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Review

Immobilization of organorhenium(VII) oxides

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Abstract

In the last decade considerable progress has been made in research on organorhenium(VII) oxide catalysts, particularly with respect to methyltrioxorhenium(VII) (MTO). Heterogeneous systems have been developed with particular emphasis on the supporting systems including inorganic and organic carrier materials. As a result efficient and reasonably selective catalysts are now available for a variety of catalytic reactions like olefin epoxidation in particular and other oxidation reactions, metathesis, etc. Besides the MTO/UHP system, polymer supports for the organometallic catalysts are now also successfully applicable. The systems exhibit in several cases the required properties of stability, selectivity, activity and recyclability.

Keywords: Catalysis; Heterogenisation; Immobilization; Oxidation; Rhenium

Contents

Abbreviations: Acac, acetylacetonate; bpy, 2,2′-bipyridyl; Cp, cyclopentadiene; dppa, bis(diphenylphosphino)amine; Et, ethyl; EXAFS, extended X-ray absorption fine structure; IR, infra red; MCM, mobile crystalline material; Me, methyl; MTO, methyltrioxorhenium; NMR, nuclear magnetic resonance; PBI, polybenzimidazole; PEO, polyethylene oxide; Ph, phenyl; PPO, polypropylene oxide; PS, polystyrene; PSHPAMP, polystyrene-divinylbenzene resin carrying an *N*-(2-hydroxypropyl)-2-aminomethylpyridine ligand; PVP, poly(4-vinylpyridine); PVPN, poly(4-vinylpyridine-*N*-oxide); RT, room temperature; EMIM, 1-ethyl-3-methylimidazolium; RTIL, room temperature ionic liquid; BMIM, 1-butyl-3-methylimidazolium; TBHP, *tert*-butyl hydroperoxide; UHP, urea hydroperoxide.

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1. Introduction

In industries heterogeneous catalysis is still far more wide spread than homogeneous catalysis. This fact is at first glance astonishing, when considering the numerous advantages of homogeneous catalysis, among them usually far milder reaction conditions, higher selectivity, defined reaction sites, comparatively easy ligand modification. However, recycling of a homogeneous catalyst and product–catalyst separation often pose serious problems, preventing large-scale industrial application.

To overcome these shortcomings and to combine the advantages of homogeneous and heterogeneous catalysis, increasing interest has been given to the immobilization of homogeneous catalysts rather than strictly homogeneous catalysis during the recent years. Homogeneous catalysts are immobilised using various carrier materials including ionic liquids, polymers and mesoporous materials.

In this work, the different techniques employed for the anchoring of organorhenium(VII) oxides on various supports are summarised. An overview of these systems particularly with respect to their application in oxidation catalysis is described.

Methyltrioxorhenium(VII) (MTO) was first described almost 30 years ago [1]. Since then it has been extensively studied as its synthesis became increasingly easy and so the compound is meanwhile available in excellent yields and large quantities [2–5]. It is particularly useful in oxidation chemistry and shows high activity for epoxidations, C–H and Si–H oxidations but it can also be applied in other types of catalytic reactions such as olefin metathesis and aldeyhyde olefinations [6,7]. Few other organometallic transition metal compounds show even remotely comparable versatility [8]. Another advantage of MTO besides its ease of production is that it activates hydrogen peroxide – which is environmentally benign since water is the only by-product of the reaction. The drawbacks of the MTO/H_2O_2 oxidation system lie in an appreciable formation of side products, diols in particular, and facile decomposition of MTO to perrhenates. These drawbacks can be overcome for several reactions by adding large excesses of aromatic Lewis bases or stoichiometric amounts of certain Schiff bases [9–11].

2. Heterogenisation of MTO and derivatives

Significant efforts have been dedicated in the recent years to the immobilisation of MTO on various supports such as niobia [12–17], zeolites [18–24], urea [25–30], polymers [31–36] and ionic liquids [37]. The immobilised catalysts were evaluated for their activity in various reactions like olefin epoxidation, silane oxidation, metathesis and Baeyer–Villiger reactions.

2.1. Inorganic supports

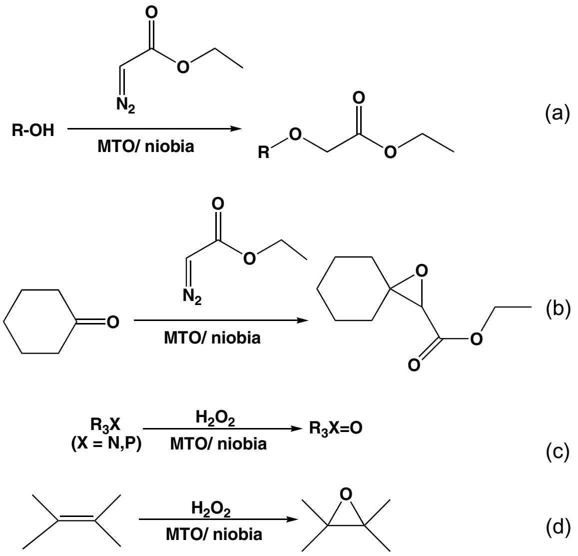
2.1.1. Unfunctionalised inorganic oxides

MTO supported on acidic metal oxides was discovered to form metathesis catalysts that are active without additives even for functionalised olefins [30]. Standard supports are zeolites and niobia (Nb_2O_5), and the activity was reportedly related to the surface acidity [38].

2.1.1.1. Niobia. Niobia supported MTO has been prepared either through sublimation of the catalyst on to the support or by the impregnation of the niobia surface with a solution of MTO. Both methods are well-described [14]. A large variety of catalytic reactions were efficiently performed with niobia-supported MTO such as olefin metathesis catalysis [13,14], reactions of ethyl diazoacetate [15], heteroatom oxidation (amine and phosphine oxidations), and olefin epoxidation with hydrogen peroxide (Scheme 1). Olefin epoxidation with the system H_2O_2/MTO, the latter being supported on niobia in the presence of urea was successfully applied with even better results than under homogeneous conditions thereby transforming simple olefin substrates to unsaturated fatty acids and esters [16,17].

2.1.1.2. Zeolites. A series of zeolite-Y hosts containing different proton concentrations has been used for MTO encapsulation [38] and the resulting materials were studied for 1-hexene metathesis. The MTO molecule is activated by the intra-zeolite protons, and subsequently blocks their isomerisation activity. The ability to tune intra-zeolite acidity and the doping levels of the intact MTO precatalyst permits control over selectivity in the metathesis reaction.

The MTO-catalysed oxidation of silanes to silanols (Fig. 1) and epoxidation of olefins by aqueous H_2O_2 exhibits product chemo-selectivities (no siloxane or diols are observed as by-products) in the presence of zeolite-Y [24]. The confinement of the oxidative species inside the 12 Å supercages of the zeolite prevents bimolecular condensation of silanol to siloxane by steric means.



Scheme 1. Examples of oxidation reactions catalysed by MTO on Niobia supports.

Fig. 1. MTO-catalysed oxidation of silanes to silanols.

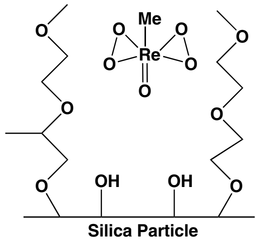
In the case of olefin epoxidation, the formation of the diol is prevented since MTO and the epoxide are topologically separated (MTO is absorbed in the zeolite whereas the epoxide remains in solution). This usually leads to very high selectivity (about 95%).

Another study shows that thermal treatment of Re_2O_7/H–MFI mixtures, leads to the selective grafting of Re-oxo species onto the zeolite via sublimation by the reactions of formed –OH groups to give $\mathrm{Si{-}O_{f}ReO_{3}{-}Al}$ [39]. The formed catalyst shows high reactivity, particularly for the oxidation of C_2H_5OH with turnover rates independent of Re loading.

2.1.2. Functionalised silica matrices

MTO has been heterogenised inside the porous systems of hybrid silica matrices [19,20]. Thus, it has been supported on silica functionalised by polyether [19]. These polyethers are covalently attached to silicate particles using sol–gel procedures and act as the solvent for the catalyst (Scheme 2). In the absence of an organic solvent, this assembly catalyses cyclohexene epoxidation with 30% aqueous H_2O_2 in high selectivity especially when the ring-opening products (diols) often observed in homogeneous media are considered. A balance between polyethylene oxide PEO (hydrophilic) and polypropylene oxide PPO (more hydrophobic) gives the best results (Fig. 2).

The oxidation of various other alkenes using the optimal heterogeneous system of 10% PEO to 10% PPO (Fig. 3) was compared to a typical homogeneous reaction using MeOH as solvent. Compared to the homogeneous standard, the polyether tethered, silica-encapsulated catalysts show somewhat lower activity but a much better selectivity.



Scheme 2. Encapsulation of MTO in silica functionalised by polyethylene oxide (PEO) and polypropylene oxide (PPO).

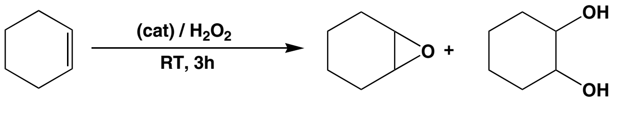


Fig. 2. Epoxidation of cyclohexene.

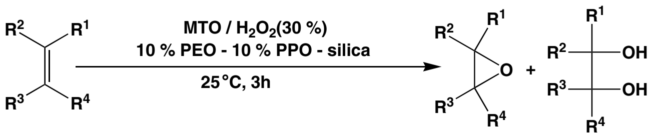


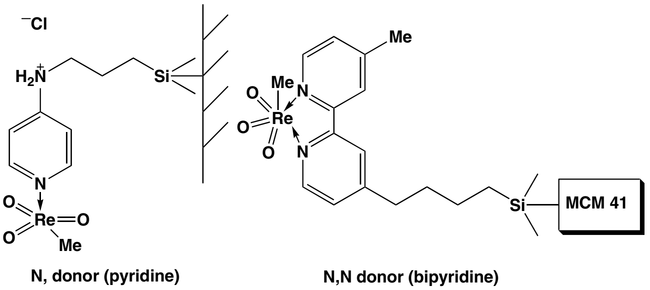
Fig. 3. Alkene oxidation using polyether tethered, silica encapsulated catalysts.

MTO has also been confined in mesoporous materials functionalised with N-donors like pyridine or *N*,*N*-donor ligands such as bipyridine. Via sol–gel methods using 1,4-bis(triethoxysilyl)benzene as a co-condensation agent and 4-[(3-triethoxysilyl)propylamino]pyridine. Hydrochloride as a hydrolysable ligand, hybrid silica matrices bearing pyridine moieties were prepared [13] (Scheme 3, *N*-donor). Combined with MTO and H_2O_2 the resulting agents were proven highly selective and recyclable as olefin heterogeneous epoxidation catalysts. MTO has also been immobilised on the mesoporous silica material MCM-41 functionalised by pendant bipyridyl groups (bpy) (4-[(-O)$_3$Si(CH$_2$)$_4$]-4′-CH$_3$-2,2′-bipyridine) to form a hybrid MCM-41-bpy/MTO material (Scheme 3, *N*,*N*-donor) [21]. When the metal loading is very high (10.24 wt.% giving an Re:N molar ratio of 1:1.1), analyses show that in fact some rhenium atoms remain uncoordinated in the MCM channels.

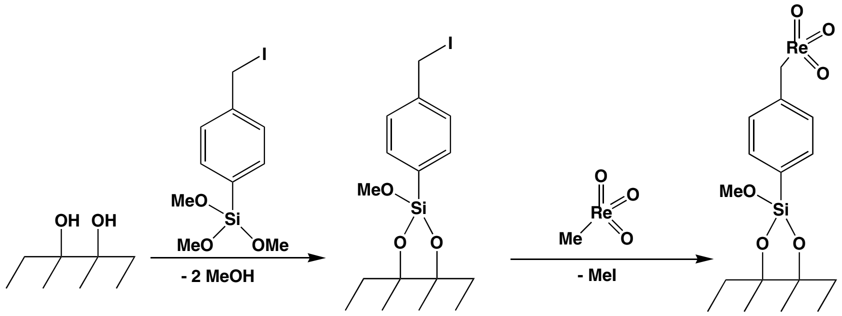
Another route to immobilise an organorhenium(VII) oxide derived from MTO on the surface of an iodosilane-modified MCM-41 was applied (Scheme 4).

The resulting material contains 1.25 wt.% Re and is actually an immobilized benzyltrioxorhenium(VII) [40]. In spite of the pronounced temperature sensitivity of pure benzyltrioxorhenium, the immobilized compound is far more stable. However, as benzyltrioxorhenium itself, it is not stable in the presence of H_2O_2, and therefore could not be used for olefin epoxidation. Instead, it was successfully utilized for aldehyde olefination reactions [22] (Scheme 5).

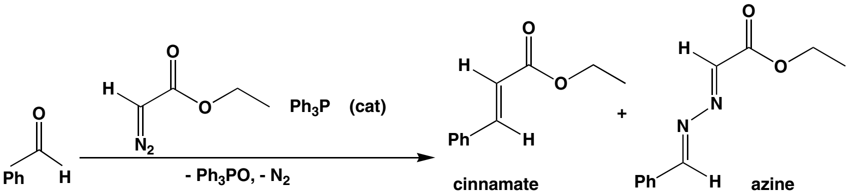
MTO immobilised on MCM-41 functionalised with a pyrazolpyridine ligand was applied [41a] after the mesostructured ligand–silica was found to be an effective solid-state complexation material for oxodiperoxo molybdenum



Scheme 3. MTO confined in silica matrices functionalised with *N*-donors and *N*,*N*-donors.



Scheme 4. Immobilisation of trioxorhenium (VII) moiety derived from MTO on a iodosilane-modified MCM.



Scheme 5. Benzaldehyde olefination with ethyl diazoacetate/triphenylphosphine/MCM-supported trioxorhenium (VII) catalyst.

and manganese acetonitrile complexes [41b,41c,41d,41e]. The resulting material had a loading of about 35%, likely due to the weak host–guest interaction of the monodentate coordination of the pyridyl nitrogen atoms of the anchored ligands to the Re(VII) centres. The catalytic properties of the material however are yet to be completely explored.

MTO has also been immobilised on the surface of an amorphous silica–alumina, which generates a catalyst for olefin metathesis [42]. The nature of the silica–alumina interaction with the grafted organometallic complex has been studied extensively and the application of the system as a catalyst with higher efficiency is being explored.

Mesoporous silicates and aluminiosilicate molecular sieves surfaces are also used for the immobilisation of acylperrhenate [43] using the available silanol and acidic hydroxy groups. The resulting material was used for olefin epoxidation with cyclooctene as the substrate and H_2O_2 as the oxidising agent. The non-aluminium surfaces (MCM-41 and MCM-48) show conversions above 80% as compared to those of the aluminium surfaces, which lie between 59% and 70%. This may be due to the stronger electron-donating capability of the Al-containing surfaces thereby reducing the Lewis acidity of the metal centre as well as the catalytic activity. Although the selectivities and activities of the catalysts are high there still remain problems of catalyst deactivation and leaching.

2.2. Organic supports

2.2.1. System MTO/UHP (urea hydroperoxide)

One large drawback of olefin epoxidation with MTO/H_2O_2 lies in the epoxide ring-opening reactions which form the corresponding diol. These undesirable reactions can be prevented partially when operating under anhydrous conditions in *tert*-butanol. The system MTO/UHP (UHP = urea hydrogen peroxide) was also proven to be a very good alternative. The urea (and therefore the inclusion complex formed by MTO with urea) is insoluble in most organic solvents. As a result, the system – MTO/UHP/organic phase is heterogenous. The MTO/UHP combination was found to be very efficient for olefin epoxidation [25] and silane oxidation [26], exhibiting higher yields and selectivities than those obtained in the homogeneous processes. This can be attributed to an increased stability of MTO when inclusion complexes with urea are formed. As the reaction is supposed to take place inside the helical urea channels, the condensation of the silanol produced is prevented for steric reasons (Fig. 4).

Even stereoidal dienes, uracil, and purine have been successfully oxidised by the MTO/UHP system [27–29]. The conversion and selectivity towards silanols are very high when a heterogeneous MTO/UHP system is used are significantly better than the homogeneous MTO/H_2O_2 (85%) combination. The presence of urea is not only beneficial for the efficiency and the chemoselectivity, but also for stereoselectivity. Thus, (+)-(α-Np)PhMeSiH is converted with retention of its configuration to (+)-(α-Np)PhMeSiOH with a high enantiomeric excess (91%) using the MTO/UHP system, whereas almost no enantioselectivity is observed with MTO/H_2O_2 (85%) (Scheme 6).

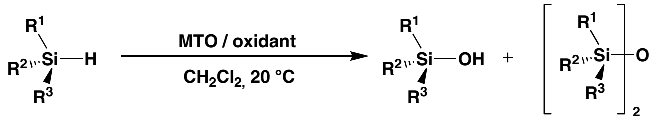
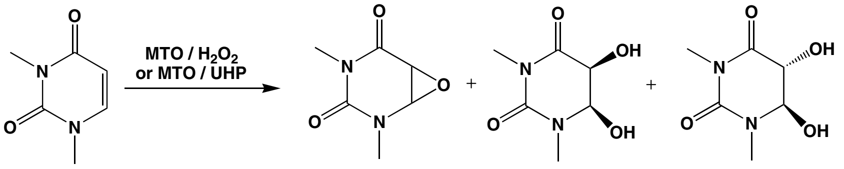


Fig. 4. Silane oxidation using the MTO/UHP system.



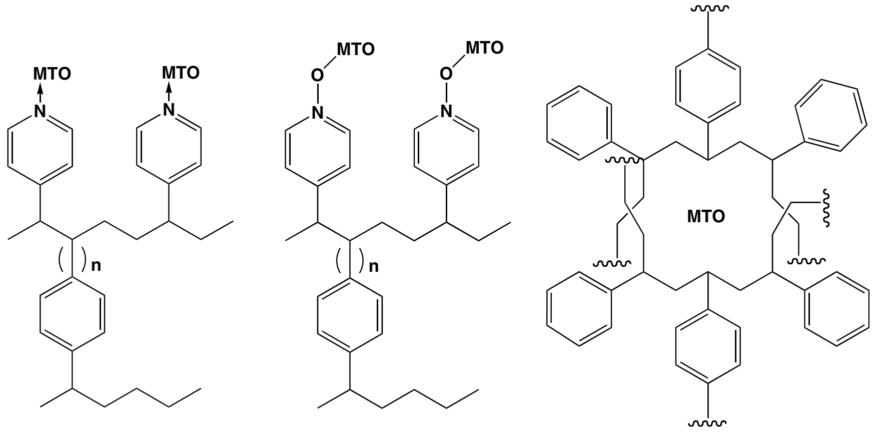
Cat. / oxidant			
MTO / H_2O_2	45 %	22 %	0 %
MTO / UHP	82 %	7 %	

Scheme 6. Oxidation of an uracil derivative by MTO/H_2O_2 system or MTO/UHP combination.

2.2.2. Organic polymers

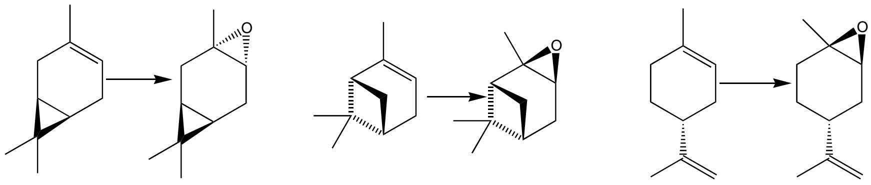
Herrmann and co-workers prepared heterogeneous MTO compounds in which MTO was assumed to be bound to the support by coordination with one nitrogen atom [30,31]. Unreticulated poly(4-vinylpyridine), poly(2-vinylpyridine), poly(vinylpyrrolidone), polyacrylamide and nylon-6 were used as organic supports. When applied to the epoxidation of olefins (cyclohexene, methyl oleate, allyl alcohols) with dried H_2O_2 in *tert*-butanol, these systems lead to low yields (20–27%) of epoxide. Ten years later, Saladino and co-workers used this concept to prepare two families of organic polymer supported MTO [32]. PVP/MTO and PVPN/MTO systems are based on poly(4-vinylpyridine) and poly(4-vinylpyridine-*N*-oxide), respectively, whereas PS/MTO are obtained from polystyrene. Cross-linkage is accomplished by divinylbenzene (Scheme 7).

Depending on the loading factor (0.5 or 1.0 mmol MTO/g support) and more importantly on the reticulation grade, these catalytic systems were proven very efficient and selective for olefin epoxidation with H_2O_2. The exceptional recycling capability of the PVP/MTO system highlights the stability of this system compared to the PS/MTO system which shows a decrease in activity during recycling. This difference in behaviour may be due to the weaker interaction between MTO and the PS polymer, which is only accomplished by the physical envelopment of the benzene ring. The PVP/MTO combination was successfully used for other compounds of biological interest such as terpenes. Even highly sensitive terpenic epoxides, like α-pinene oxide, can been obtained in excellent yields using polymer supported MTO catalysts [33] (Scheme 8). Compared to homogeneous conditions with MTO in the



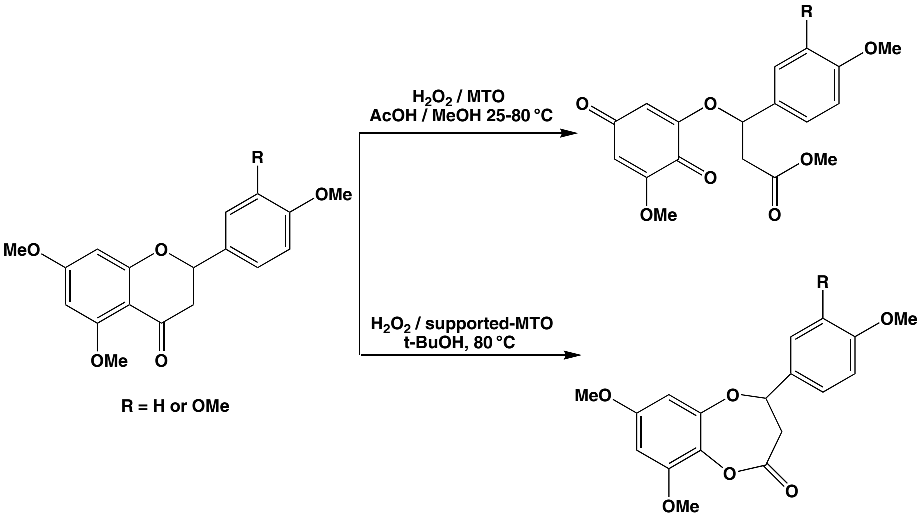
PVP-n % / MTO **PVPN-n % / MTO** **PS-n % / MTO**

Scheme 7. MTO on polyvinylpyridine and polystyrene supports (*n* is the cross-linkage percent with divinylbenzene).



***S*-(+)-carene** **1(*R*)-α–pinene** ***R*-(+)-limonene**

Scheme 8. Epoxidation of terpenes with H_2O_2/polymer supported MTO at room temperature in CH_2Cl_2/MeCN.



Scheme 9. Baeyer–Villiger reaction catalysed by the PVP/MTO/H_2O_2 system.

presence of pyridine, selectivities improve using polymer supported MTO.

The heterogeneous PVP/MTO/H_2O_2 system was additionally proven efficient and selective for the conversion of naringenin and hesperetin into lactones by a Baeyer–Villiger reaction [27] (Scheme 9). In less than 8 h, 75–100% conversion was reached with 35–80% selectivity.

C–H insertion reactions with H_2O_2 catalysed by PVP/MTO were also achieved starting from hydrocarbons and producing ketones and alcohols [28] (Scheme 10).

Polymer-supported MTO systems were shown to be efficient catalysts for the oxidative functionalisation of cyclohexane and cyclopentane derivatives with H_2O_2 as the oxygen donor [44]. Using poly(4-vinyl)pyridine and poly(4vinyl)pyridine-*N*-oxide as MTO supports, cycloalkanol, cycloalkanediol, cycloalkanone and ω-hydroxy methyl ketone derivatives were obtained. The selectivity of the reactions was found to be correlated both to the structural properties of the poly(4-vinyl)pyridine support and to the stereochemical properties of the substrate.

Saladino et al. followed their previous work [32,44] with another publication with MTO immobilised on polymer supports [45]. Poly(4-vinylpyridine)/MTO catalysts poly(4-vinylpyridine) *N*-oxide/MTO catalysts and micro-encapsulated polystyrene/MTO and MTO-2-(aminomethyl)pyridine catalysts were used for the oxidation of various hydrocarbon derivatives to the corresponding alcohols or ketones (Fig. 5).

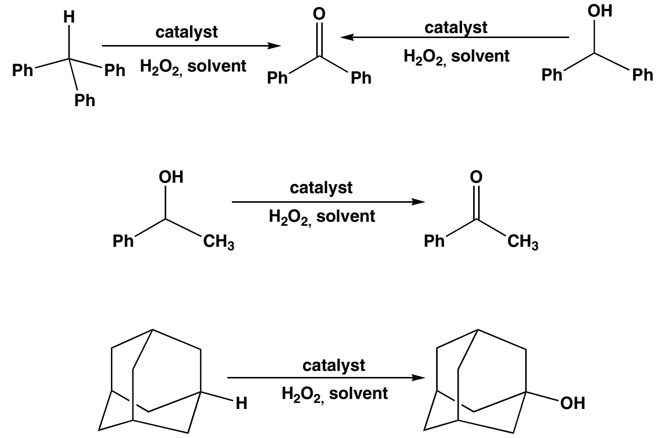
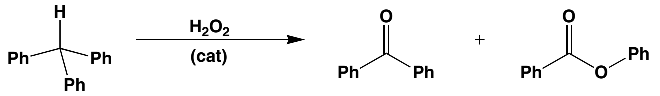


Fig. 5. Examples of oxidation reactions with MTO supported on polymers.

2.3. Ionic liquids

The catalytic potential of the MTO/UHP oxidation system has also been tested in the room temperature ionic liquid [EMIM][BF_4], in which it is soluble [37] (Fig. 6). In contrast the olefin is poorly soluble in such solvents and so the whole system is bi-phasic. Excellent conversions and selectivities for the epoxides of a wide number of olefinic substrates were reached under these anhydrous conditions. The exception was 1-decene, which displayed poor



Scheme 10. Example of C–H insertion reactions catalysed by the PVP/MTO/H_2O_2 system.

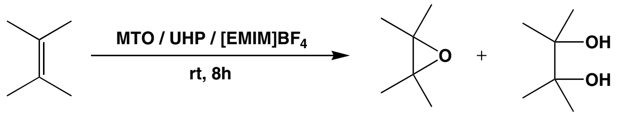
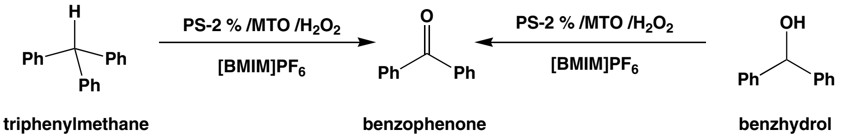
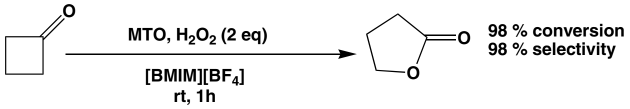


Fig. 6. Epoxidation of various substrates with MTO/UHP in [EMIM]BF_4.



Scheme 11. Recyclability of PS-2%/MTO/H_2O_2/RTIL [BMIM]PF_6 system used for oxidation reactions.



Scheme 12. Example of Baeyer–Villiger oxidation achieved by MTO (2%)/H_2O_2 (50% aqueous) system in RTIL [BMIM][BF_4].

conversion resulting in phase transfer problems as it is the least soluble substrate in the ionic liquid.

Remaining reactants and products are both easily removed from the reaction mixture via extraction with an organic solvent such as diethyl ether, which is immiscible with the ionic liquid. Unfortunately, MTO cannot be retained in ionic liquids during the liquid/liquid extraction of the reaction mixture for recycling due to its high solubility in a wide range of molecular solvents. However, when MTO is additionally supported by an organic polymer, recycling becomes possible. For example, the system PS-2%/MTO/H_2O_2 in RTIL [BMIM]PF_6 which is an efficient and selective catalytic system for various oxidation reactions can be fully recovered [36] (Scheme 11).

The Baeyer–Villiger oxidation of cyclic ketones was also achieved by the MTO/H_2O_2 system in the ionic liquid [BMIM][BF_4] [31] (Scheme 12). Kinetic investigations have additionally been performed in order to follow the formation of the catalytically active peroxorhenium intermediates in the RTIL's [46,47].

That the Baeyer–Villiger oxidation of cyclic ketones can be effected by methyltrioxorhenium/hydrogen peroxide in the ionic liquid [bmim]BF_4 was later confirmed by Bernini et al. [48]. After simple extraction of the lactone with diethyl ether, the catalyst can be repeatedly recycled and efficiently reused for the lactonisation process in the same reaction medium.

2.4. Mesoporous alumina

Very recently work on the immobilisation of MTO on a mesoporous alumina carrier material [49] was reported. A zinc chloride-modified mesoporous alumina, $ZnCl_2$//meso-Al_2O_3, with a high surface area, relatively uniform mesopores, and Lewis acidic character carrier material was made. Using this material it was found that MTO doped on the alumina, MTO/$ZnCl_2$//meso-Al_2O_3, demonstrated higher catalytic performance for the metathesis of functionalized olefins than the system of MTO on SiO_2-Al_2O_3 (MTO/SiO_2–Al_2O_3). $ZnCl_2$//meso-Al_2O_3 immobilizes MTO on its solid surface and activates MTO enough to accelerate the metathesis of functionalized olefins. The authors of this work claim their methodology to be with the first outstanding activation of organometallic complexes with an acidic carrier composed of mesoporous alumina and immobilized Lewis acidic zinc chloride reported in the literature.

Methyltrioxorhenium (MTO) has also been immobilized on various commercially available supporting materials (like AlO–SiO and NbO) via sublimation under vacuum [50]. Up to 15 wt.% MTO (10 wt.% Re) can be immobilized on the different supporting materials. Metathesis experiments using *cis*-cyclooctene as substrate were performed aiming at a high yield of low molecular weight metathesis products (dimers, trimers, and tetramers), which are interesting for aroma and flavor industries. Up to ca. 60% of these desired products can be obtained. A high rhenium loading leads usually to good catalytic activities of the materials in the cyclooctene metathesis. Prolonged reaction times lead to higher yields of the high molecular weight metathesis products. When the same catalyst material is used repeatedly in several catalytic runs, leaching of the grafted Re compounds plays an increasing role, resulting in a reduction of the catalyst performance. None of the examined commercially available carrier materials, however, present an ideal means for the heterogenization of MTO to obtain particularly high amounts of the desired low molecular weight metathesis products of cyclooctene.

2.5. Resins

Novel heterogeneous aminated polystyrene and polyacrylate resins and vinylpyridine copolymerized with methylmethacrylate and buthylmethacrylate, were synthesized, characterized and used as supports for MTO immobilization [51]. The amount of rhenium incorporated and the interaction between N and Re varied with the ligand type and the polymer. It was seen that MTO immobilized on oxidized supports was more prone to leaching than non-oxidized supports. MTO supported on copolymers was more effective for the epoxidation of α-pinene than MTO supported on tertiary amines or commercial polyvinylpyridine.

3. Conclusion

Considerable progress has been made in research on organorhenium oxide catalysts in the last 10 years. Heterogeneous systems have been developed with particular emphasis on the supporting systems including zeolites, mesoporous materials and others. As a result efficient and reasonably selective catalysts are now available for various reactions like olefin epoxidation in particular and other oxidation reactions, metathesis etc. Besides the combination system of MTO with UHP, polymer supports for catalysts are also successfully used. The systems exhibit the required properties of selectivity, activity and recyclability. There is also high possibility in the future of having highly enantioselective heterogeneous epoxidation catalysts tolerating a broad variety of substrates.

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