A Review on Heterogeneous Solid Catalysts and Related Catalytic Mechanisms for Epoxidation of Olefins with H_2O_2

H. L. Xie,[a] Y. X. Fan,[a] C. H. Zhou,[a,*] Z. X. Du,[b] E. Z. Min,[b] Z. H. Ge,[a] and X. N. Li[a]
[a] Advanced Materials & Catalytic Conversions for Renewable
Feedstocks Research Group, College of Chem. Eng. & Mater. Sci.,
Zhejiang University of Technology, Hangzhou 310014, China
[b] Research Institute of Petroleum Processing, SINOPEC, Beijing 100083

Original scientific paper
Received: January 11, 2007
Accepted: December 10, 2007

The epoxidation reaction using heterogeneous solid catalysts with H_2O_2 as oxidants are environmentally friendly routes to produce extensively useful epoxides which are traditionally obtained from capital-intensive or environmentally polluted processes. In this paper, various types of solid catalysts for the epoxidation of olefins with H_2O_2 as oxidants are reviewed. The efficient catalysts reported include microporous and mesoporous molecular sieves, layered-type materials, inorganic oxides, supported catalysts, zeolite encapsulated metal complexes, polyoxometalates, and supported organometallic catalysts. The proposed reaction mechanisms over different solid catalysts are summarized. The problems and perspectives to further efficiently improve the catalytic performances of the concerned heterogeneous catalysts for epoxidation reaction are remarked.

Key words:
Epoxidation, olefins, heterogeneous catalyst, hydrogen peroxide, reaction mechanism

Introduction

The epoxidation of olefins are a class of important chemical processes because epoxides are widely used as raw materials or intermediates for production of epoxy resins, paints, surfactants and medicines.[1] The traditional epoxidation processes are: (i) the chlorine-using non-catalytic process, (ii) co-epoxidation processes and (iii) catalytic processes based on organic peroxides and peracids.[2] These processes are very capital-intensive. The chlorine-using process has environmental disadvantages due to the large output of chloride-laden sewage. The employment of peracids is not a clean method as an equivalent amount of acid waste is produced. Furthermore, the homogeneously catalytic processes usually suffer from the difficulty of separation. As to the co-epoxidation processes, the coupling product should be an equivalently commercial desired one.

Hydrogen peroxide (H_2O_2) is an attractive option of oxidants that can epoxidize olefinic compounds in the presence of various transition metal-containing catalysts (Ti, V, Cr, and Mo etc.). It gives water as the only waste product. Another desirable thing is to use heterogeneous catalysts because of their easy separation, regeneration and operation. Therefore, development of heterogeneous catalytic processes for epoxidation using H_2O_2 as oxidants is very demanding.[3] In this aspect, the development of solid and recyclable catalysts with high performance is a key issue. The major types of solid catalysts with catalytic activity and selectivity in the epoxidation of olefins will be reviewed in the following subsections, along with its catalytic reaction mechanisms.[4–14]

Heterogeneous epoxidation catalysts

Microporous and mesoporous molecular sieves

Framework-substituted MFI and MEL zeolites

Microporous zeolite-based catalysts have normally shown great potential for the epoxidation of various olefins.[15] Especially, the heteroatom-substituted variant of ZSM-5, titanosilicate TS-1, is a very active and versatile oxidation catalyst under mild conditions.[16–21] Early studies carried out by Clerici and coworkers[22] showed that TS-1 is an efficient catalyst in the epoxidation reaction of various lower olefins, such as C_4-C_8 linear olefins, allyl chloride,[23] and allyl alcohol (with up to 86 % yield).[24] Some attractive results have been obtained in the case of propylene with H_2O_2 in the liquid phase.[25] When the reaction is carried out in methanol/water solution at 40 °C for 90 min, 95 % of the H_2O_2 is consumed, with 90 % selectivity to propylene oxide with propylene glycol and its monomethyl ethers as main byproducts. With a mixed

---

* To whom correspondence should be addressed.
Tel:/Fax 86-571-88254568. E-mail: catalysis8@yahoo.com.cn

solvent system of methanol and acetonitrile, TS-1 efficiently catalyzes the epoxidation of allyl chloride to the corresponding epichlorohydrin in excellent yields (up to 99 % when at the temperature of 30 °C for 1 h) using dilute H_2O_2 (45 %) as oxidizing agent. Because the TS-1 is usually inherently acidic, it is sometimes previously modified to prevent the inactivation of the catalyst or the epoxide-decomposition. When modified the TS-1 samples with small amounts (w = 0.3–1.7 %) of alkali, alkaline-earth and lanthanide ions, the selectivity to epoxide can be higher. The reason could be the neutralization of the surface acidity of the TS-1 zeolite by the metal oxide, thus leading to subsequent inhibition of the solvolysis reaction of the epoxide normally taking place on the acid sites.[26] Hölderich and coworkers[27] reported that propylene epoxidation was carried out with an O_2–H_2 mixture instead of the relative high cost of H_2O_2 over a precious metal containing TS-1, preferably palladium and platinum. However, results of the catalyst for the epoxidation of propylene are low, with the propylene oxide yield and the selectivity 11.7 % and 46 % respectively.

Although TS-1 gives excellent catalytic activity of the propylene epoxidation, the deactivation of the catalyst occurs with time on stream. The major cause of the deactivation of TS-1 catalyst for epoxidation is the blocking of micropores by bulky organic byproducts formed from consecutive reactions of target reaction, such as dimerization or oligomerization of epoxides, etherification of epoxides with alcohol solvents. Leaching of framework titanium could also result in the deactivation of the catalyst.[28] And the methods of generating deactivated TS-1 are mainly focused on:[28] (1) heat treatment at temperatures from 300 to 700 °C in the presence of different media, such as air, vapor and inert gas; (2) oxidation by diluted H_2O_2 at temperature below 100 °C, (3) extraction by different solvents such as methanol in the temperature range from 140 to 240 °C. However, the regeneration effectiveness with the solvent washing was lower, because this method could only partly remove the deposits in the micropores of TS-1.

TS-1 has also been indicated as a catalyst to selective epoxidation of styrene,[29] but the styrene oxide selectivity was very poor (5 ~ 10 %) using aqueous H_2O_2 as oxidants, mainly due to its isomerization into phenylacetaldehyde. Its catalytic performances can be improved by using anhydrous urea-H_2O_2 as an oxidizing agent (S = ~85 %).[30] Xu and his co-worker[31] successfully synthesized TS-1 with microwave heating which had better catalytic properties for epoxidation reaction of 1-hexene and styrene with H_2O_2.

The encouraging results in epoxidation reaction using TS-1 catalyst gave rise to a number of isomorphous substitutions of crystalline materials with other transition metals. A vanadium-containing zeolite with MFI structure, VS-1[31,32] and a zinc-containing one, ZS-1,[33] have been used in epoxidation reactions (such as trans-2-hexen-1-ol) with H_2O_2.

However, the application of MFI zeolites-based catalyst is generally limited to production of small, fairly stable epoxides because its pores only are suitable for transformations of molecules small enough to enter the relatively small pores (0.53 nm ~ 0.55 nm). For example, cyclohexene cannot be epoxidized efficiently by this system.[34]

While the catalyst TS-2 with MEL structure, nearly has the same pore size (0.53 · 0.54 nm)[35] with TS-1, it was shown to be active in the epoxidation of simple olefins with H_2O_2. 100 % selectivity was obtained for the epoxidation of 1-octene, while in the epoxidation of styrene, the main product was the epoxide with a selectivity of 55 %.[36]

Titanium silicalites with MFI and MEL structure have been extensively studied as catalysts with H_2O_2, even relatively unreactive olefins, such as propylene and allyl chloride mentioned above are smoothly epoxidized under mild conditions. However, several challenges still exist when using these nanosized catalysts, such as higher production cost and relatively difficult separation from the reaction mixture.

Framework-substituted BEA zeolite

The BEA-type framework, Ti-β, has a relatively low framework density and a three dimensional large pore system that make the material particularly attractive when relatively bulky molecules are processed. Bekkum *et. al.*[15] performed a study in which aluminum-free zeolite Ti-β catalyst was compared with TS-1, Ti/Al-β and Ti-MCM-41 in the epoxidation of 1-octene and norbornene with H_2O_2. Their results showed that Ti-β was highly active and selective for several branched alkenes. In addition, the alkenes with an internal double bond are oxidized faster than the alkenes with a terminal double bond. Ti-β has a higher catalytic activity in the epoxidation of bulky alkenes while Ti/Al-β and Ti-MCM-41 showed poorer activity for linear alkenes than TS-1 because of their interior hydrophilicity. Furthermore, Ti-β does not have any preference when two double bonds are present.

The traditional synthesis of zeolite Ti-β is hydrothermal synthesis with only a very low yield. Improved synthesis methods, e.g., co-gel method,[37] seeding techniques,[38,39] and fluoride method[40,41] have been developed to obtain the Ti-β zeolites with high yield. Recently, Jappar *et al.*[42] succeeded in synthesizing Ti-β zeolites with a yield of more than 95 % in the presence of a certain amount of sodium by the dry-gel conversion (DGC) method using TEAOH as template. NH_4^+ exchange before calcination[43] was found an effective route for reducing the amount of adsorbed H_2O and removing Na^+, resulting in high hydrothermal stability, and creating Ti sites surrounded by a hydrophobic environment, leading to higher catalytic activity for cyclohexene epoxidation with H_2O_2, selectivity toward epoxide up to 98 %.

Framework-substituted MWW zeolite

The structure of Ti-MWW consists of the open spaces of side cups, supercages and independent 10-MR channels, it could make Ti-MWW much more active than TS-1 and Ti-β in the epoxidation of linear alkenes with H_2O_2.[44,45] It also showed unique shape selectivity in the epoxidation of cis/trans geometric isomers.[46] Besides its pore structure and high stability, such unusual activity of Ti–MWW is ascribed to the nature of the framework. The supercages within the crystals and the exterior pockets directly related to the crystal form of the thin platelets make the Ti species in Ti–MWW highly accessible to both the substrate and the oxidant. However, for the oxidation of bulky molecules, it is still inferior to Ti-β owing to severe steric restrictions.

Therefore, some materials which cannot only make the active sites within the supercages more accessible to bulky molecules but are also endowed with the capability of promoting the oxidation reactions with an aqueous solution of H_2O_2 as an oxidant seem so important. Tatsumi *et al.*[53] have succeeded in preparing such a novel titanosilicate catalyst (denoted as Ti-YNU-1), with a lamellar structure analogous to a MWW precursor, and have found that this material shows substantially improved oxidation ability, selectivity, and stability in the liquid-phase epoxidation of cycloalkenes.

The high-yield synthesis of epichlorohydrin from the weakly nucleophilic allyl chloride is indicative of the effectiveness of the Ti-MWW in the epoxidation of alkene,[54,55] with both the conversion of allyl chloride and the selectivity for epichlorohydrin up to 99 %. Ti-MWW favors protic solvent of acetone and acetonitrile because both can restrain the solvolysis of epichlorohydrin.

Aluminum-phosphate molecular sieves

Aluminophosphate ($AlPO_4$) materials were first disclosed by Wilson *et al.*[56] in 1982. Many practical utilities were found by incorporation with various heteroatoms, including epoxidation of olefins (Table 1). Tetrahedral Sn present in the aluminophosphate framework can act as oxidation catalyst in the presence of dilute H_2O_2 oxidants. However, due to a very high charge structure, these materials have relatively poor chemical and thermal stability. This could be overcome through the incorporation of Si in tin phosphate-based materials similar to the incorporation of Si in $AlPO_4$ (SAPO based molecular sieves).[47]

Thomas and coworkers[57] have achieved good conversion and selectivity for the epoxidation of cyclohexene and other alkenes with H_2O_2 as oxidants using framework-substituted metal ions (M) in microporous aluminum phosphate, MAlPO-36 (M = Mn or Co) catalysts. The conversions are consistently higher for both the MnAlPO-36 and CoAlPO-36 catalysts compared with those of their larger-pore (AlPO-5) analogues while MgAlPO-36 is inactive totally.

Ti-substituted aluminophshpates (TAPOs) are efficient epoxidation catalyst systems using aqueous H_2O_2 in the presence of acetonitrile. The activity and H_2O_2 selectivity for the epoxidation of 1-octene and cyclohexene were in the order

Table 1 – *Various transition-metal substituted alumino-phosphate molecular sieves & MCM-41 used in the epoxidation of olefins with H_2O_2 as oxidant*

Catalysts	Substrate	Reaction conditions and catalytic activity				Ref.
		solvent	T/°C	t/h	X/%	
Sn-AlPO	styrene	acetonitrile	80	36	88.5	47
	cycloctene	acetonitrile	60	20	94	
	1-octene	acetonitrile	60	20	99	
	cyclododecene	acetonitrile	60	20	98	
TAPO	norbornene	acetonitrile	60	20	> 99	48
	styrene	acetonitrile	60	20	100	
	(+)-α-Pinene	acetonitrile	60	20	72	
	limeonene	acetonitrile	60	20	63	
TAPSO-5	cycloohexene	acetone	70	6	97	9
Ti-MCM-41	1-hexene	methanol	45	5	40	49
Nb-MCM-41	cyclohexene	acetonitrile	45	30	~70	50
V-MCM-41	cyclooctene	acetonitrile	70	12	20~50	51
Fe-MCM-41	styrene		73	2	13.8	52

TAPO-5 > TAPO-11 > TAPO-36.[58] TAPSO-5 has been used as a catalyst for the liquid-phase epoxidation of cyclohexene.[8] VAPO can also be an active and very selective catalyst for epoxidation of 3-phenyl-2-ol, allylic alcohols and simple alkenes with *tert*-butyl hydroperoxide (TBHP).[59,60]

Transition-metal substituted mesoporous materials

Transition-metal substituted MCM-41 molecular sieves with highly ordered hexagonal array of one-dimensional pores, such as Ti, V, Nb, Fe, Cr, Sn, Mn, Mo is another representative of molecular sieve active for epoxidation of bulky reactants with both H_2O_2 and alkyhydroperoxides as oxidants.[61,62] MCM-41 can be modified by various transition metals, *via* post synthesis or tethering, or *via* inclusion of metal during the synthesis (isomorphous substitution).[63] MCM-41 materials, especially Ti-MCM-41, have less activity and selectivity in reactions using aqueous H_2O_2 as oxidant than metal-containing zeolites, because of their hydrophilicity,[34] the nature of Ti species. It has been reported that silylation can be applied to increase the hydrophobicity of the catalysts.[64] Additionally, the leaching of metal species from the solid unables the recovery of the catalysts.[64] However, when using TBHP as oxidant instead of H_2O_2, MCM-41 is more effective for the epoxidation of olefins.[65]

Ti-SBA-15,[66] synthesized from the fluoride-accelerating hydrolysis of tetramethoxysilane (TMOS), was tested for the epoxidation of styrene, in which the conversion and epoxidation selectivity are appreciatively higher than those of Ti-MCM-41 prepared under acidic conditions. Ti-SBA-15, synthesized by grafting titanium on a structured mesoporous SBA-15 using titanium tetrachloride in the gas phase was also tested in the selective epoxidation of olefins, such as cyclooctene, cyclohexene, (R)-limonen and α-pinene. Whatever the oxidant, H_2O_2, TBHP, or cumyl hydroperoxide, the selectivity is 100 %. However, the yield is low with H_2O_2 and the active species is partially leached out.[67]

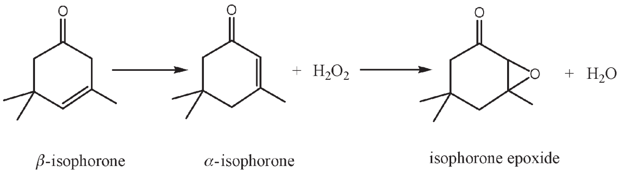
Other Ti-containing mesoporous catalysts are Ti-ZSM-11,[68] Ti-HMS,[69] Ti-TUD-1,[70] Ti-ITQ-6,[71] V-MWW,[72] Ti-SBA-1,[73] etc. Ti-ZSM-11 has a good performance for propylene epoxidation with the conversion of H_2O_2 and the selectivity of propylene oxide as high as 90 % and 100 %, respectively.[68] The catalytic activity of mesoporous Ti-HMS was lower than that of TS-1 for the epoxidation of 1-butylene with dilute H_2O_2 solution as oxidants.[69] The catalytic activity for the epoxidation of cyclohexene over Ti-TUD-1 is about 5-6 times higher than that over Ti-MCM-41 and similar to that over Ti-grafted MCM-41. Ti-ITQ-6 has been synthesized and showed activities and selectivities similar to those of Ti-β for the epoxidation of 1-hexene, owing to the good accessibility of the reactants to the active sites achieved by delamination of the Ti-PREER laminar precursor.[71]

Layered-type materials

Hydrotalcites are used as efficient heterogeneous catalysts for the epoxidation of various olefins using H_2O_2 as oxidants and isobutyramide as co-catalyst.[11] The activity was attributed to the *O-tert*-Bu paired with Mg and Al atoms of hydrotalcite. These catalyst systems can effectively epoxidize both electron-rich and electron-deficient olefins.

Kaneda *et al.*[74] studied $Mg_{10}Al_2(OH)_{24}CO_3$ hydrotalcite catalyst for the epoxidation of olefins using H_2O_2 in the presence of nitriles. It is likely that the hydrotalcite acts as a solid base and promotes the formation of peroxycarboximidic acid, leading to the high yield of the epoxides. It can be reused without an appreciable loss of catalytic activity. The hydrotalcites are basic enough to promote some nucleophilic epoxidation with H_2O_2. The reaction is not particularly sensitive to steric hindrance. Most cyclic and acyclic, α,β-unsaturated carbonyl compounds, including β-disubstituted, can also be efficiently oxidized. For example, $Mg_{10}Al_2(OH)_{24}CO_3$ and $Mg_{9.5}Al_{2.6}(OH)_{24.8}CO_3$ mediate epoxidation of α,β-unsaturated ketones with H_2O_2 in the absence of other inorganic bases. β-isophorone is not an activated olefin and cannot be epoxidized by a basic mechanism. The epoxidation of α-isophorone is in principle possible, with a low reactivity compared to that of the epoxidation of cyclohexenone. The oxidation with H_2O_2 was studied using rehydrated MgAl hydrotalcite: the isomerization of β-isophorone to α-isophorone was complete in a few minutes, then producing the epoxide of the α-isophorone (Scheme 1). Toluene and methanol were preferred as solvents and the best yield of epoxide was reported to be 66 % after 72 h, with a selectivity limited to 41 %.[75]

Many efforts have been devoted to improve the epoxidation properties of hydrotalcite-derived catalysts. One is the addition of an anionic surfactant, sodium dodecyl sulfate, which can remarkably enhance the reaction rate. However, cationic surfactants inhibit the reaction and non-ionic surfactants



Scheme 1 – *Reactions of α- and β-isophorone with H_2O_2*

have no effect. In these cases, hydrocarbons can be used as solvents, and 1,2-dichloroethane gives higher conversions for cyclooctene epoxidation. However, owing to the use of equivalent amounts of amide or nitrile additive[76,77] to act as a peroxide carrier, which is consumed during the reaction to the corresponding acids, this catalytic system complicates the separation of the desired epoxide.[76] More recently, heating by microwave radiation in the hydrotalcite catalyzed epoxidation of olefins with H_2O_2 has proved to be a significant way to accelerate the reaction rates and has resulted in higher yield of epoxides, so reaction time can be reduced from 1 day to 1 min.[77,78]

Tungstates and tungstic acid, which have long been studied in epoxidation reactions with H_2O_2,[79] intercalated into the interlayer of hydrotalcite could be an alternative for developing reusable catalysts and also avoiding the use of additional organic solvents. W (VI)-based hydrotalcite, either by anionic exchange or by complexation with phosphonic acids previously incorporated between the sheets, was evaluated in the epoxidation of cyclohexene with H_2O_2 or TBHP as external oxidants. The materials prepared by anionic exchange gave only epoxycyclohexane with moderate yield, whereas those prepared from previously incorporated phosphonic acids gave a selectivity in the range of 50–72 % in allylic oxidation products.[80]

The bromide-assisted epoxidation, with bromohydrin as an intermediate, using WO_4^-–LDH as catalyst is a new and unique chemocatalytic reaction.[81] Suitable substrates for bromide-assisted epoxidation include geminally di-, tri-, and tetrasubstituted olefins. The reaction is simply switched from bromohydroxylation to epoxidation by the solvent choice, while mono-substituted and *cis* and *trans* disubstituted olefins are not converted into their epoxides, but the bromohydrins can readily be isolated and transformed into the epoxide in an additional base workup. Bromide-assisted epoxidation is characterized by much higher turnover frequencies than classical W-catalyzed epoxidation.

Inorganic oxides and supported catalysts

Mixed Oxides

A variety of mixed oxides, such as Al_2O_3-ZrO_2, Al_2O_3-TiO_2, SiO_2-TiO_2 and ZrO_2-TiO_2, Nb_2O_5-SiO_2, can be used as epoxidation catalysts.[32,82–85] Hutter *et al.*[86] compared the catalytic activities of mixed oxides, silica-supported titania and Ti-substituted molecular sieves (TS-1, Ti-β and Ti-MCM-41) in the epoxidation of 1-hexene, 1-octene, cyclohexene, cyclododecene and norbornene. The activities vary in a broad range of several orders of magnitude. It is shown that at low temperature, aerogel containing w = 20 % TiO_2 is superior to any other Ti- and Si-containing catalyst for the epoxidation of cyclic olefins. Many efforts have been devoted to the application of these catalysts in demanding epoxidation of deactivated alkenes, alkenones, and alkenols. Addition of even weak bases, such as $NaHCO_3$, led to significant improvements in the catalytic performance for several reactions. Recently, modification of mesoporous TiO_2-SiO_2 mixed oxides with amines has proved an excellent tool for improving the selectivity and activity in the epoxidation of allylic alcohols,[87] cyclohexene and cyclohexenol.[88] Another new heterogeneous system to enhance the epoxidation catalytic activity is by means of fluorination and alkylsilylation of a titanium-containing catalyst.[89] This fluorine is expected to further activate an active site by making the active site more electrophilic, easier to be attacked by nucleophile substrates like alkenes. On the other hand, alkylsilylation is aimed to induce hydrophobicity of the catalyst, which is a prerequisite in any epoxidation using H_2O_2 as oxidant. The amphiphilic fluorinated titania-silica and zirconia-silica mixed oxides were more active and more efficient than the conventional ones in linear alkene epoxidation.[89]

The sol-gel method is used to synthesize Ti, Si mixed oxides at atomic scale with a tunable pore distribution.[90] Compared to conventional evaporative, drying resulting in microporous aerogels, solvent extraction with supercritical CO_2 yields the mesoporous solid. The appropriate choice of the sol-gel conditions can lead to a high proportion of isolated $Ti(OSi)_4$ species. The surface of mixed oxides can be modified organically by introducing apolar surface functional groups *via* Si-C bonds or subsequent hydrophobization of the material by trimethylation. All these methods can extend the application of these materials in the aqueous epoxidation with H_2O_2[6,91] which can be often regenerated without loss in activity, indicating high stability as catalysts compared with conventional Ti-zeolite.[90]

The MgLa mixed oxide is not as active as Mg-Al-O-*t*-Bu hydrotalcite,[75] which reaches a yield of 90 % in 5 min for the epoxidation of cyclohexene with 2-cyclohexen-1-one as a byproduct. However, interestingly it shows a possibility of recycling after being obtained from activation at 923 K – the solid is thermally stable and can therefore be regenerated by calcination.

More recently, Strukul *et al.*[92] reported that the preparation of mesoporous heterogeneous WO_3-SiO_2 catalysts made by sol-gel techniques allow the incorporation of W in the silica network, thereby avoiding the problems of leaching which were made by impregnation of a sol-gel-made silica with ammonium tungstate. These materials are very promising catalysts for the selective epoxidation of allylic alcohols. The surface modification of the catalysts with apolar and moderately polar organic groups can improve the accessibility on the active sites to molecules that enhance the activity and selectivity.

Among the mixed oxides, mixed titania-silica oxides show more promise due to their activity, selectivity and economic feasibility. Future effort should be focused on further optimizing the preparation method to enhance their catalytic activities.

Re_2O_3-supported catalysts

Methyltrioxorhenium ($MeReO_3$, MTO) represents a rhenium catalyst to selectively epoxidize olefins at high catalytic turnovers at low temperature.[93] The main disadvantage in MTO/H_2O_2 epoxidation is that they are inherently acidic and this tends to cause ring opening of sensitive epoxides to diols. This can be solved by addition of a base, such as pyridine,[94] pyridine derivatives,[95] pyrazole,[96] fluorinated alcohols, which can effectively enhance the reaction rate and selectivity of epoxidation of di-, tri- and tetra-substituted alkenes with 30 % H_2O_2 as oxidants ($Y > 95$ %). The excess of ligand can be a synthetic limitation in the case of expensive and chiral Lewis bases. MTO can form adducts with ligands immobilized on an inorganic and organic host. Therefore, one strategy to improve heterogeneous MTO-catalyzed epoxidation can involve the immobilization of previously synthesized Lewis base adducts of MTO on polystyrene by the use of the micro-encapsulation technique. The reactivity and selectivity of MTO in these compounds can be tuned by the chemical-physical properties of the ligand and of the support, showing the advantages of the ligand accelerated catalysis and the environmental benefits of heterogeneous systems. Micro-encapsulated Lewis base adducts of MTO with nitrogen containing ligands are highly efficient and selective catalysts for the epoxidation of several olefins and monoterpenes with H_2O_2 even in the case of the most sensitive substrates. The catalysts can be recovered easily from the reaction mixture and used for more transformations.[97]

It was found that a urea-H_2O_2 (UHP) complex[98,99] is a very effective oxidant in heterogeneous olefin epoxidation catalyzed by MTO. Even steroidal dienes, uracil and purine have been successfully oxidized by the MTO/H_2O_2-urea system. The system of epoxidation by urea-H_2O_2 has also been catalyzed by MTO on niobia (Nb_2O_5).[100] The heterogeneous MTO can be supported on silica functionalized with polyether tethers[101] or polymer.[102] The polymer supported MTO proved to be an efficient and selective catalyst for the olefin epoxidation, even the highly sensitive terpenic epoxides were obtained in excellent yield (> 90 %). The catalytic activity was reported to be maintained for at least five recycling experiments. MTO has also been immobilized in mesoporous silica MCM-41 functionalized with pendant bipyridyl groups of the type [4-($Si(CH_2)_4$)-40-methyl-2,20-bipyridine].[103]

Schuchardt *et al.*[104,105] successfully supported rhenium oxides Re_2O_7 and ReO_4^- on zeolite Y, mixed alumina-silica and pure alumina as epoxidation catalysts with anhydrous H_2O_2 (solvent EtOAc). Low conversions (X = 40 %) were obtained for the epoxidation of cyclooctene due to the ring opening promoted by the acidic Re centers and cyclohexane diol with high selectivity ($S > 96$ %) was obtained as the main oxidation product.

Immobilizing the homogeneous MTO catalysts on an insoluble support is still an ongoing endeavor to increase the reusability of catalysis in industrial settings.

Al_2O_3 and Al_2O_3-supported catalysts

Alumina has been shown to have attractive catalytic activity in the epoxidation of several alkenes ranging from unreactive (terminal) alkenes to the highly reactive terpenes using H_2O_2 under nearly anhydrous conditions, which can be dried *in situ* by performing the reaction under reflux with Dean-Stark water separation. The conversion of the various alkenes is slightly lower (16 % ~ 60 %), but the selectivity is really high ($S > 97$ %) after reaction of 5 h.[106] Completely anhydrous conditions result in lower selectivity, as alumina catalyzed decomposition of epoxide and H_2O_2 is prevented by the presence of only a small amount of water. The system is not very reactive, however, for the epoxidation of cycloalkenes.[107] As to the epoxidation of several terpenic diolefins in anhydrous conditions using alumina as a heterogeneous catalyst, basic alumina was the catalyst that gave better activity and selectivity. The reactivity of the substrate increases with the nucleophilic character of its double bonds, and the regioselectivity to some monoepoxides is also related to this nucleophilic character.[108] The ultrapure γ-Al_2O_3 obtained by the calcination of precursors synthesized by sol-gel routes showed significantly higher epoxidation activity compared to commercial chromatographic neutral alumina.[109] The surface hydrophilicity and the amount of weak to moderate Brønsted acid sites are among the responsible factors for the catalytic activity of alumina.

There are also various Al_2O_3 supported catalysts in the epoxidation of olefin, such as Ag-Cs/α-Al_2O_3,[110] Ag/α-Al_2O_3 catalysts promoted by Ba, Cs and Cl,[111] Au-Ag/Al_2O_3[112] using air or oxygen as oxidants. Three heterogeneous systems were tested in the epoxidation of α-isophorone to the epoxides. The results obtained using H_2O_2-urea were limited by the low selectivity, while with TBHP-KF/Al_2O_3 the selectivity was higher. The best result was obtained with an excess of oxidant, leading to conversion of up to X = 96 %.[113] However, H_2O_2 cannot be used with KF/Al_2O_3 because of the solubility of KF.

Al_2O_3 is an inexpensive and simple catalyst for alkene epoxidation, the amount of water has a critical influence on the rate of the reaction. Almost no activity was observed in the case of 60 % H_2O_2, due to the ring open of the epoxide and the decomposition of H_2O_2 due to the surface acidity of the alumina. However, when the reaction is under absolutely anhydrous conditions, the epoxide decomposition is also strong.[107]

Porous materials encapsulated metal complexes

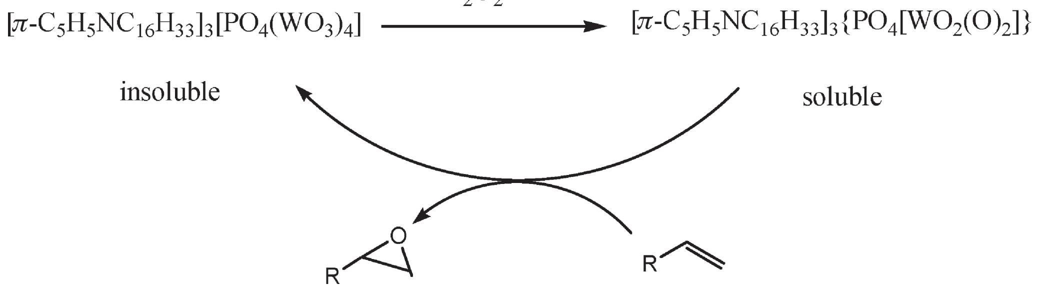
The ship-in-bottle concept involves physical entrapment of metal complexes in the cage of zeolites, which can be free to move about within the confine of the cavities of appropriate molecular sieve host but are prevented from leaching by restrictive pore openings. It can be anticipated that metal complexes not bound to the zeolite surface will retain activity, and the crystalline microporous host is expected to impart size and shape selectivity to the catalyst. Most of the ship-in-bottle complexes such as Mnsalen/NaY, CoPc/NaY, FePc/NaY, RuF_{16}Pc/NaX, CoPc/EMT, Cosalophen/NaY/Pd$(OAc)_2$, RuF_{16}Pc/MCM-41 usually have been tested as catalysts for the epoxidation of various olefins with PhIO, *t*-BOOH, O_2 as oxidant.[114,115] However, the use of this type of catalyst is restricted to relatively small reactants, considering smaller pores after the encapsulated metal complex. Additionally, the zeolite should provide a stabilizing effect since multimolecular deactivation pathways such as formation of μ-oxo or -peroxo bridged species will be precluded.[115] There were few reports for the epoxidation of olefins with H_2O_2, one example was a manganese-bis(bipyridyl) complex encapsulated within the cages of zeolite Y. The resulting material catalyzed the epoxidation of cyclohexene,[116] which not only retained the reactivity but also enhanced the catalyst stability.

Although these materials seem to be stable under oxidative conditions, their main disadvantage is the relatively low loading of metal and limited accessibility.

Polyoxometalates

The catalytic function of polyoxometalates has been attracting much attention because their acidic and redox properties can be controlled at atomic or molecular levels. Various catalytic systems for H_2O_2-based epoxidation catalyzed by polyoxometalates can be classified into two groups according to the structural and mechanistic aspects of polyoxometalates: (1) catalyst precursors of peroxotungstate or peroxomolybdate: the monomeric, dimeric and tetrameric peroxo species are generated by the reaction of polymetalates with H_2O_2 and the peroxo species can catalyze the epoxidation. The polyoxometalates act as catalyst precursors; (2) transition-metal-substituted polyoxometaltates: transition-metal-substituted polyoxometalates are oxidatively and hydrolytically stable, and various kinds of catalytically active sites can be introduced. The sites influence the catalytic activity and selectivity for the epoxidation.[2]

Various transition-metal-substituted polyoxometalates can effectively catalyze the epoxidation of olefins with H_2O_2 under mild conditions. Heterogenization of this kind of catalysts is very desirable. Xi *et al.* developed π-$[C_5H_5NC_{16}H_{33}]_3$-$[PO_4(WO_3)_4]$ based catalyst with special solubility characteristics for the epoxidation of 1-hexene and cyclohexene at high selectivities (S > 87 %).[117] In their system, the initially insoluble catalyst becomes soluble in aqueous H_2O_2-toluene due to the *in situ* formation of π-$[C_5H_5NC_{16}H_{33}]_3\{PO_4[W(O)_2(O_2)]_4\}$ (Scheme 2). At



S c h e m e 2 – *Reaction-controlled phase-transfer catalyst:* π-$[C_5H_5NC_{16}H_{33}]_3[PO_4(WO_3)_4]$

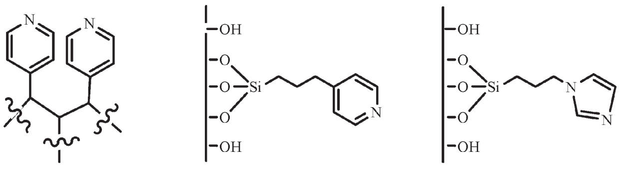
the end of the reaction in the absence of H_2O_2, the catalyst precipitates out, facilitating its recovery from the reaction mixture. The catalyst is stable and can be recycled without loss of activity (Scheme 2). This system combined the high reactivity of the homogeneous catalyst and the easy separation of the heterogeneous one. As a so-called reaction-controlled catalyst, there are many aspects that should be explored before it can be really used in industrial scale.

Another direction to fully use the favorable catalyst is to immobilize the catalyst to some special supports. Functionalized silica particles were always used to support the active transition-metal-substituted polyoxometalates. The catalyst could well dispense the organic solvent, because the silica surface was modified with the suitable hydrophilicity and hydrophobicity. In addition, catalyst recovery is simplified by use of filtration of silica particle.[118–120] Similarly, the dinuclear peroxotungstate $[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$ was recently immobilized on an imidazolium ion liquid-modified silica. The resulting catalyst was highly efficient in the epoxidation of various olefins with H_2O_2 as an oxidant in CH_3CN at 100 °C, affording high yields (up to 99 %) of the epoxides, together with easy recovery of catalyst by a simple filtration. The catalyst was reused several times without loss of activity and selectivity.[121] The immobilization of tungsten and phosphotungsten (PW) catalytic species on both organic resins such as Amberlite IRA-900 and hybrid silica materials has been examined in the epoxidation of bulky olefins.[122] *In situ* formation of peroxo-W species bound to the immobilized P group results in the most active catalyst and epoxidizes bulky olefins such as cyclooctene, norbornene and geraniol with good conversions and high selectivities ($S > 93$ %). Especially the $\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3\text{-}(PW_{12}O_{40})^{3-}$/silica showed good performance in the epoxidation of terminal, cyclic, highly substituted and aromatic olefins with the corresponding epoxides selectivity $S > 97$ %. More recently, Xi *et al.* reported a reversible supported catalyst, quarternary ammonium heteropolyphosphatotungstate compounds supported on silanized silica gel, for the epoxidation of allyl chloride to epichlorohydrin with H_2O_2 under solvent-free conditions. The selectivity to epoxide and conversions of inactive allyl chloride based on H_2O_2 were both high, with $S = 94.4$ %, and $X = 90.6$ % respectively.[123]

Supported porphyrins

Immobilization of metalloporphyrins onto a solid support is another catalyst family for alkene epoxidation. However, the synthesis of metalloporphyrins is challenging and low-yielding. Immobilization onto a solid support can counteract this problem, enabling easier recovery and reuse of the catalysts, and reducing the instability of the metalloporphyrins during the epoxidation reaction.

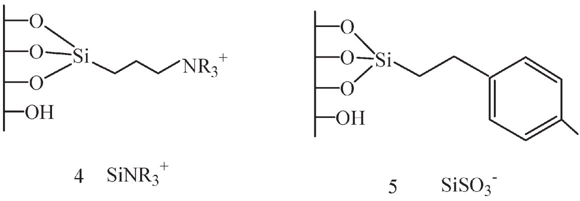
Miguel *et al.*[124] have reviewed the supported metalloporphyrin catalysts for alkene epoxidation with kinds of oxidants such as PhIO, $NaIO_4$, $KHSO_5$, NaOCl, and also H_2O_2. The performance of the catalysts is usually lower using H_2O_2 as an oxidant than using other organic oxidants. Several synthetic strategies and a wide range of supports can be used. Metalloporphyrins can be immobilized *via* coordinative binding between their metal centre and a nitrogenous axial ligand (Scheme 3), which is covalently anchored to a support. Pyridine ligands have been anchored onto organic supports to form polyvinylpyridines (PVP) **1**[125] and have also been immobilized on inorganic supports, such as silica gel (Si–Py) **2**. Imidazole attached to polystyrene (PS–Im)[126,127] or silica gel (Si–Im) **3**, have also been utilized. Several different metalloporphyrins have been anchored to these supports and have been investigated mainly in the epoxidation of cyclooctene with PhIO as the oxidant to replace H_2O_2, which always requires the presence of an additional ligand such as imidazole. However, lower yields are usually achieved. The best system so far involved iron monosulfonated porphyrin immobilized on Si-Im, which formed epoxycyclooctane with a good yield of $Y = 50$ % (compared to only $Y = 12$ % with the homogeneous analogue).



1 PVP **2** Si-Py **3** Si-Im

Scheme 3 – *Immobilized axial ligands*

There are also some inorganic supports such as aminopropyl silica (APS), montmorillonite K_{10} and some organic supports such as PEG. Electrostatic interactions between an ionic metalloporphyrin and a counterionic group situated on the support have been shown to be stronger than the coordinative ones. Anionic metalloporphyrins containing sulfonate groups have been developed and anchored onto silica gel containing ammonium groups ($SiNR^{3+}$) **4** and anionic silica gel ($SiSO^{3-}$) **5** (Scheme 4). Compared with coordinative bound manganese porphyrins, these immobilized catalysts have a shorter reaction time. One novel heterogeneous catalyst was developed by immobilization of the robust Mn porphyrin on a modified silica which



Scheme 4 – *Ionic silica gels*

covalently bonded at the β-pyrrolic position of the macrocycle.[128] The efficiency of the catalyst system was evaluated for the epoxidation of *cis*-cyclooctene with H_2O_2, X = 89 % of substrate and $S \geq$ 99 % can be obtained. H_2O_2 has also been used as oxidant for the epoxidation of the deactivated double bond of an allylic alcohol (3-penten-2-ol) catalyzed by manganese porphyrin encapsulated in polydimethylsiloxane (a dense hydrophobic elastomer)[129] and by the manganese porphyrins immobilized on (Si–Im)(SiSO^{3-}) **5**, but low yields were obtained. Few studies have been carried out on the epoxidation of alkenes other than cyclooctene.

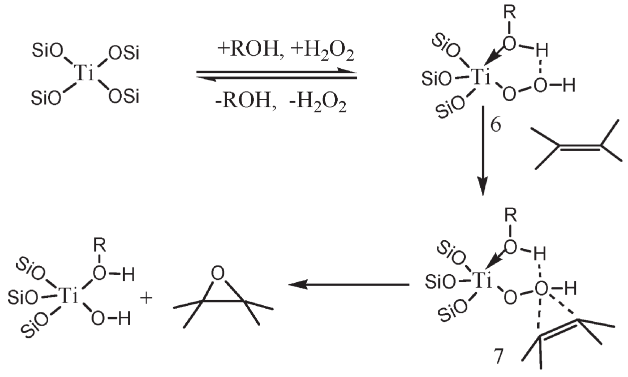
Zhang *et al.*[130] reported the encapsulation of chiral Ru-porphyrin into uniform mesopores of ordered mesoporous molecular sieves (MCM-41 and MCM-48). When these catalysts were used in the asymmetric epoxidation of olefins, *ee* values ranging 43–77 % could be achieved. Notably, chiral Ru-porphyrin immobilized on MCM-48 showed a better reactivity for *cis*-alkenes than for *trans*-counterparts, closely similar to the case of free chiral Ru-porphyrin complex.

The reuse of supported metalloporphyrins remains challenging, leaching of the catalysts into solution can be observed due to cleavage of the spacer chain between the porphyrin and the support.[131] Nevertheless, some catalysts are already recyclable several times without loss of activity.[132] In particular, ruthenium porphyrins have shown excellent results in terms of recyclability.[133]

Catalytic epoxidation mechanisms

Catalytic epoxidation mechanisms over titanium silicates

Due to the exclusive properties of TS-1 on olefin epoxidation, a lot of work has been devoted to the study on the mechanism of titanosilicate catalyzed epoxidation.[134,135] A mechanistic rationalization was proposed based on species **7** as an intermediary (Scheme 5).[136] The titanium is teterahedrally coordinated in TS-1 catalyst, which coordinate the solvent and is transformed into pentahedral and/or octahedral. The solvent efficiency series can be justified by the result of decreasing electrophilicity



Scheme 5 – *Proposed mechanism for the TS-1 epoxidation of olefins*

and increasing steric constraint of species **7**. The increasing of R group size in the alcohol facilitates the formation of **6** and favors the approach of the olefin. The catalytic activity is decreased by higher concentration of basic substrates and is improved by the presence of acids. The epoxidation of terminal double bond is very slow when compared to internal ones. These selectivity differences can be explained in terms of the double bond ability to coordinate to the Ti active site as well as by steric demands. More recently, Limtrakul *et al.*[137] used the 65T nanocluster, $TiSi_{64}O_{97}H_{74}$, and calculated at the 9T/65T two-layered ONIOM level to investigate the mechanism of alkene oxidation with H_2O_2 over titanium silicalite-1(TS-1) defect. The intermediate titanium hydroperoxo in the bidentate form, Ti(η^2-OOH), occurring through the single-step double proton-transfer mechanism aided by a neighboring silanol group, is proffered as the active species in the oxidation process.

TS-1 was confirmed stable towards H_2O_2, in agreement with its well-known catalytic applications, while Ti-β is not stable.[138] In TS-1, Si-O-Ti bonds can react at room temperature with water or other protic molecules, producing reversible Si-OH and Ti-OH (or Ti-OOH in the case of H_2O_2), while thermal treatment restores the initial Si-O-Ti bonds. On the other hand, in Ti-β, H_2O_2 gives rise to a high amount of defects and to a partial removal of Ti from the framework.

It is reported that tetrahedral Ti isolated by SiO groups **7**[139] in a silica matrix is also the most active site for the supported oxides.

As to the silica supported Ti-catalyst, modification of the silica surface with HCl could show a surprisingly better performance as support for the titanium centre than the parent silica. The use of a weaker electrophilic species, such as an acyl chloride, allows the modulation of the support properties in such a way that it can be prepared as the best silica-supported titanium catalyst for epoxidation with diluted H_2O_2.[140]

Catalytic epoxidation mechanisms over mixed oxides

It is assumed that several different active Ti sites[141] may be present in the mixed oxides and the most active and selective site for olefin epoxidation is the isolated tetrahedral Ti **8** (Scheme 6). Their structures can cover the whole range from tetrahedral Ti isolated by four SiO groups **8** to octahedral Ti surrounded by six TiO groups **9** (titania nanodomains). The transformation of isolated, tetrahedral Ti to octahedral TiO_2 nanodomains may be visualized by a gradual replacement of SiO ligands by TiO groups, and a change from 4 to 5 to 6 coordination. The first "step" in this direction is the bidentate Ti site. This structural unit is present in the soluble titanosilsesquioxane prepared from $Ti(O^iPr)_4$ and trisilanols **10**, and also in silica-supported $Ti(O^iPr)_4$ **11**. The last step in the "hypothetic" change from isolated Ti to anatase titania is a Ti site that contains only Ti-O-Ti connectivity except one Ti-O-Si bond (species **12)**. This structure was assumed to be formed when the surface OH groups of the titania aerogel were silylated.

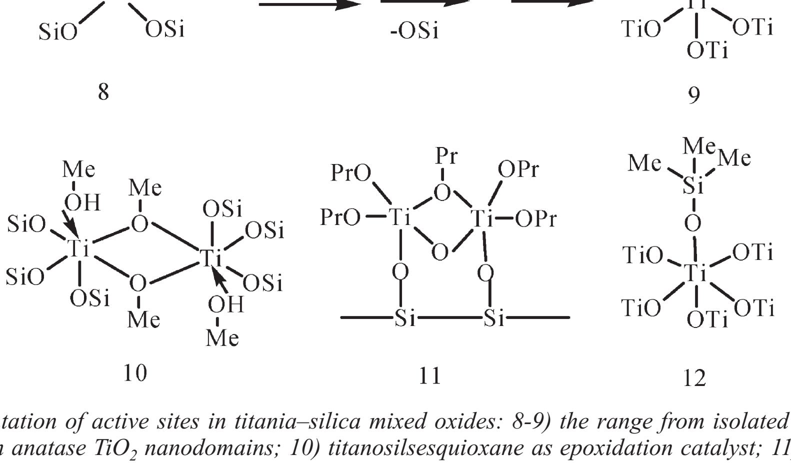
Mesoporous mixed oxides containing tetrahedral Ti were the most active catalysts for the epoxidation reaction with organic hydroperoxide due to the ease of access of bulky reactants to the Ti sites. However, the same mesoporous mixed oxides were ineffective for the epoxidation reaction with aqueous H_2O_2 compared to titanosilicalite TS-1. Apparently, the hydrophobicity of a mesoporous sample is not adequate to screen out water from the active Ti site.[142] Interestingly, the poisoning of acidic centers yields a decreasing activity while increasing selectivity.

Catalytic epoxidation mechanisms over layered hydrotalcite

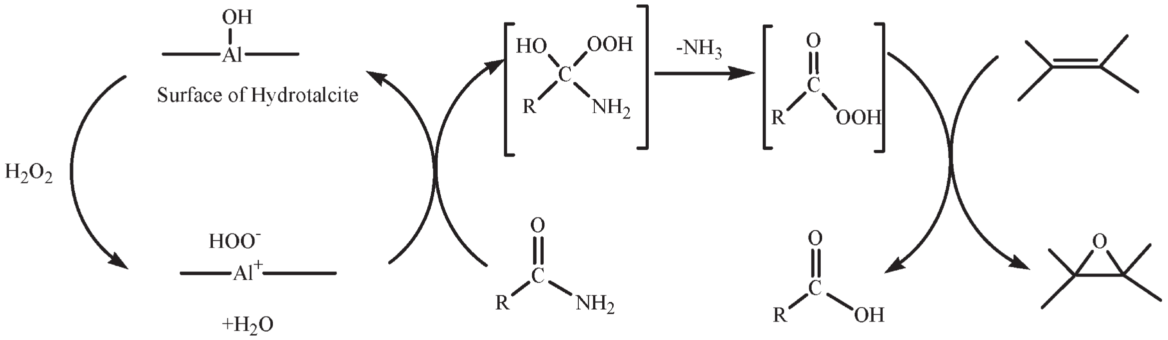
Yamaguchi, K. *et al.*[76] depicted a possible scheme of the epoxidation catalyzed by layered hydrotalcite (Scheme 7). H_2O_2 attacks a basic hydroxyl function on the surface of hydrotalcites to form an HOO- species, which reacts with an amide to generate a peracid together with NH_3 in the aqueous phase. Further, the oxygen transfer from the peracid to an olefin occurs at the surface boundary between aqueous and organic phases. In addition, anionic surfactant should be added to increase the contact area of the interface between the aqueous and organic phases and to enhance the transfer of a lipophilic olefin from the organic phase to the interface between the above two phases.

Ilham *et al.*[143] reported Mg/Al hydrotalcite-like materials for the epoxidation of styrene, using a combined oxidant of H_2O_2 and acetonitrile in the presence of acetone and water as solvents. When in the absence of nitriles, no activity is observed. A combined effect between the oxidant, acetonitrile and the hydroxyl groups of the hydrotalcite sample is necessary to improve the epoxidation reaction (Scheme 8).

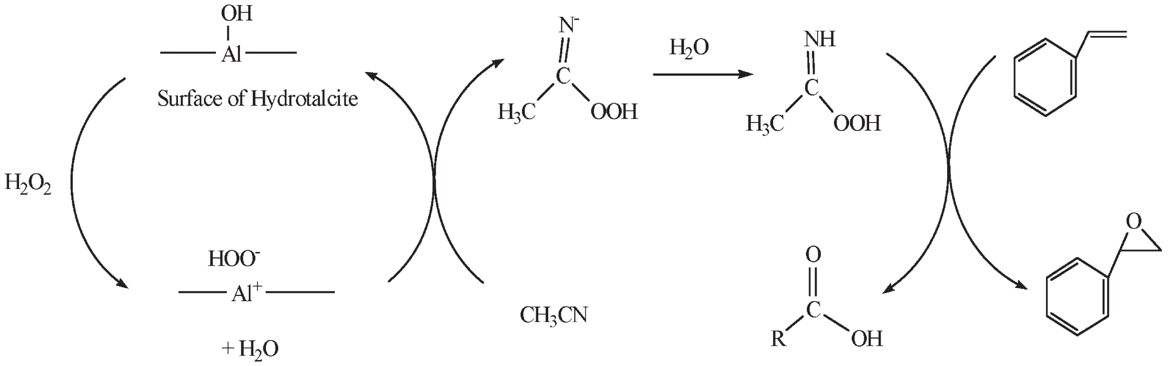
The tungstate-exchanged hydrotalcite showed good activity in the epoxidation of olefins with the assistance of bromide. Scheme 9 illustrates the proposed epoxidation mechanism.[81,144] Note that Br^- anions can be recycled from bromohydrin, making water the only byproduct. The main differences with the industrial two-step halohydrin processes are the controlled catalytic production of "Br^+", which replaces the addition of element halogen, and the *in situ* transformation of bromohydrin. Thus, isolation of bromohydrin is no longer needed. Moreover, the bromide-assisted epoxidation is char-



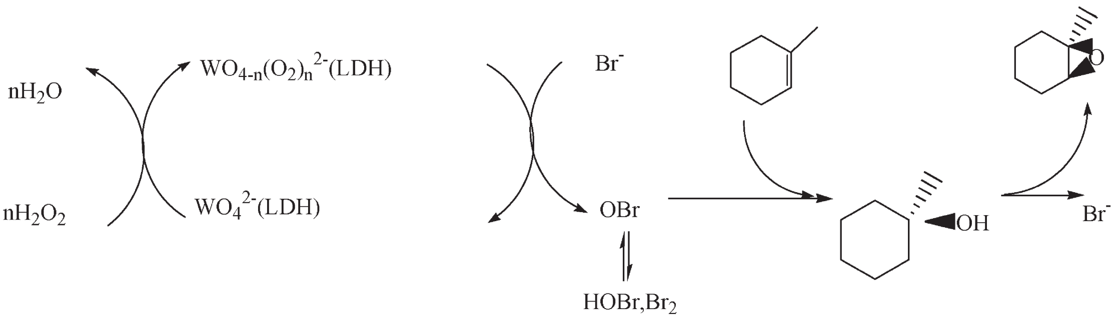
Scheme 6 – *Representation of active sites in titania–silica mixed oxides: 8-9) the range from isolated tetrahedral Ti to octahedral Ti in anatase TiO_2 nanodomains; 10) titanosilsesquioxane as epoxidation catalyst; 11) the proposed active site in silica-supported $Ti(O^iPr)_4$); and 12) silylated octahedral titania*



S c h e m e 7 – *Proposed mechanism for the hydrotalcites catalyzed epoxidation of olefins with isobutyramide as additive*



S c h e m e 8 – *Proposed mechanism for hydrotalcites used in the epoxidation of styrene with acetonitrile as solvent*



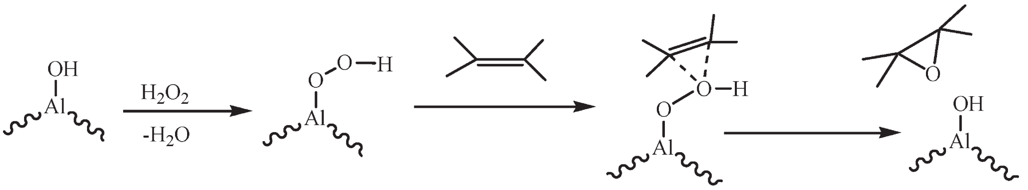
S c h e m e 9 – *Proposed epoxidation mechanism for* WO_4^- *– LDH catalyzed epoxidation of olefin*

acterized by much higher turnover frequencies than classical W-catalyzed epoxidation.

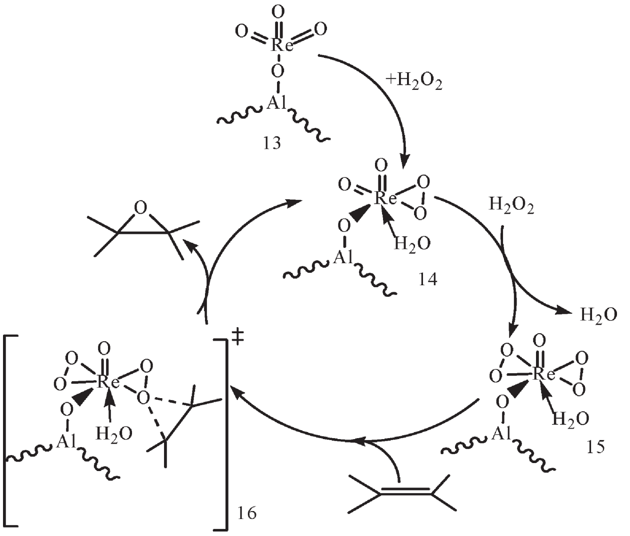
Catalytic epoxidation mechanisms over Al_2O_3 and supported rhenium oxide

The reaction mechanism of the Al_2O_3/H_2O_2-catalyzed alkene epoxidation probably involves Al-OOH species[106] (Scheme 10). First, the alumina reacts with the H_2O_2, forming the active species Al-OOH, which further react the olefins with the oxygen transferred to produce the resulting peroxide. The deactivation of Al_2O_3 is not straightforward. Some chemical and physical changes associated with the deactivation of the alumina used for catalytic epoxidation with H_2O_2 are attributed to the presence of water in the reaction mixture and to the adsorption of organic moleculars on the alumina surface. On the other hand, water plays an important role related to prolonging catalyst lifetime by shifting the equilibriums of the adsorption of byproducts.[145]

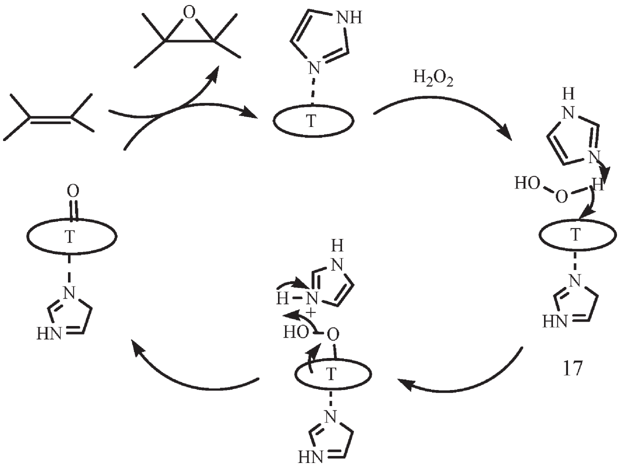
Tetrahedral ReO_4^- species are attached to alumina surfaces by covalent Al-O-Re bonds. The proposed mechanism[104] of ReO_4-Al_2O_3 catalysts was depicted in Scheme 11. Reaction of surface-Al-O-ReO_3 **13** with H_2O_2 gives the peroxo species **14**, which reacts further with H_2O_2 to form complex **15**. Oxygen transfer from **15** to the olefin yields the epoxide and complex **14**.



Scheme 10 – *Proposed mechanism of Al_2O_3-catalyzed alkene epoxidation*



Scheme 11 – *Proposed mechanism for the re-catalyzed epoxidation of alkenes at the surface of alumina*



Scheme 12 – *Proposed mechanism of metalloporphyrin-catalyzed olefin epoxidation using H_2O_2 as oxidants*

Catalytic epoxidation mechanisms over ship-in-bottle materials and metalloporphyrin-based catalysts

Kenneth and coworkers[146] assumed the mechanism of the ship-in-bottle material is radical in nature. The FePc/NaY catalyzed oxidation of alkanes in acetone was reported to involve a radical mechanism, while changing the solvent to a polymer membrane results in activity, which has been described as a mimic of enzyme P-450 which involves oxo chemistry.

The proposed mechanism of metalloporphyrin-catalyzed olefin epoxidation using H_2O_2 as oxidant is shown in Scheme 12. The catalytic reaction requires the presence of an additional ligand such as imidazole. This co-catalyst helps cleave the O-O of the metal hydroperoxoporphyrin **17** heterolytically, formed by reaction between the metalloporphyrin and H_2O_2.[124]

Besides, transition-metal-substituted Keggin-type polyoxometalates (Zn, Ti, Fe, and Mn-substituted) can act as effective catalysts for H_2O_2-based epoxidation. Yamase and coworkers[147] proposed that the intermediate from the synergistic interaction between η^2-peroxo $Ti(O_2)$ species with $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ acted as an electrophilic center for the olefin on the catalyst. The coordination of Ti^{4+} in Ti-polyoxometalate is octahedral-like geometry, which is different from the Ti, Si-catalyst with tetrahedral coordination.[148] In addition, the solvent nature had a strong effect on the stability of Ti-POM toward H_2O_2 and, therefore, on its catalytic activity in epoxidation of olefins.

Conclusions and prospects

A broad range of solids including framework-substituted molecular sieves, inorganic oxide and supported catalysts, porous materials encapsulated metal complexes, layered-type materials, peroxometalates, supported porphyrin catalysts and some others have been tested as catalysts for the liquid phase epoxidation with H_2O_2 as oxidants. All these catalyst systems have shown potential in olefin epoxidation, sometimes depending on the reaction conditions. Among these, the catalyst systems with W, Ti and Mo have a much better prospect of industrial application from the economical viewpoint, although these catalysts and reaction conditions should be further optimized.

However, the catalytic performance of most catalysts still cannot satisfy all requirements of commercialization. Further improvements should still be sought to meet the need of industrial processes with H_2O_2 as oxidants. For supported metal catalysts, the problem of leaching of active species must be overcome. Since a variety of possible products may be obtained under catalytic oxidation, one of the key problems is to invent novel catalysts with much higher selectivity to an objective product. In the meantime, the treatment technologies of byproducts or recycling of co-products should be improved. For some catalysts, only the oxidants such as PhIO, *t*BOOH, benzaldehyde, and *m*-chloroperoxo benzoic offer more efficient properties rather than H_2O_2. Modification of such kinds of catalysts could perhaps offer an alternative to obtaining new catalysts, which could be used in the presence of H_2O_2. For epoxidation of some functionalized olefins to high value-added chemicals, the activity and selectivity should be a priority.

The merger of the advantageous properties of homogeneous and heterogeneous catalysis bears great potential and a few attempts have been made to heterogenize homogeneous transition metal catalysts, such as the use of reaction-controlled phase-transfer catalyst, and the immobilization of homogeneous catalysts, etc. Still, the number of satisfying catalyst systems, which are robust, recyclable and afford rates and selectivities comparable to those of their homogeneous counterparts is rather limited.

The deep understanding of the mechanisms is of great importance for the design of solid epoxidation catalysts, which is still underdeveloped.[90,149] To the best of our knowledge, the mechanisms for the epoxidation catalysts reported previously only involve the activation of H_2O_2 over catalysts first to form usually peroxo- active sites, and then react with the olefins by transforming the oxygen to produce the epoxides. Is there any reaction initiated with the activation of olefins first, followed by the reaction with H_2O_2? More efforts should be made to investigate the mechanisms to afford a guideline for the novel catalyst design and facilitate realization of greener epoxidation processes with H_2O_2 as oxidant.

Besides, the interaction of substrate and solvents,[150] the effect of water, the leaching of the active transition metal in the heterogeneous catalysts, the deactivation of the catalysts, and the kinetics of the reaction are significant for the guidance of good design of catalysts for epoxidation. All of these need further study. Finally, future development of industrial catalysts for green epoxidation should also take into consideration production costs, easy separation and regeneration besides high catalytic activity and selectivity.

ACKNOWLEDGMENT

Funded by the national natural science foundation of China (No. 20773110 and No. 20541002), SINOPEC basic research foundation (X 504034) and Zhejiang provincial natural science foundation (No. Y405064; Y405025, Y407200) are acknowledged.

List of symbols

S – selectivity, %
T – temperature, °C
t – time, h
w – mass fraction, %
X – conversion, %
Y – yield, %

References

1. *Grigoropoulou, G., Clark, J. H., Elings, J. A.,* Green Chem. **5** (2003) 1.
2. *Mizuno, N., Yamaguchi, K., Kamatab, K.,* Coord. Chem. Rev. **249** (2005) 1944.
3. *Dusi, M., Mallat, T., Baiker, A.,* Catal. Rev. Sci. Eng. **42** (2000) 213.
4. *Kochkar, H., Figueras, F.,* J. Catal. **171** (1997) 420.
5. *Kumar, P., Kumar, R., Pandey, B.,* Syn. Lett. **4** (1995) 289.
6. *Camblor, M. A., Corma, A., Pérez-Pariente, J.,* Zeolites **13** (1993) 82.
7. *Xiao, F. S., Han, Y., Yu, Y., Meng, X. J., Yang, M., Wu, S.,* J. Am. Chem. Soc. **124** (2002) 6.
8. *Niaki, Z., Kapoor, M. P., Kailiaguine, S.,* J. Catal. **177** (1998) 231.
9. *Tuel, A.,* Zeolites **15** (1995) 228.
10. *Prakash, A. M., Hartmann, M., Zhu, Z. D., Kevan, L.,* J. Phys. Chem. B **104** (2000) 1610.
11. *Cativiela, C., Figueras, F., Fraile, J. M., Garcia, J. I., Mayoral, J. A.,* Tetrahedron Lett. **36** (1995) 4125.
12. *Sels, B. F., De Vos, D. E., Jacobs, P. A.,* J. Chem. Soc., Chem. Commun. **123** (1990) 8350.
13. *Oldroyd, R. D., Sankar, G., Thomas, J. M., Özkaya, D.,* J. Phys. Chem. B **102** (1997) 1849.
14. *Paez-Mozo, E., Gabriunas, N., Maggi, R., Acosta, D., Ruiz, P., Delmon, B.,* J. Mol. Catal. **91** (1994) 251.
15. *van der Waal, J. C., Rigutto, M. S., van Bekkum, H.,* Appl. Catal. A: Gen. **167** (1998) 331.
16. *Wang, X. S., Guo, X. W., Li, G.,* Catal. Today **74** (2002) 65.
17. *Cativiela, C., Fraile, J. M., Garaia, F. I., Mayoral, J. A.,* J. Mol. Catal. B **112** (1996) 259.
18. *José, M. F., José, I. G., José, A. M., Louis, C. de M., Férid, R.,* J. Chem. Soc. Chem. Commun. **1995** 539.
19. *Shul'pin, G. B., Sooknoi, T., Romakh, V. B., Süss-Fink, G., Shul'pina, L. S.,* Tetrahedron Lett. **47** (2006) 3071.
20. *Thomas, M., Fernando, R., Gopinathan, S., John, M. T.,* Nature **9** (1995) 159.
21. *Xu, C. H., Jhung, S. H., Chang, J. S., Hwang, J. S., Park, S. E.,* Catal. Today **111** (2006) 366.
22. *Clerici, M. G., Ingallina, P.,* J. Catal. **140** (1993) 71.
23. *Pandey, R. K., Kumar, R.,* Catal. Commun. **8** (2007) 379.
24. *Höft, E., Kosslick, H., Fricke, R., Hamann, H. J.,* J. für Praktische Chemie / Chemiker-Zeitung **338** (1996) 1.
25. *Clerici, M. G., Bellussi, G., Romano, U.*, J. Catal. **129** (1991) 159.

26. *Capel-Sanchez, M. C., Campos-Martin, J. M., Fierro, J. L. G.,* Appl. Catal. A: Gen. **246** (2003) 69.
27. *Meiers, R., Dingerdissen, U., Hölderich, W. F.,* J. Catal. **176** (1998) 376.
28. *Wang, Q., Wang, L., Chen, J., Wu, Y., Mi, Z.*, J. Mol. Catal. A: Chem. **273** (2007) 73.
29. *Laha, S. C., Kumar, R.,* J. Catal. **204** (2001) 64.
30. *Cheng, W. G., Wang, X. S., Li, G., Guo, X. W.*, Cuihua Xuebao **25** (2004) 513.
31. *Rigutto, M. S., Van Bekkum, H.,* Appl. Catal. **68** (1991) L1.
32. *Moussa, N., Ghorbel, A.,* J. Sol-Gel Sci. Tech. **33** (2005) 127.
33. *Bhaumik, A., Mal, N. K.,* Stud. Surf. Sci. Catal. **145** (2002) 223.
34. *Ziolek, M.,* Catal. Today **90** (2004) 145.
35. *Arends, I. W. C. E., Sheldon, R. A., Wallau, M., Schuchardt, U.,* Chem. Int. Engl. **36** (1997) 1144.
36. *Kustova, M. Y., Hasserlriis, P., Christensen, C. H.,* Catal. Lett. **96** (2004) 205.
37. *Camblor, M. A., Costantini, M., Corma, A., Gilbert, L., Esteve, P., Martinez, A., Valencia, S.,* Appl. Catal. A: Gen. **133** (1995) L185.
38. *van der Waal, J. C., Kooyman, P. J., Jansen, J. C., van Bekkum, H.,* Microporous Mesoporous Mater. **25** (1998) 43.
39. *Blasco, T., Camblor, M. A., Corma, A., Esteve, P., Martinez, A., Valencia, S.,* Chem. Commun. **1996** 2367.
40. *Cambor, M. A., Costantini, M., Corma, A., Gilbert, L., Esteve, P., Martinez, A., Valencia, S.,* Chem. Commun. **1996** 1339.
41. *Blasco, T., Miguel, A. Camblor, Corma, A., Esteve P., Martinez, A., Prieto, C., Valencia, S.,* J. Catal. **180** (1998) 132.
42. *Jappar, N., Xia, Q. H., Tatsumi, T.,* J. Catal. **180** (1998) 132.
43. *Ogura, M., Nakata S., Kikuchi, E., Matsukata, M.,* J. Catal. **199** (2001) 41.
44. *Wu., P., Tatsumi, T., Komatsu, T., Yashima, T.,* J. Catal. **202** (2001) 245.
45. *Kholdeeva, O. A., Derevyankin, A. Y., Shmakov, A. N., Trukhan, N. N., Paukshtis, E. A., Tuel, A.,* J. Mol. Catal. A: Chem. **158** (2000) 417.
46. *Wu, P., Tatsumi, T.,* Catal. Surv. From Asia **2** (2004) 137.
47. *Chandr, D., Malb, N. K., Bhaumik, A.,* J. Mol. Catal. A: Chem. **247** (2006) 216.
48. *Kapoor, M. P., Raj A.,* Appl. Catal. A: Gen. **203** (2000) 311.
49. *Corma, A., Navarro, M. T., Pariente, J. P.,* J. Chem. Soc., Chem. Commun. (1994) 147.
50. *Kilos, B., Aouine, M., Nowak, I., Ziolek, M., Volta, J. C.,* J. Catal. **224** (2004) 314.
51. *Shylesh, S., Singh, A. P.,* J. Catal. **233** (2005) 359.
52. *Wang, Y., Zhang, Q. H., Shishido, T., Takehira, K.,* J. Catal. **209** (2002) 186.
53. *Fan, W., Wu, P., Namba, S., Tatsumi, T.,* Angew. Chem. Int. Ed. **43** (2004) 236.
54. *Wang, L., Liu, Y., Zhang, H., Wu, H., Jiang, Y., Wu, P.,* Chin. J. Catal. **27** (2006) 656.
55. *Wang, L., Liu, Y., Xie, W., Zhang, H., Wu, H., Jiang, Y., He, M., Wu, P.,* J. Catal. **246** (2007) 205.
56. *Wilson, S. T., Lok, B. M., Messina, C. A., Cannan, T. R., Flanigen, E. M.,* J. Am. Chem. Soc. I **104** (1982) 1146.
57. *Raja, R., Sankar, G., Thomas, J. M.,* Chem. Commun. **1999** 829.
58. *Zahedi-Niaki, M. H., Kapoor, M. P., Kaliaguine, S.,* J. Catal. **177** (1998) 231.
59. *Rigutto, M. S., Bekkum, H. V.,* J. Mol. Catal. **81** (1993) 77.
60. *Haanepen, M. J., van Hooff, J. H. C.,* Appl. Catal. A: Gen. **152** (1997) 183.
61. *Chaudhari, K., Das, T. K., Rajmohanan, P. R., Lazar, K., Sivasanker, S., Chandwadkar, A. J.,* J. Catal. **183** (1999) 281.
62. *Masteri-Farahani, M., Farzaneh, F., Ghandi, M.,* J. Mol. Catal. A: Chem. **l 243** (2006) 170.
63. *Li, J., Zhou, C. H., Xie, H. L., Ge, Z., Yuan, L., Li, X.,* J. Nat. Gas Chem. **15** (2006) 164.
64. *Cagnoli, M. V., Casuscelli, S. G., Alvarez, A. M., Bengoa, J. F., Gallegos, N. G., Crivello, M. E., Herrero, E. R., Marchetti, S. G.,* Catal. Today **107** (2005) 397.
65. *Tatsumi, T., Koyano, K. A., Igarashi, N.,* Chem. Commun. **1998** 325.
66. *Zhang, W. H., Lu, J. P., Li, M. J., Xiu, J. H., Ying, P. L., Li, C.,* Chem. Mater. **14** (2002) 3413.
67. *Chiker, F., Launay, F., Nogier, J. P., Bonardet, J. L.,* Green Chem. **5** (2003) 318.
68. *Wang, X. S., Guo, X. W.,* Catal. Today **51** (1999) 177.
69. *Ma, S. O., Li, G., Wang, X. S., Jin, C. Z., Liu, M.,* J. Fuel Chem. Tech. **33** (2005) 509.
70. *Shan, Z. P., Jansen, J. C., Marchese, L., Maschmeyer, T.,* Microporous Mesoporous Mater. **48** (2001) 181.
71. *Corma, A., Diaz, U., Domine, M. E., Fornés, V.*, Chem. Commun. **2000** 137.
72. *Trukhan, N. N., Derevyankin, A. Y., Shmakov, A. N., Paukshtis, E. A., Kholdeeva, O. A., Romannikov, V. N.,* Microporous Mesoporous Mater. **44** (2001) 603.
73. *Ji, D., Zhao, R., Lv, G., Qian, G., Yan, L., Suo, J.,* Appl. Catal. A: Gen. **281** (2005) 39.
74. *Ueno, S., Yamaguchi, K., Yoshida, K., Ebitani, K., Kaneda, K.,* Chem. Commun. (1998) 295.
75. *Palomeque, J., Lopez, J., Figueras, F.,* J. Catal. **211** (2002) 150.
76. *Yamaguchi, K., Ebitani, K., Kaneda, K.,* J. Org. Chem. **64** (1999) 2996.
77. *Pillai, U. R., Sahle-Demessie, E., Varma, R. S.,* Tetrahedron Lett. **43** (2002) 2909.
78. *Zhou, C. H., Ge, Z., Li, X., Tong, D., Li, Q., Guo, H.,* Chin. J. Chem. Eng. **12** (2004) 388.
79. *Maheswari, P. U., Tang, X. H., Hage, R., Gamez, P., Reedijk, J.,* J. Mol. Catal. A: Chem. **258** (2006) 295.
80. *Palomeque, J., Figueras, F., Gelbard, G.,* Appl. Catal. A: Gen. **300** (2006) 100.
81. *Sels, B. F., De Vos, D. E., Jacobs, P. A.,* J. Am. Chem. Soc. **123** (2001) 8350.
82. *de Farias, R. F., Arnold, U., Martínez, L., Schuchardt, U., Jannini, M. J. D. M., Airoldi, C.,* J. Phys. Chem. Solids **64** (2003) 2385.
83. *Palazzi, C., Oliva, L., Signoretto, M., Strukul, G.,* J. Catal. **194** (2000) 286.
84. *Gan, L., Wang, Y., Hao, Z., Xu, Z., Chen, L.*, Chin. J. Chem. Eng. **13** (2005) 758.
85. *Somma, F., Puppinato, A., Strukul, G.,* Appl. Catal. A: Gen. **309** (2006) 115.
86. *Hutter, R., Mallat ,T., Dutoit, D., Baiker ,A.,* Top. Catal. **3** (1996) 421.
87. *Samantaray, S. K., Parida, K.,* Catal. Commun. **6** (2005) 578.
88. *Müller, C. A., Schneider, M., Mallat, T., Baiker, A.*, Appl. Catal. A: Gen. **201** (2000) 253.
89. *Ng, Y. H., Izwan, I., Nur, H., Muhid, M. N. M., Hamdan, H.,* J. Fluorine. Chem. **128** (2007) 12.
90. *Klein, S., Thorimbert, S., Mairer, W. F.,* J. Catal. **163** (1996) 476.
91. *Shan, Z. P., Jansen, J. C., Marchese, L., Maschmeyer, T.,* Microporous Mesoporous Mater. **48** (2001) 181.
92. *Somma, F., Strukul, G.,* J. Catal. **227** (2004) 344.

93. *Herrmann, W. A., Fischer, R. W., Rauch, M. U., Scherer, W.,* J. Mol. Catal. **86** (1994) 243.
94. *Adolfsson, H., Converso, A., Sharpless, K. B.,* Tetrahedron Lett. **40** (1999) 3991.
95. *Herrmann, W. A., Kühn, F. E., Mattner, M. R., Artus, G. R. J., Geisberger, M. R., Correia, J. D. G.,* J. Organomet. Chem. **538** (1999) 203.
96. *Herrmann, W. A., Kratzer, R. M., Ding, H., Thiel, W. R., Glas, H.,* J. Organomet. Chem. **555** (1998) 293.
97. *Saladino, R., Andreoni, A., Neri, V., Crestini, C.,* Tetrahedron **61** (2006) 1069.
98. *Bouh, A. O., Espenson, J. H.,* J. Mol. Catal. A: Chem. **200** (2003) 43.
99. *Li, M., Espenson, J. H*., J. Mol. Catal. A: Chem. **208** (2004) 123.
100. *Li, M., Espenson, J. H.,* J. Mol. Catal. A: Chem. **208** (2004) 123.
101. *Neumann, R., Wang, T. J.,* Chem. Commun. **1997** 1915.
102. *Saladino, R., Neri, V., Pelliccia, A. R., Mincione, E.,* Teterahedron **59** (2003) 7403.
103. *Nunes, C. D., Pillinger, M., Valente, A. A., Goncalves, I. S., Rocha, J., Ferreira, P., Kühn, F. E.,* Eur. J. Inorg. Chem. **2002** 1100.
104. *Mandelli, D., van Vliet, M. C. A., Arnold U., Sheldon, R. A., Schuchardt, U.,* J. Mol. Catal. A: Chem. **168** (2001) 165.
105. *Adam, W., Saha-Moller, C. R., Weichold, O.,* J. Org. Chem. **65** (2000) 2897.
106. *Mandelli, D., van Vliet, M. C. A., Sheldon, R. A., Schuchardt, U.,* Appl. Catal. A: Gen. **219** (2001) 209.
107. *van Vliet, M. C. A., Mandelli, D., Arends, I. W. C. E., Schuchardt, U., Sheldon, R. A., Green Chem.* **3** (2001) 243.
108. *Uguina, M. A., Delgado, J. A., Rodríguez, A., Carretero, J., Gómez-Díaz, D.,* J. Mol. Catal. A: Chem. **256** (2006) 208.
109. *Cesquini, R. G., de S. e Silva, J. M., Woitiski, C. B., Mandelli, D., Rinaldi, R., Schuchardt, U.,* Adv. Synth. Catal. **344** (2002) 911.
110. *Lafarga, D., Al-Juaied, M. A., Bondy, C. M., Varma, A.,* Ind. Eng. Chem. Res. **39** (2000) 2148.
111. *Song, H. L., Chen, G. X., Li, S. B., Luo, S. W., Yao, C. L.,* React. Kinet. Catal. Lett. **85** (2005) 45.
112. *Rojluechai, S., Chavadej, S., Schwank, J. W., Meeyoo, V.,* J. Chem. Eng. Jap. **39** (2006) 321.
113. *Fraile, J. M., García, J. I. , Mayoral, J. A., Figueras, F.,* Tetrahedron Lett. **37** (1996) 5995.
114. *Ernst, S., Selle, M.,* Microporous Mesoporous Mater. **27** (1999) 355.
115. *Balkus, K. J., Khanmamedova, A. K., Dixon, K. M., Bedioui, F.,* Appl. Catal. A: Gen. **143** (1996) 159.
116. *Knops-Gerrits, P. P., De Vos, D. E., Thibault-Starzyk, F., Jacobs, P. A.,* Nature **369** (1994) 543.
117. *Xi, Z. W., Zhou. N., Sun, Y., Li, K. L.,* Science **292** (2001) 1139.
118. *Neumann, R., Khenkin, A. M., Juwiler, D., Miller, H., Gara, M.,* J. Mol. Catal A: Chem. **117** (1997) 169.
119. *Cohen, M., Neumann, R. J.,* J. Mol. Catal. A: Chem. **146** (1999) 291.
120. *Sakamoto, T., Pac, C.,* Tetrahedron Lett. **41** (2000) 10009.
121. *Yamaguchi, K., Yoshida, C., Uchida, S., Mizuno, N.,* J. Am. Chem. Soc. **127** (2005**)** 530.
122. *Hoegaerts, D., Sels, B. F., de Vos, D. E.,* Catal. Today **60** (2000) 209.
123. *Li, J., Zhao, G., Gao, S., Lv, Y., Li, J., Xi., Z.,* Org. Process Res. Dev. **10** (2006) 876.
124. *Brulé, E., de Miguel, Y. R.,* Org. Bio. Mol. Chem. **4** (2006) 599.
125. *Tangestaninejad, S., Moghadam, M.,* J. Chem. Res. **1998** 242.
126. *Tangestaninejad, S., Mirkhani, V.,* J. Chem. Res. **1998** 788.
127. *Tangestaninejad, S., Habibi, M. H., Mirkhani, V., Moghadam, M.,* Syn. Commun. **32** (2002) 3331.
128. *Rebelo, S. L. H., Gonçalves, A. R., Pereira, M. M., Simões, M. M. Q., Neves, M. G. P. M. S., Cavaleiro, J. A. S.,* J. Mol. Catal. A: Chem. **256** (2006) 321.
129. *Neys, P. E. E., Severeyns, A., Vankelecom, I. F. J., Ceulemans, E., Dehaen, W., Jacobs, P. A.,* J. Mol. Catal. A: Chem. **144** (1999) 373.
130. *Zhang, J. L., Liu, Y. L., Che, C. M.,* Chem. Commu. **2002** 2906.
131. *Rebelo, S. L. H., Gonçalves, A. R., Pereira, M. M., Simões, M. M. Q., Neves, M. G. P. M. S., Cavaleiro, J. A. S.,* J. Mol. Catal. A: Chem. **256** (2006) 321.
132. *Sacco, H. C., Iamamoto, Y., Smith, J. R. L.,* J. Chem. Soc., Perkin Trans. **2** (2001) 181.
133. *Yu, X., Huang, J., Yu, W., Che, C.,* J. Am. Chem. Soc. **122** (2000) 5337.
134. *Perego, C., Carati, A., Ingallina, P., Mantegazza, M. A., Bellussi, G.,* Appl. Catal. A: Gen. **211** (2001) 63.
135. *Zhidomirov, G. M., Yakovlev, A. L., Milov, M. A., Kachurovskaya, N. A., Yudanov, I. V.,* Catal. Today **51** (1999) 397.
136. *Candeias, N. R., Afonso, C. A. M.,* J. Mol. Catal. A: Chem. **242** (2005) 195.
137. *Panyaburapa, W., Nanok, T., Limtrakul, J.,* J. Phys. Chem. **111** (2007) 3433.
138. *Carati, A., Flego, C., Massara, E. P., Millini, R., Carluccio, L.,* Microporous Mesoporous Mater. **30** (1999) 137.
139. *Sheldon, R A.,* J. Mol. Catal. **7** (1980) 107.
140. *Fraile, J. M., García, J. I., Mayoral, J. A., Vispe, E.,* Appl. Catal. A: Gen. **276** (2004) 113.
141. *Beck, C., Mallat, T., Bürgi, T., Baiker, A.,* J. Catal. **204** (2001) 428.
142. *Liu, Z. F., Crumbaugh, G. M., Davis, R. J.,* J. Catal. **159** (1996) 83.
143. *Kirm, I., Medina, F., Rodríguez, X., Cesteros, Y., Salagre, P., Sueiras, J.,* Appl. Catal. A: Gen. **272** (2004) 175.
144. *Sels, B., De Vos, D., Buntinx, M., Pierard, F., Mesmaeker, A. K., Jacobs, P.,* Lett. Nat. **400** (1999) 855.
145. *Rinaldi, R., Fujiwara, F. Y., Schuchardt, U.,* J. Catal. **245** (2007) 456.
146. *Kenneth, J., Balkus Jr., Alla K. Khanmamedova, Kathleen M. D., Fethi, B.,* Appl. Catal. A: Gen. **143** (1996) 159.
147. *Yamase, T., Ishikawa, E., Asai, Y., Kanai, S.,* J. Mol. Catal. A: Chem. **114** (1996) 237.
148. *Kholdeeva, O. A.,* Topics Catal. **40** (2006) 229.
149. *Barf, G. A., Sheldon, R. A.,* J. Mol. Catal. A: Chem. **102** (1995) 23.
150. *Liu, S., Xiao, J.,* J. Mol. Catal. A: Chem. **270** (2007) 1.