Graphical abstract

The epoxidation of propene to propene oxide at mild conditions using molecular rhenium and molybdenum catalysts is presented.

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Efficient epoxidation of propene using molecular catalysts

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The epoxidation of propene is performed in homogeneous phase using different molecular catalysts and H_2O_2 or *tert*-butyl hydroperoxide as oxidants. A comparison between molybdenum catalysts and methyltrioxorhenium (MTO) shows that the well known Re catalyst is the best among the examined catalysts.

The epoxidation of olefins is of high relevance in both industry and academia. Epoxides are very important intermediates in the chemical industry, particularly for the synthesis of various polymers (polyglycols, polyamides, polyurethanes, etc.), and they are also used in the synthesis of fine chemicals, such as pharmaceuticals, food additives, and flavor & fragrance compounds.[1] Propene oxide (PO) is currently produced on a scale of 8 million tons/year with an expected annual increase of 5%.[2] Heterogeneous catalysts, such as Ag/Al_2O_3 (for ethylene oxide) and titania-doped zeolite TS-1 (for PO) are the state-of-the-art epoxidation catalysts.[3] On the other hand, a plethora of highly active organometallic molecular transition metal catalysts for homogeneous epoxidation have been developed in the last 40 years.[4] So far they have mainly been applied for proof of principle and for a general comparison of relative activities of the different catalysts.[5] It is intriguing that only few reports deal with the homogeneous epoxidation of propene.[6,7]

Methyltrioxorhenium (MTO) is one of the best-studied catalysts for olefin epoxidation in homogeneous phase.[5] It is arguably the most versatile and widely applicable catalyst compound, covering a broad range of catalytic reactions, among them olefin metathesis,[8] aldehyde olefination,[9] dehydration of alcohols,[10] deoxydehydration of diols and the C–O cleavage in lignin model compounds.[11]

The catalytic epoxidation of propene with MTO was briefly mentioned in 1991, showing moderate conversion and poor selectivity, suggesting diol formation.[6a] A similar study by Subramaniam, Busch et al.[6b] was conducted in 2007 where MTO stabilised by pyridine-*N*-oxide was used with hydrogen peroxide as oxidant in methanol solution. Beyond these two studies, there is no protocol for the epoxidation of basic, industrially relevant olefins with MTO. It is well known that stability and catalytic performance of catalytically active methyl rhenium peroxo/bis(peroxo) complex is improved by addition of excess Lewis base.[12] Pyridine- and pyrazol derivatives are the most efficient Lewis basic additives, and they are typically used in a five- to tenfold excess vs. MTO, as the Re–N bond is rather weak.[13] The acidity of the Re centre is also somewhat reduced upon addition of these Lewis bases, which in turn suppresses the catalytic ring opening of the epoxide product to the (usually undesired) 1,2-diol (Scheme 1).[12]
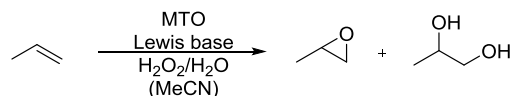
Scheme 1 MTO-catalysed epoxidation of propene using H_2O_2 as oxidant in acetonitrile.

The immobilisation of MTO either by covalent binding to a solid support[14] or by two-phase catalysis in ionic liquids to enable its recycling[15] has been reported. The two-phase (liquid-liquid) catalysis, however, suffers from high solubility of the catalytically active Re species in all solvents (organic, water). In this report, the catalytic activity of MTO for the epoxidation of propene is examined and its performance is compared to related, well-known molybdenum-based catalysts, which are also efficient epoxidation catalysts with *tert*-butyl hydroperoxide (TBHP).[16] So far, there are no reports on homogeneous epoxidations of industrially relevant bulk olefins with

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Catal. Sci. Technol., 2014, **4**, 1-5 | 1

COMMUNICATION

molecular, organometallic molybdenum based catalysts.[5,15] Since some organometallic molybdenum compounds, however, have been shown to be highly active catalysts, comparable to MTO in epoxidations of standard-olefins such as cyclohexene, it is interesting to examine them for their performance in the context of this work. In order to address the problems of recycling and epoxide ring opening (i.e. the product selectivity), the effect of different Lewis-basic ionic additives on selectivity and reusability of the MTO-H_2O_2 system has been tested. A protocol for formation of propene oxide from propene under mild conditions (25 °C, 3 bar) is presented.
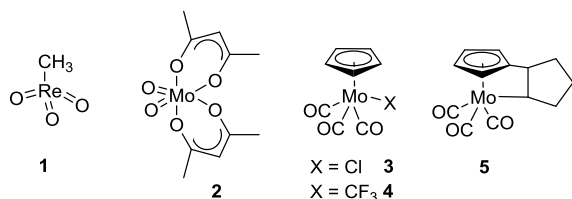
Figure 1 Catalysts used in this study for the epoxidation of propene.

Catalysts **1**-**5** (Figure 1) exhibit high conversions and selectivity for epoxidation of *cis*-cyclooctene.[4] For the reaction with propene, NMR with an internal standard was used for quantification. The reactions were carried out either in a Fisher-Porter bottle equipped with a digital manometer, or directly in pressure-stable NMR tubes. Table summarizes the results obtained for the conversion of propene to propene oxide using molybdenum catalysts **2**-**5**. While aqueous hydrogen peroxide was used for the reactions with MTO (Table 2, Entry 1), the molybdenum complexes **2**-**5** were activated by TBHP, since it is known that MTO decomposes with TBHP to perrhenate,[17] and Mo complexes **2**-**5** are not active catalysts for epoxidation with H_2O_2. All examined Mo catalysts show a propene conversion of up to 35 % with a PO selectivity of >99 % independent of catalyst and solvent (Table 1, Entries 1, 2, 4, 6, and 7). Despite the excellent selectivity, the conversion using Mo catalysts could not be enhanced by variation of the solvent nor with addition of an ionic liquid (Table 1, Entries 3 and 5). Discoloration of the yellow solution was observed during the reaction with catalysts **2**-**5**, indicating that decomposition of the catalytically active species is taking place. This is very likely the reason for the comparatively low conversion of propene.

Table 1 Epoxidation of propene using catalysts **2**–**5**.[a]

Entry	Cat.	Solvent	t [h]	Conv. [%]	Sel. [%]
1	2	CH_2Cl_2	24	23	> 99
2	3	CH_2Cl_2	24	33	> 99
3	3	[omim][NTf$_2$][b]	24	35	> 99
4	3	HFI[b]	24	28	> 99
5	4	[omim][NTf$_2$][b]	24	23	> 99
6	4	HFI[c]	24	26	> 99
7	5	CH_2Cl_2	24	32	> 99

[a] Reaction conditions: molar ratio cat:propene:TBHP 1:100:250, 25 °C, 0.5 mL solvent or IL
[b] [omim][NTf$_2$] = 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide.
[c] HFI = 1,1,1,3,3,3-hexafluoroisopropanol.

The catalytic epoxidation of propene using MTO (**1**) was also examined, particularly concerning optimisation of conversion and selectivity. The ideal reaction medium for MTO should be a solvent which is not miscible with water nor product, but at the same time exhibits a functionality for binding the Re species – i.e. a functionalised ionic liquid, which would then allow for separation of the catalyst-containing ionic liquid phase from water and the product phases, respectively. Thus, imidazolium-based ionic liquids bearing pyridine substituents were selected as objects of study.[18] Pyridine was selected as a representative *N*-donor base.
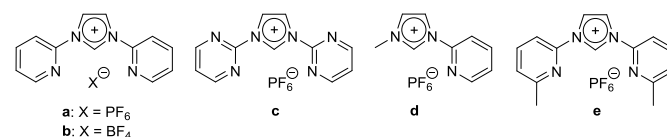
Figure 2 Ionic compounds **a**-**e** used as additives for the epoxidation of propene with MTO as catalyst.

The pyridine- and pyrimidine-functionalised imidazolium salts **a**-**e** (Figure 2) are solid at the reaction temperature; thus, the reactions were carried out in acetonitrile using the salts only as additives. Table summarises the results for epoxidation of propene using MTO with different additives in acetonitrile solution.

Table 2 Effect of Lewis-basic ionic additives on the catalytic performance of MTO for the epoxidation of propene.[a]

Entry	Additive	Equiv. additive	Conv. [%]	Sel. [%]
1	-	-	75	80
2	Pyridine	10	42	98
3	a	2	79	76
4	a	5	68	73
5	b	2	69	79
6	b	5	72	73
7	c	2	81	50
8	d	2	51	72
9	e	2	80	82
10[b]	-	-	86	91
11[b]	Pyridine	10	52	98
12[b]	a	2	96	89
13[b]	d	2	79	90
14[b]	e	2	86	92

[a] Reaction conditions: molar ratio MTO:propene:H_2O_2 (50 % aq. solution) 1:100:250, 25 °C, 6 h reaction time.
[b] Results obtained at 40 °C after 3 h during ^{1}H-NMR kinetic measurements.

Without any additive (Table 2, Entry 1), a conversion of 75 % and a selectivity of 80 % is reached. Using pyridine (Table 2, Entry 2), the conversion decreases to 42 %, but the selectivity rises to 98 %. Furthermore, 4-*tert*-butylpyridine, which is known as the best N-donor base in combination with MTO, was used as additive.[18b] In comparison to pyridine, no enhancement in conversion nor in selectivity was observed. For this reason, 4-*tert*-butylpyridine was not further investigated and excluded from further studies. Additives **a**-**e** do not significantly change neither conversion nor selectivity (Table 2, Entries 3-9) compared to the additive-free reaction (Table 2, Entry 1), despite being pyridine analogues. Changing the anion from PF_6^- to BF_4^- (Table 2, Entries 3 and 5) leads to a slight increase in conversion

with comparable selectivities. Increasing the amount of additive **a** and **b** from 2 to 5 molar equivalents per mole (Table 2, Entries 3-6), MTO does not lead to a significant change in conversion and selectivity (Table 2, Entries 4 and 6). Changing the pyridyl substituent to a pyrimidyl group (additive **c**) has a negative effect on the selectivity (Table 2, Entry 7), c.f. 76 % using additive **a** vs. 50 % for **c**, attributed to the lower basicity of the pyrimidyl groups. Additive **d** behaves similarly to pyridine-substituted **a** during catalysis, although with a lower conversion (51 %) (Table 2, Entry 8). Compound **e** was used to investigate if steric factors have an effect on conversion or selectivity (Entry 9).
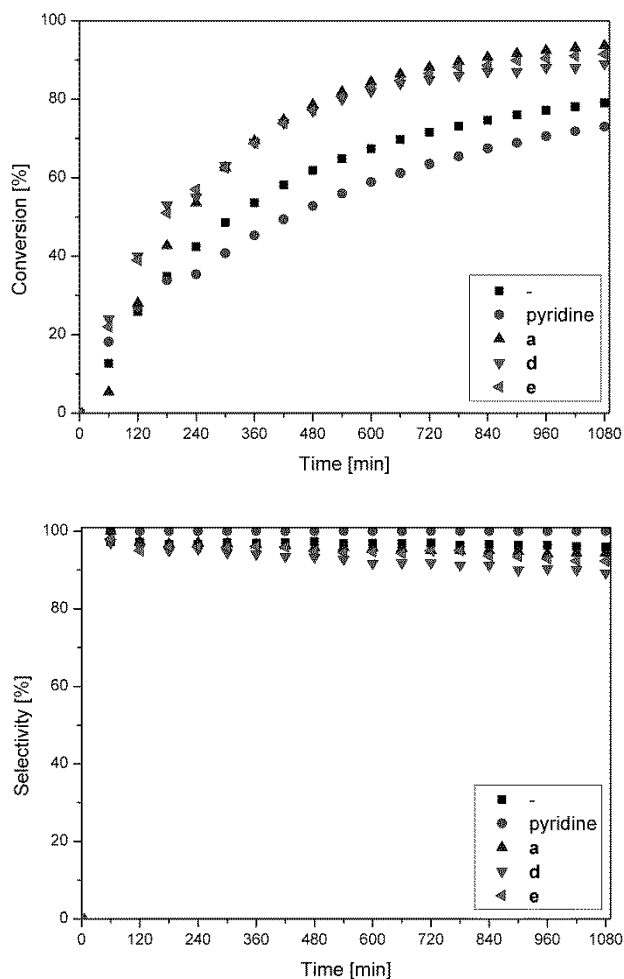
Figure 3 Kinetic plots of the propene conversion and PO selectivity using MTO as catalyst and different additives at 25 °C.

Surprisingly, it has a slightly positive impact on conversion and selectivity compared to additive **a**. Pyridine as additive has the highest basicity of the used *N*-donor bases, which has a positive influence on selectivity, but lowers the conversion. The opposite effect is seen with additive **c**, which is the least basic of the additives, but it also provides a hydrophobic environment like the other additives, which may exert a positive influence on the stability of the catalytically active species. For better understanding of the reaction kinetics, a series of parallel reactions were carried out in pressure-stable NMR tubes. Conversion and selectivity were monitored via ^{1}H-

NMR spectroscopy (see Figure 3 and 4, and Table 2, Entries 10-14). By raising the temperature to 40 °C, it was possible to decrease the reaction time to 3 h, leading to superior conversions and selectivities. Figure 3 shows the conversion and selectivity at 25 °C, respectively. However, it is apparent from Figure 3 that the reactions are not finished after 3 h or after 6 h, as recorded before (Table 2, Entries 1-9). After 3h reaction time, additives **a**, **d** and **e** have conversions of 42 %, 53 % and 51 % compared to 35 % and 34 % without any additive and with pyridine, respectively. Even after 18 h at room temperature, the substitution pattern of the additives has little influence on the conversion, but they perform markedly better than without additive or using pyridine as additive.The observed selectivities follow the same pattern as given in Table 2 (Entries 1-9). Pyridine as additive leads to a selectivity of nearly 99 %, followed by the reaction without additive with a selectivity of around 95 %. By the use of additives **a**–**e** only moderate selectivities are achieved, where additive **d** results in the lowest selectivity of 90 %.
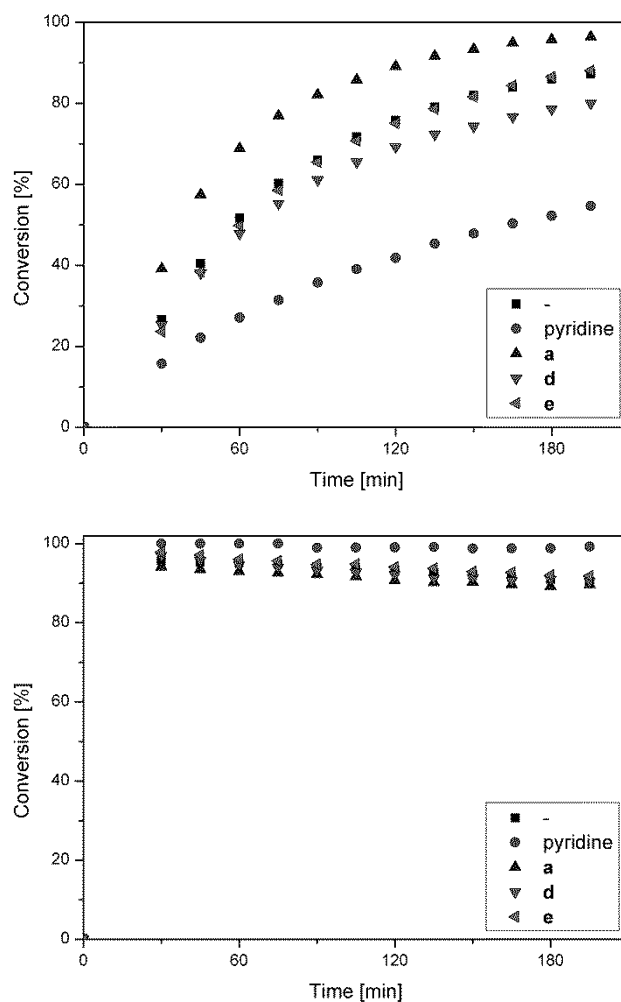
Figure 4 Kinetic plots of the propene conversion and PO selectivity using MTO as catalyst and different additives at 40 °C.

At 40 °C (Figure 4, and Table 2, Entries 10-14) both conversions and selectivities have been enhanced drastically. Additive **a** has a particularly high increase in conversion of 96 % after just 3 h. In

comparison, the additive-free reaction and the reaction with pyridine as additive yield 86 % and 52 % conversion after 3 h. Additive **e** performs comparably to the additive-free reaction, and additive **d** has a slightly lower conversion with comparable selectivity – the same pattern as seen above, where steric hindrance surprisingly accelerates the reaction. Once again, pyridine shows superior selectivity, although selectivities are at least 90% for all additives at 40 °C. In summary, a combination of both, pyridine and **a**, should lead to high conversions and selectivities. For this reason a reaction using both as additives was performed, but no reaction was observed. Instead of an enhanced reactivity, the solution turned colourless and gas evolution was observed, which indicates the decomposition of MTO.

Addition of an N-donor base may therefore suppress diol formation, and if grafted on an ionic liquid, the catalyst can potentially be recycled. This was tested with additive **a**, where, after the reaction completed, an additional amount of H_2O_2 and propene was added to the reaction mixture and the reaction was monitored for the next 3 h. In this way the reaction mixture could be reused 2 times with a decrease in conversion and selectivity of about 30 and 20 %, respectively after each run (see the ESI). We attribute the loss in activity to decomposition of the active species during catalysis. It is noteworthy that the recycling experiments could only be performed with the addition of compound **a**. With all other additives or no additives at all, the catalytic system shows no further conversion of propene after the first run.

Conclusions

Although MTO is well known as an efficient epoxidation catalyst, it has not been examined for the epoxidation propene in any detail. Here, a new protocol for the epoxidation of propene under mild conditions (40 °C, 3 bar propene) is reported, showing a conversion of 85 % after 3 h. In contrast, all examined molecular Mo-catalysts exhibit by far lower conversions. ^{1}H-NMR experiments have shown that by addition of pyridyl-functionalised imidazolium salts nearly quantitative conversions are obtained. Moreover, the selectivity towards the epoxide remains unaffected by the additive. Further work will include the comparison of the catalytic performance of MTO with other molecular transition metal catalysts, as well the optimization of the additive in terms of recycling.

Notes and references

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Catal. Sci. Technol., 2014, **4**, 1-5 | **5**