-template/metal-exchange method (Scheme 21).

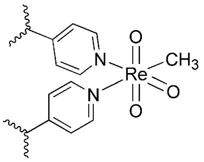
Olefin epoxidation with peracetic acid shows that these catalysts have an improved product selectivity for epoxides, a greater substrate scope, a more efficient use of oxidant, and a higher reactivity than their homogeneous analogues. Avoiding the template strategy generates manganese sites co-ordinated with just one phenanthroline ligand (the remaining coordination sites at Mn are covered by surface Si–O groups), which gives remarkably poorer results in olefin epoxidation.



Scheme 21. Synthesis of a grafted manganese phenanthroline catalyst by a template strategy.

Rhenium

In 1991, Herrmann et al. published a simple and efficient synthesis for methyltrioxidorhenium (MTO), which turned out to be highly active in the catalytic epoxidation of unfunctionalized olefins.[88] They claimed in a patent the heterogenization of MTO by usage of a series of polymers such as polypyridines, polyvinylpyrrolidone, and polyamides.[89] Unfortunately, only poor epoxide yields could be obtained and the polymer/MTO systems were not completely characterized. These problems were overcome by Saladino et al. who carefully investigated the heterogenization of MTO on crosslinked polyvinylpyridine and polystyrene.[90] The resulting polymeric catalyst were thoroughly investigated by means of IR spectroscopy, SEM imaging and especially wide-angle X-ray diffraction (WAXS) to determine the local geometry of the rhenium atom. In the polystyrene system, the rhenium centre is sixfold coordinated, with two *cis* positions occupied by pyridine donors (Scheme 22), as observed in low molecular coordination complexes of MTO, too.[91]



Scheme 22. Coordination of MTO in crosslinked polyvinylpyridine.

All these polymeric MTO systems were efficient and selective heterogeneous catalysts for the olefins epoxidation with environmentally friendly aqueous H_2O_2 as the oxygen source. The catalysts maintained their activity for at least five recycling experiments.

Novel heterogeneous aminated polystyrene and polyacrylate resins used as supports for MTO immobilization were reported by Gelbard et al.[92] They proved spectroscopically that the *N*-oxides of tertiary amines and pyridine can act as ligands for MTO anchoring onto polymeric resins. MTO immobilized on these oxidized supports was more stable against leaching than on non-oxidized supports.

Adam et al. succeeded in heterogenizing MTO in zeolites, which also dramatically increased the stability of the catalyst in the presence of aqueous H_2O_2.[93] It seems that the restricted volume of the cavities in such system hinders decomposition. A similar effect is addressed to the combination of urea and H_2O_2 as the oxygen source, where the helical urea channels may serve as an host confined stabilizing environment for MTO.[94] Grafting of organorhenium oxides was reviewed by Kühn et al.[95]

Conclusions

The above described series of examples highlights the high catalytic activity and selectivity of Mo-, W-, Mn- and Re-based catalyst systems for various industrially relevant epoxidation reactions. The activity, selectivity and stability were found to be extremely sensitive to the oxidant and solvents used as well as preparation procedures. Even though a myriad of heterogenized metal catalysts over porous solid supports were reported in due time, successful examples of highly, active, stable catalysts without significant leaching of metal/metal complexes and having long term stability however have yet not often been described in the literature for liquid phase epoxidation reactions. One probably outstanding example in this context was published by Arnold et al.[96] Because of the entirely different reaction conditions used, it often remains difficult to trace out a better epoxidation catalyst for a particular reaction and the heterogeneity tests needs to be conclusive. Meantime, the heterogenization of homogeneous catalysts over hybrid mesoporous materials can: (a) help to enhance the stability of the homogeneous catalysts and hence limit leaching under liquid phase reaction conditions, (b) help also to immobilize homogeneous catalysts without additional modifications of the homogeneous catalysts or the mesoporous support, (c) will enhance the selectivity of speculated products because of pore confinement effect and enhance higher catalyst turnovers brought about by the stabilization of the catalyst in the nanocages of the mesoporous supports and thus greater specificity for targeted reactions as compared to attachment over non-porous disordered silica supports, (d) the solid catalyst can be easily separated, regenerated and recycled and (e) various metal complexes can be immobilized in a similar way over the mesoporous supports for other important reactions like asymmetric epoxidation reactions.

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