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# Metal-Doped Epoxy Resins – New Catalysts for the Epoxidation of Alkenes with High Long-Term Activities

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**Abstract:** For the first time, the use of epoxy resins for the immobilisation of catalytically active metal species is reported. The resins were cured using metal acetylacetonates and alkoxides as polymerisation initiators and the thus obtained thermosets were tested as epoxidation catalysts. Outstanding long-term catalyst activities and selectivities were observed for molybdenum-containing resins in the epoxidation of cyclohexene with *tert*-butyl hydroperoxide. Mechanistic investigations indicate a superposition of heterogeneous and homogeneous catalysis and a heterogeneous contribution to the catalytic activity of at least 15% can be estimated. Metal leaching is extremely low and depends on the catalyst preparation mode. The catalysts were employed batchwise in up to 60 reactions exceeding an application period of 50 days. Based on these results catalyst lifetimes of approximately 1500 days can be expected. They were applied without any reconditioning and loss of activity thus offering promising perspectives for industrial applications in continuously operating processes.

**Keywords:** catalyst recycling; epoxidation; epoxy resins; heterogeneous catalysis; molybdenum; polymer-supported catalysts

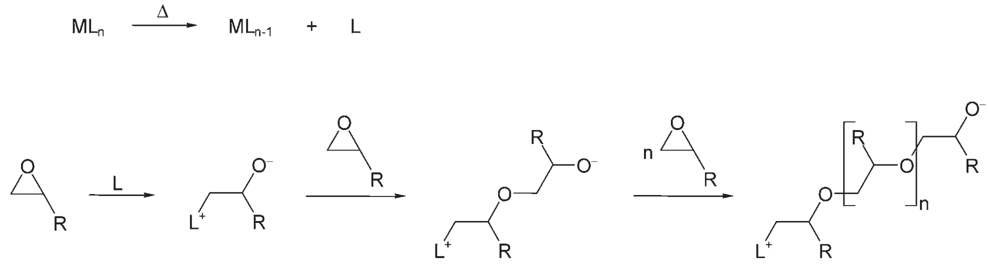
## Introduction

In spite of intensive research on the immobilisation of catalytically active metal species on organic polymers during the last decades[1] there is still a lack of highly stable catalyst systems suitable for long-term applications, e.g., in continuously operating processes. Indispensable conditions for any technological relevance of a polymer-supported catalyst are, apart from high activities and selectivities, economic criteria such as cost efficiency and a high catalyst lifetime. A high catalyst lifetime implies high thermal as well as chemical resistance and, especially in the case of oxidation reactions, high resistance to oxidative decomposition. Numerous catalysts were shown to be recyclable in principle. However, data on the long-term performance of polymer-supported catalysts is almost unavailable. In a recent review[2] on heterogeneous catalysts for epoxide production De Vos et al. pointed out that the development of highly stable catalysts and the evaluation of their long-term stability remains a challenge in the field of heterogeneous liquid phase epoxidation.

Epoxy resins combine some unique features considering their excellent mechanical and electrical properties as well as high resistance to numerous chemicals and high temperatures. Due to their versatility and outstanding properties this class of thermosetting resins is widely used in high performance applications, e.g., protective coatings, insulating materials for electrical and electronic equipment, composites or adhesives.[3]

The resins can be cured by anionic polymerisation promoted by small amounts of Lewis bases. Metal complexes are also well-known polymerisation initiators[4] (Scheme 1) due to their intrinsic ability to liberate ligands, i.e., Lewis bases upon heating. Thus, thermally latent formulations can be prepared that are processed safely at elevated temperatures and cured at high temperatures, usually above 100 °C. According to the concept outlined in Scheme 1, a broad variety of metal species can be incorporated in the network of cured epoxy resins.

The emergence of the Halcon-Arco process for the epoxidation of propylene with organic hydroperoxides[5] stimulated intensive research in the field of molybdenum-catalysed homogeneous alkene epoxidations.[6] These early investigations revealed that simple catalyst precursors, e.g., $Mo(CO)_6$ or $MoO_2(acac)_2$, give excellent activities. In the meantime numerous molybdenum compounds were reported to be active epoxidation catalysts.[7] Recently, cyclopentadienyl-molybdenum complexes were described as highly active catalysts.[8] Turnover frequencies in the epoxidation of cyclooctene up to



**Scheme 1.** Anionic polymerisation of epoxides initiated by metal complexes.

21000 mol/mol$^{-1}$ (Mo) h$^{-1}$ were reported using *tert*-butyl hydroperoxide (TBHP) as oxidant.

Several epoxidation catalysts have been developed in the past by immobilisation of molybdenum on various supports. Inorganic supports such as sol-gel derived silicates[9] or organo-functionalised MCM-41[10] have been employed. Among some attempts to immobilise molybdenum on organic polymers[11] the work of Sherrington et al. is outstanding. Highly active as well as recyclable and stable catalysts based on polybenzimidazole[12] and polyimides[13] have been reported. Recently, cross-linked poly(4-vinylpyridine-*co*-styrene)[14] was used as support for the immobilisation of $\text{MoO}_2\text{(acac)}_2$. Furthermore, polyaniline-supported $\text{MoO}_2\text{(acac)}_2$[15] was shown to be an active and recyclable catalyst for the oxidation of alcohols to aldehydes and ketones using molecular oxygen.

Here we report for the first time on the catalytic potential of metal-doped epoxy resins, especially molybdenum-doped resins. The liquid phase epoxidation of cyclohexene with TBHP as oxidant was chosen as test reaction with a main focus on catalyst stabilities. A rigorous long-term testing for periods of weeks up to months was accomplished to gain insight into their long-term applicability. The question of metal leaching, its accurate determination and whether the reactions are catalysed heterogeneously or homogeneously are discussed.

## Results and Discussion

### Catalyst Preparation and Characterisation

Commercially available epoxy resins such as the tetraglycidyl derivative of 4,4′-methylenedianiline (TGMDA) and the triglycidyl derivative of 4-aminophenol (TGAP) were used (Figure 1) for the build-up of catalyst matrices by metal complex-initiated polymerisation.

TGMDA was cured with a series of metal acetylacetonates [$\text{TiO(acac)}_2$, $\text{VO(acac)}_2$, $\text{MoO}_2\text{(acac)}_2$] and metal alkoxides [$\text{Ti(OPr)}_4$, $\text{VO(OPr)}_3$, $\text{Mo(OEt)}_5$]. Metal contents of 1.5 wt % were adjusted by dispersing the corresponding amount of metal complex in the resin. The resins were cured in aluminium molds at temperatures between 120 and 230 °C and thin plates with about 1 mm thickness were obtained. The curing reactions were monitored by differential scanning calorimetry (DSC) and strong exothermic reactions with reaction enthalpies between 600 and 700 J/g were observed. Furthermore, DSC measurements with the polymeric materials revealed high glass transition temperatures, usually above 160 °C. These observations indicate a high cross-linkage in the polymers. In the case of the metal acetylacetonates, which are sparingly soluble in TGMDA, solvent polymerisation was also applied. Saturated solutions of the acetylacetonates in DMF were added to the resin to get a homogeneous metal dispersion in the resin matrix. The solvent was allowed to evaporate at 160 °C simultaneously with the polymerisation. The resin plates were ground with an analytical mill and the thus obtained fine grained plastics (particle diameter $<800$ μm) were annealed at 230 °C.

The polymer surfaces were analysed by scanning electron microscopy coupled with electron-dispersive X-ray spectroscopy (SEM-EDX). Figure 2 shows SEM images of materials containing 1.5 wt % of molybdenum. Bright spots with molybdenum contents up to 50% are visible in the case of $\text{TGMDA-MoO}_2\text{(acac)}_2^{1.5\%\text{Mo}}$ (Figure 2a) and $\text{TGMDA-Mo(OEt)}_5^{1.5\%\text{Mo}}$ (Figure 2c). The number of these agglomerates is significantly lower in the latter. This can be explained by the lower resin solubility of $\text{MoO}_2\text{(acac)}_2$ compared to the liquid metal alkoxide $\text{Mo(OEt)}_5$. By reacting $\text{MoO}_2\text{(acac)}_2$ with stoichiometric amounts of TGMDA we observed the formation of

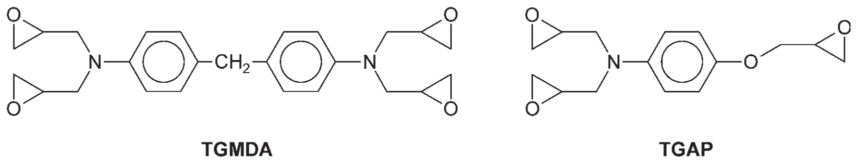


**Figure 1.** Structures of epoxy resin monomers.

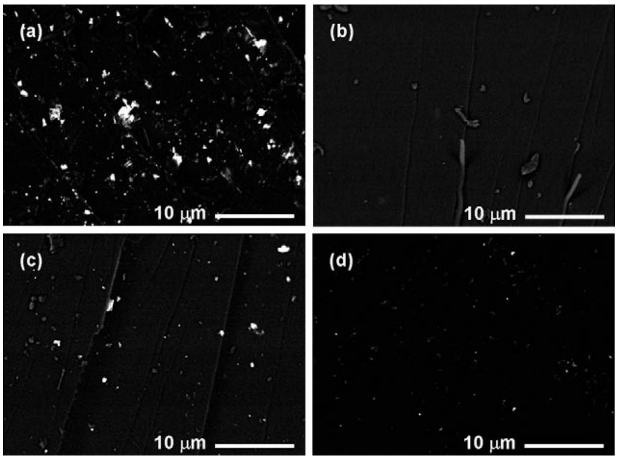
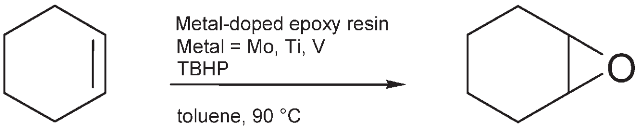


**Figure 2.** SEM images of (**a**) TGMDA-$MoO_2(acac)_2^{1.5\%Mo}$, (**b**) TGMDA-$MoO_2(acac)_2^{1.5\%Mo\text{-}DMF}$, (**c**) TGMDA-$Mo(OEt)_5^{1.5\%Mo}$ and (**d**) TGAP-$Mo(OEt)_5^{0.75\%Mo}$.

polyoxo complexes such as $[Mo_8O_{26}]^{4-}$. The structure of this polyoxo cluster was elucidated by XRD and reveals an oxygen-bridged cubic arrangement of molybdenum centres. This suggests that the surface agglomerates comprise polyoxo compounds. In the matrices of both polymers metal contents between 1 and 2% were detected. The surface of the material obtained by solvent polymerisation TGMDA-$MoO_2(acac)_2^{1.5\%Mo\text{-}DMF}$ is uniform (Figure 2b) thus indicating a homogeneous metal distribution in the matrix. EDX analysis confirms the expected average metal content of 1.5%. Using TGAP as epoxy resin and reducing the amount of $Mo(OEt)_5$ (0.75% metal loading) a catalyst with an homogeneous surface (TGAP-$Mo(OEt)_5^{0.75\%Mo}$, Figure 2d) can be obtained without use of any solvent.

## Catalytic Performance of Metal-Doped Epoxy Resins

The materials were tested as heterogeneous catalysts in the liquid-phase cyclohexene epoxidation using anhydrous TBHP as oxidant[16] (Scheme 2). In order to evaluate the stability of the polymers they were tested in a series of consecutive reactions. Metal contents of the reaction solutions were determined by atomic emission spectroscopy (ICP-AES) after filtering the reaction mixtures through PTFE-filters (0.45 µm pore width). The thus separated catalysts were subjected to the next run without any reconditioning.



**Scheme 2.** Epoxy resin-catalysed epoxidation of cyclohexene.

The epoxy resins were initially tested in a series of 10 consecutive reactions with a reaction time of 7 h, respectively. The catalytic activities of the titanium-containing polymers are negligible and only slightly above the level of the blank reaction while the vanadium-containing resins give conversions up to 80% with epoxide selectivities around 50% and show a strong trend towards allylic oxidation. Best activities, selectivities and stabilities were observed for polymers containing molybdenum. Some results of these initial catalytic runs are summarised in Table 1 (entries 1–10). All catalysts show a strong decrease of metal leaching during the first reactions indicating the removal of weakly bound surface species. Furthermore, the catalysts strongly differ in metal loss thus showing a strong influence of the preparation conditions on the catalyst stabilities. In the case of TGMDA-$MoO_2(acac)_2^{1.5\%Mo}$ metal leaching is comparatively high and reflects the low solubility of the metal acetylacetonate in the resin and consequently the heterogeneous nature of the polymerised material (Figure 2a). Using TGAP-$Mo(OEt)_5^{0.75\%Mo}$ no metal loss is detectable by ICP-AES. Metal contents in the nanogram range were quantified by atomic absorption spectroscopy (AAS) after removal of volatile components and investigation of the reaction residues. This suggests that metal enrichment and the application of sensitive AAS techniques should be applied as a matter of routine in an accurate study of metal leaching.

In order to gain insight into their long-term applicability, the pre-used catalysts were subjected to another 10 catalytic runs with a reaction time of 24 h/run (Table 1 entries 11–20). TGMDA-$MoO_2(acac)_2^{1.5\%Mo}$ is remarkably stable and reaches a steady-state performance after 13 reactions. Molybdenum leaching decreases to an average amount of 6 µg/run starting with run 12. Conversions and selectivities increase and reach values of 95% or higher in the fourteenth and the following reactions.

An excellent long-term performance was observed for TGMDA-$Mo(OEt)_5^{1.5\%Mo}$. Except for reactions 11 and 13, where the values are higher, metal leaching is around 6 µg/run. Alkene conversions and epoxide selectivities are higher than 96%. This catalyst was tested in 40 additional reactions with a reaction time of 24 h respectively, extending its application period to a total of almost 53 days. TBHP consumption was monitored by iodometric titration[17] and non-productive TBHP decomposition was proven to be negligible (below 1.5%/run). Alkene conversions and metal leaching are summarised in Figure 3 and details are given in Table 2. Metal contents in the reaction solutions decrease from 6 to around 4 µg/run (reactions 21 to 30) and subsequently (reactions 31 to 40) to values around 1 µg/run (around 0.02% of molybdenum originally present in the resin and around 0.3 ppm in the reaction mixture) while conversions and selectivities remain high with values between 90 and 100%. It is noted that the catalyst was

**Table 1.** Catalytic long-term performance of molybdenum-containing epoxy resins in the epoxidation of cyclohexene.[a, b]

| TGMDA-$MoO_2(acac)_2^{1.5\%Mo}$ | | | TGMDA-$Mo(OEt)_5^{1.5\%Mo}$ | | | TGAP-$Mo(OEt)_5^{0.75\%Mo[c]}$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| Run no. | Alkene conversion[d] [%] | Epoxide selectivity[d] [%] | Mo leached[e] [μg] | Alkene conversion[d] [%] | Epoxide selectivity[d] [%] | Mo leached[e] [μg] | Alkene conversion[d] [%] | Epoxide selectivity[d] [%] | Mo leached[f] [μg] |
| 1 | >99 | 88 | 972 (12.96)[g] | >99 | 98 | 20 (0.27) | 46 | 89 | 0.19 (0.005) |
| 2 | >99 | 94 | 132 (1.76) | 96 | 98 | 11 (0.15) | 37 | 86 | 0.13 (0.003) |
| 3 | >99 | 93 | 37 (0.49) | 92 | 98 | 5 (0.07) | 40 | 86 | 0.14 (0.004) |
| 4 | 98 | 88 | 22 (0.29) | 89 | 97 | 3 (0.04) | 39 | 86 | 0.11 (0.003) |
| 5 | 94 | 83 | 14 (0.19) | 86 | 98 | 2 (0.03) | 33 | 84 | 0.12 (0.003) |
| 6 | 93 | 86 | 19 (0.25) | 84 | 98 | 2 (0.03) | 33 | 84 | 0.10 (0.003) |
| 7 | 81 | 77 | 15 (0.20) | 83 | 97 | 2 (0.03) | 43 | 88 | 0.15 (0.004) |
| 8 | 83 | 81 | 13 (0.17) | 82 | 98 | 2 (0.03) | 43 | 88 | 0.12 (0.003) |
| 9 | 97 | 91 | 22 (0.29) | 83 | 97 | 3 (0.04) | 36 | 87 | 0.13 (0.003) |
| 10 | 68 | 71 | 9 (0.12) | 82 | 97 | 2 (0.03) | 37 | 86 | 0.10 (0.003) |
| 11 | 90 | 89 | 16 (0.21) | 99 | 97 | 14 (0.19) | 64 | 91 | 0.66 (0.018) |
| 12 | 87 | 92 | 6 (0.08) | 97 | 98 | 7 (0.09) | 69 | 93 | 0.67 (0.018) |
| 13 | 90 | 93 | 6 (0.08) | 99 | 97 | 15 (0.20) | 71 | 93 | 0.71 (0.019) |
| 14 | 96 | 95 | 5 (0.07) | 98 | 98 | 8 (0.11) | 66 | 92 | 0.56 (0.015) |
| 15 | 98 | 96 | 7 (0.09) | 97 | 97 | 6 (0.08) | 63 | 92 | 0.56 (0.015) |
| 16 | 96 | 96 | 5 (0.07) | 96 | 97 | 5 (0.07) | 57 | 90 | 0.46 (0.012) |
| 17 | 97 | 95 | 5 (0.07) | 98 | 97 | 7 (0.09) | 60 | 91 | 0.49 (0.013) |
| 18 | 99 | 96 | 8 (0.11) | 97 | 97 | 6 (0.08) | 56 | 91 | 0.43 (0.011) |
| 19 | 99 | 96 | 7 (0.09) | 97 | 97 | 5 (0.07) | 58 | 90 | 0.45 (0.012) |
| 20 | 98 | 95 | 5 (0.07) | 97 | 97 | 6 (0.08) | 64 | 92 | 0.60 (0.016) |

[a] Reaction times of 7 h for entries 1–10 and reaction times of 24 h for entries 11–20.

[b] Reaction conditions: 10 mmol cyclohexene, 16 mmol TBHP (3.2 M solution in toluene), 500 mg catalyst, 90 °C; no precautions against moisture and air.

[c] 12 mmol TBHP (3.2 M solution in toluene) used instead of 16 mmol.

[d] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard.

[e] Determined by ICP-AES from solutions of the reaction residues in concentrated $HNO_3$.

[f] Determined by AAS from solutions of the reaction residues in concentrated $HNO_3$.

[g] Values in parentheses: percentage of Mo originally loaded on the polymer.

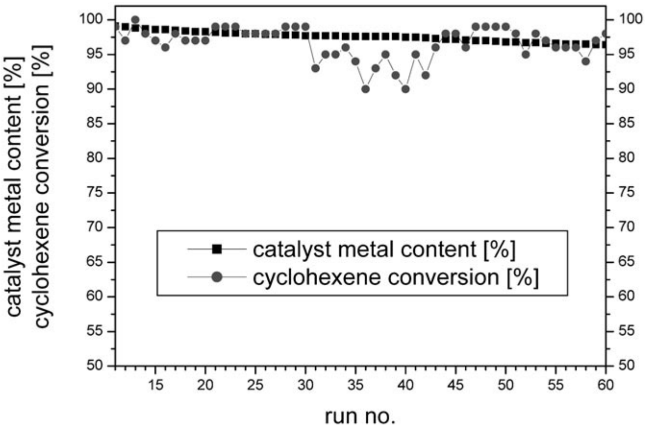


**Figure 3.** Catalytic long-term performance of TGMDA-$Mo(OEt)_5^{1.5\%Mo}$ in the epoxidation of cyclohexene during a period of 50 days. Reaction conditions: see Table 2.

not used during a period of 3 months between run 30 and 31. The slight decrease of conversion starting with run 31 is probably due to this interruption. However, after further application an increase in activity was observed resulting in conversions and selectivities higher than 95% (reactions 45 to 60) associated with an average leaching of around 4 μg/run. The catalyst metal content after 60 reactions is 96.4% of metal originally present in the resin. Provided that the catalytic activity stays unchanged, a catalyst lifetime of approximately 1500 days can be predicted. Using this catalyst, less reactive alkenes such as 1-octene or styrene were also successfully epoxidised in 10 runs with epoxide yields up to 78 and 82%, respectively. To ensure that dissolved metal species are not absorbed on the catalyst during cooling down after the reaction, control experiments were carried out. ICP-AES samples were taken from the hot reaction mixture immediately after completion of the reaction and from the reaction mixture after cooling down to room temperature. Metal concentrations were in all cases the same indicating that reabsorption (boomerang effect) does not take place.

To elucidate the nature of the catalytically active species, other filtration experiments were carried out. From run nos. 31 to 40 the hot reaction mixtures were filtered

**Table 2.** Catalytic long-term performance of TGMDA-Mo(OEt)$_5^{1.5\%\mathrm{Mo}}$ in the epoxidation of cyclohexene.[a]

| Run no. | Alkene conversion[b] [%] | Epoxide selectivity[b] [%] | Mo leached[c] [μg] | Run no. | Alkene conversion[b] [%] | Epoxide selectivity[b] [%] | Mo leached[c] [μg] |
|---|---|---|---|---|---|---|---|
| 21 | 99 | 96 | 5 (0.07)[d] | 41 | 95 | 90 | 4 (0.05) |
| 22 | 99 | 96 | 4 (0.05) | 42 | 92 | 92 | 4 (0.05) |
| 23 | 99 | 96 | 4 (0.05) | 43 | 96 | 90 | 5 (0.07) |
| 24 | 98 | 96 | 4 (0.05) | 44 | 98 | 93 | 6 (0.08) |
| 25 | 98 | 96 | 4 (0.05) | 45 | 98 | 97 | 6 (0.08) |
| 26 | 98 | 97 | 4 (0.05) | 46 | 96 | 97 | 4 (0.05) |
| 27 | 98 | 96 | 3 (0.04) | 47 | 99 | 97 | 6 (0.08) |
| 28 | 99 | 96 | 4 (0.05) | 48 | 99 | 97 | 4 (0.05) |
| 29 | 99 | 97 | 4 (0.05) | 49 | 99 | 97 | 4 (0.05) |
| 30 | 99 | 96 | 5 (0.07) | 50 | 99 | 97 | 5 (0.07) |
| 31 | 93 | 95 | 1 (0.01) | 51 | 98 | 97 | 5 (0.07) |
| 32 | 95 | 95 | 1 (0.01) | 52 | 95 | 97 | 3 (0.04) |
| 33 | 95 | 93 | 2 (0.03) | 53 | 98 | 97 | 4 (0.05) |
| 34 | 96 | 93 | 2 (0.03) | 54 | 97 | 97 | 4 (0.05) |
| 35 | 94 | 93 | 1 (0.01) | 55 | 96 | 98 | 4 (0.05) |
| 36 | 90 | 93 | 1 (0.01) | 56 | 96 | 97 | 3 (0.04) |
| 37 | 93 | 93 | 1 (0.01) | 57 | 96 | 97 | 3 (0.04) |
| 38 | 95 | 93 | 2 (0.03) | 58 | 95 | 98 | 3 (0.04) |
| 39 | 92 | 97 | 1 (0.01) | 59 | 97 | 97 | 4 (0.05) |
| 40 | 90 | 94 | 1 (0.01) | 60 | 98 | 97 | 4 (0.05) |

[a] Reaction conditions: 10 mmol cyclohexene, 16 mmol TBHP (3.2 M solution in toluene), 500 mg catalyst, 90 °C, 24 h; no precautions against moisture and air.

[b] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard.

[c] Determined by ICP-AES from solutions of the reaction residues in concentrated $HNO_3$.

[d] Values in parentheses: percentage of Mo originally loaded on the polymer.

after 24 h through PTFE-filters and analysed by GC (see Figure 3 and Table 2 entries 31 to 40). Subsequently, fresh cyclohexene as well as TBHP were added to the filtrate, readjusting the initial amount of 10 mmol of cyclohexene and 16 mmol of TBHP. The mixtures were analysed by GC and the reactions were run again under exactly the same reaction conditions. Significant cyclohexene conversions varying between 32 and 64% were determined and the average conversion of these 10 second runs is 50%. Filtration experiments from run no. 55 to 60 where leaching is higher revealed conversions between 68 and 82% (76% average conversion). The correlation between leaching and catalytic activity indicates catalysis in the homogeneous phase. However, conversions observed in the presence of the solid catalyst were not reached, suggesting a rapid deactivation of catalytically active species in solution and/or a heterogeneous contribution to the catalytic activity.

It is noteworthy that no more metal is detectable by ICP-AES when the reaction solutions are filtered through aluminium oxide filters with a pore width of 0.02 μm. This clearly shows that filtration experiments can be problematic. One should keep in mind that, on the one hand, filtration experiments are a state-of-the-art technique to prove a heterogeneous reaction mechanism. On the other hand, metal species can be removed almost quantitatively during filtration by absorption and/or retention of nano-sized particles thus pretending metal-free reaction solutions.

To gain further information on the correlation between metal leaching and catalytic activity, highly leaching-resistant catalysts were investigated. Using TGAP-Mo(OEt)$_5^{0.75\%\mathrm{Mo}}$ no metal loss is detectable by ICP-AES even after reaction times of 24 h. Molybdenum contents between 0.43 and 0.71 μg were quantified by AAS after metal enrichment in the reaction residues (Table 1 entries 11–20). Conversions are between 56 and 71% with epoxide selectivities around 91%. The major by-products are cyclohexenol (up to 4%), due to allylic oxidation, and cyclohexanediol (up to 3%) arising from oxirane ring-opening. The low metal contents in the reaction solutions suggest a heterogeneous contribution to the catalytic activity. Shorter reaction times of 7 h (Table 1 entries 1–10) afforded an extremely low metal leaching. It is close to the AAS detection limit (~0.05 μg) and values between 0.10 and 0.19 μg were observed. There is a linear correlation between the amount of metal in the reaction solution and the cyclohexene conversion (Figure 4). Extrapolation to 0 μg of metal and considering a blank conversion without catalyst of around 5% allow us to estimate a heterogeneous contribution of at least 15%.

If one assumes that in the case of TGAP-Mo(OEt)$_5^{0.75\%\mathrm{Mo}}$ reactions are catalysed exclusively by

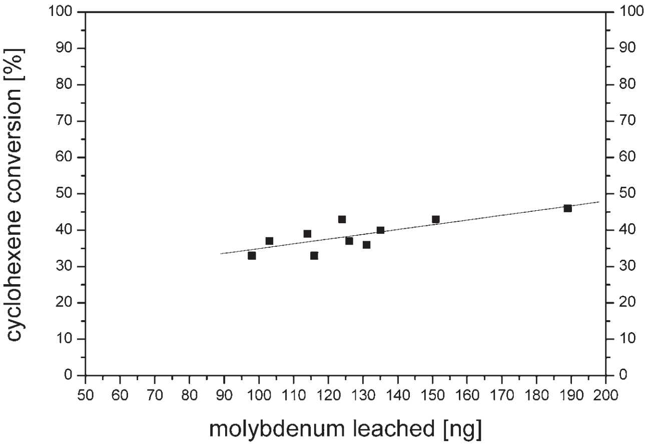


**Figure 4.** Epoxidation of cyclohexene with TGAP-Mo(OEt)$_5^{0.75\%Mo}$ as catalyst: correlation between cyclohexene conversion and metal leaching. Reaction conditions: see Table 1.

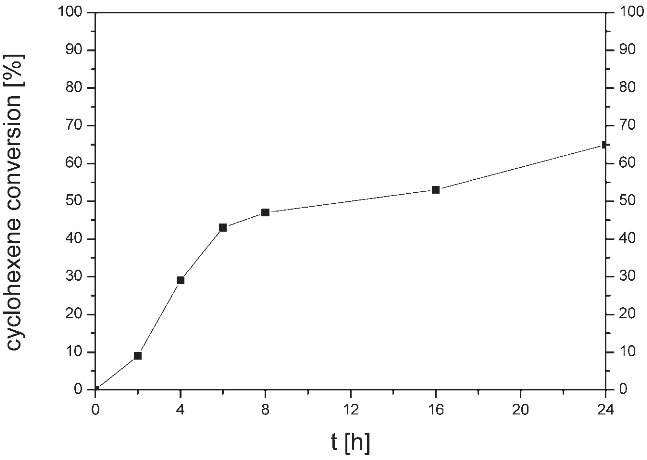


**Figure 5.** Homogeneously catalysed epoxidation of cyclohexene with MoO$_2$(acac)$_2$ as catalyst (metal:alkene molar ratio of $1:3\times10^6$). Reaction conditions: 100 mmol cyclohexene, 160 mmol TBHP (3.2 M solution in toluene), 21.7 $\mu$L of a $1.533\times10^{-3}$ M solution of MoO$_2$(acac)$_2$ in DMF (33.3 nmol Mo), 90 °C, 24 h; no precautions against moisture and air.

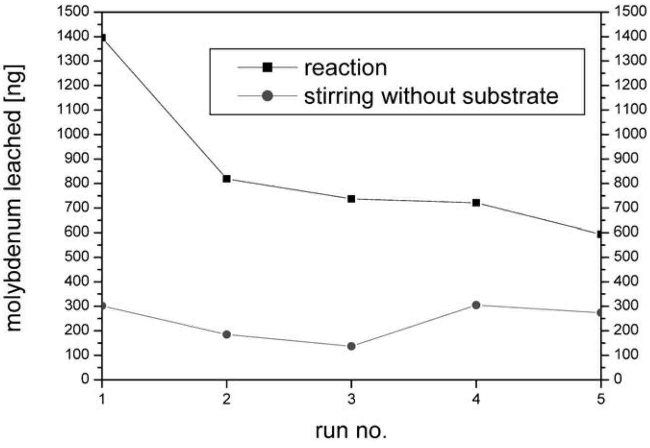


**Figure 6.** Epoxidation of cyclohexene with TGMDA-Mo(OEt)$_5^{0.75\%Mo}$ as catalyst: metal leaching in the presence and absence of cyclohexene. Reaction conditions: (10 mmol cyclohexene), 12 mmol TBHP (3.2 M solution in toluene), 500 mg catalyst, 90 °C, 7 h; no precautions against moisture and air.

metal traces in the homogeneous phase, high turnover numbers around $3\times10^6$ after reaction times of only 7 h corresponding to turnover frequencies around 420000 mol/mol$^{-1}$ (Mo) h$^{-1}$ can be calculated from the slope of the straight line in Figure 4. Activities in this range would exceed those reported for the most active homogeneous catalysts,[6a,8] thus corroborating a heterogeneous contribution to the catalytic activity.

In this context control experiments with an extremely low metal:alkene molar ratio of $1:3\times10^6$ were carried out using MoO$_2$(acac)$_2$, one of the most efficient catalyst precursors for homogeneously catalysed epoxidations. The results are summarised in Figure 5. Turnover numbers in the range of $3\times10^6$ were not reached after 7 h and even after reaction times of 24 h cyclohexene conversions remained below 70%. These results also corroborate a heterogeneous contribution to the catalytic activity in reactions catalysed by molybdenum-doped epoxy resins. Surprisingly, when this reaction was run in the presence of the metal-free epoxy resin TGMDA-DMI (TGMDA cured with 5 wt % of 1,2-dimethylimidazole as polymerisation initiator) no catalytic activity was observed probably due to absorption and deactivation of molybdenum species on this resin.

When the catalysts are treated with TBHP under reaction conditions but without any substrate the amount of metal loss is remarkably lower than in the presence of an alkene (around one fourth). This suggests that epoxidation reactions on the catalyst surface cause detachment of the metal. A comparison of metal leaching from TGMDA-Mo(OEt)$_5^{0.75\%Mo}$ in the presence and absence of cyclohexene is shown in Figure 6.

To ensure that there is no influence of the polyether matrix on the catalytic properties of the molybdenum-doped resins, experiments in the presence of metal-free TGMDA-DMI and without any metal in the reaction solutions were also run. Using this polymer under standard reaction conditions (see Table 1) cyclohexene conversions below 5% were observed after reaction times of 7 h with low epoxide selectivities (around 20%). The same results were obtained in blank reactions without any polymer indicating that there is no significant influence of the catalyst matrices on the catalytic properties.

The catalysts are highly cross-linked, non-porous thermosets that swell only slightly in the reaction solutions (weight gain by uptake of liquid components of a few percent under reaction conditions). Their catalytic activities are determined substantially by particle sizes and the resulting surfaces of the catalyst powders. Catalyst powders with particle diameters between 150 and 300 μm were used in this study and catalyst loadings that correspond to metal:alkene ratios of about 1:100 were adopted. Employing catalysts with smaller particles, similar conversions can be obtained with much lower catalyst loadings. Using TGMDA-Mo(OEt)$_5$$^{1.5\%Mo}$ with particle diameters below 150 μm, cyclohexene conversions above 95% were obtained after reaction times of 24 h in a series of reactions with catalyst loadings that correspond to metal:alkene ratios of 1:1000.

Comparing the molybdenum-doped epoxy resins with the established molybdenum catalysts mentioned above, it can be stated that they are superior with respect to ease of preparation and long-term activities. Molybdenum-loaded sol-gel derived silicates[9] or organo-functionalised MCM-41[10] were shown to be recyclable. However, activities are decreasing during recycling and the catalysts were tested up to a few days only. Catalysts based on organic supports such as polybenzimidazole[12] were used up to 40 h in the epoxidation of cyclohexene and a decrease of activity was observed,[12b] whereas an increase in activity was reported in the epoxidation of propylene during 10 h.[12c, d] Polyimide-based catalysts[13] showed a retention of activity in the epoxidation of cyclohexene during 20 h. Metal leaching was investigated by AAS but a comparatively high detection limit expressed as a percentage of molybdenum originally loaded on the polymer (0.2%) was reported and this is in the microgram range. In the case of $MoO_2(acac)_2$ supported on poly(4-vinylpyridine-*co*-styrene)[14] or polyaniline[15] metal leaching was not investigated in detail and data on the catalytic long-term performance of these catalysts are not available.

## Conclusion

Metal-doped epoxy resins are, to our knowledge, the first example of catalysts based on organic polymers that operate for a period of several weeks. Metal leaching is extremely low and can vary during such a long-term test. On the basis of results obtained during an application period of about 50 days catalyst lifetimes of approximately 1500 days can be expected. Using highly leaching-resistant catalysts, it is possible to show that the reactions proceed at the boundary between heterogeneous and homogeneous catalysis. A heterogeneous contribution to the catalytic activity of at least 15% can be estimated. Metal enrichment and application of sensitive AAS techniques are necessary for an accurate determination of metal leaching in the nanogram range. Filtration experiments can be problematic since dissolved or nano-sized metal species can be removed during filtration thus pretending metal-free reaction solutions.

Catalyst preparation is simple, time- and cost-saving. Good resin solubilities of the metal precursors are crucial to get homogeneous metal dispersions in the resin matrix. Metal leaching highly depends on the catalyst preparation conditions. Since epoxy resins are predominantly applied as protective coatings, surfaces of reactors as well as packing materials could easily be coated with catalytically active resin layers. These possibilities together with their outstanding long-term activities offer promising perspectives for industrial applications. From a technological point of view the extremely low metal leaching is more than compensated by very high catalyst lifetimes of up to months under thermo-oxidatively demanding reaction conditions. Currently the reaction is being extended to a series of other alkenes including propylene and the catalysts as well as the reaction conditions are being optimised. Furthermore, a series of catalysts is undergoing tested in continuously operating experiments. Taking into account that this concept could easily be extended to other catalytic reactions, we conclude that a great variety of new catalysts based upon thermosetting resins is accessible.

## Experimental Section

### General Remarks

The epoxy resins TGMDA and TGAP as well as $MoO_2(acac)_2$ and cyclohexene were purchased from Aldrich whereas $Mo(OEt)_5$ was purchased from Gelest. All compounds were used without further purification. Anhydrous TBHP in toluene was prepared by azeotropic drying of TBHP (T-HYDRO® solution 70 wt % TBHP in water from Aldrich) as described in the literature.[16] TBHP concentrations were determined by iodometric titration.[17] Rotilabo® (PTFE, 0.45 μm pore width) and Whatman® (aluminium oxide, 0.02 μm pore width) syringe filters were used for catalyst separation. SEM images were recorded on a Leo 982 digital scanning microscope coupled with an Oxford Instruments ISIS 300 EDX unit. ICP-AES and AAS analyses were carried out on Varian Liberty 150 and Varian SpectrAA 800 instruments, respectively. Reaction mixtures were analysed by GC-FID using an Agilent 6890N gas chromatograph equipped with a PHENOMENEX ZB-1 column (60 m × 0.32 mm; 1 μm film thickness). Products were quantified using calibration curves obtained with standard solutions and dodecane as external standard. Unknown products were identified by GC-MSD using an Agilent 6890N instrument (J & W SCIENTIFIC DB5 column; 30 m × 0.25 mm; 0.25 μm film thickness) coupled with an Agilent 5973 mass selective detector.

### Typical Procedure for Catalyst Preparation

***Preparation of TGMDA-Mo(OEt)$_5$$^{1.5\%Mo}$*:** $Mo(OEt)_5$ (0.483 g, 1.503 mmol) was added to TGMDA (9.045 g, 21.407 mmol) and the mixture was stirred vigorously at 50 °C for 30 min. The dispersion was transferred to an aluminium mold and a thin layer, being approximately 1 mm thick, was cured by raising the temperature successively from 120 to 230 °C (120 °C, 1 h – 180 °C, 3 h – 200 °C, 2 h – 230 °C, 1 h). The thus obtained resin plate was cut and ground with an analytical mill yielding a fine grained polymer with particle diameters below 800 μm. Finally, the material was annealed for 7 h at 230 °C and sieved. The catalytic reactions were run using the fraction with particle diameters between 150 and 300 μm.

### Typical Procedure for the Catalytic Epoxidation

All reactions were carried out without precautions against moisture and air. In a typical experiment a mixture of cyclohexene (0.821 g, 10 mmol), a 3.2 M solution of TBHP in toluene (5 mL, 16 mmol) and 500 mg of catalyst was magnetically stirred at 90 °C for 24 h. The catalyst was separated by filtration (PTFE filters, 0.45 μm pore width) and subjected to the next catalytic run without any reconditioning. The filtrate was analysed by GC and liquid components were distilled off. The reaction residue was dissolved in 2 g of concentrated $HNO_3$. The solution was diluted with an appropriate volume of water, depending on the metal content, and then analysed by atomic spectroscopy. Control experiments were performed where 1 g of the filtrate was filtered again through aluminium oxide filters with a pore width of 0.02 μm and analysed separately by atomic spectroscopy.

### Long-Term Testing of TGMDA-Mo(OEt)$_5^{1.5\%Mo}$

A mixture of cyclohexene (0.821 g, 10 mmol), a 3.2 M solution of TBHP in toluene (5 mL, 16 mmol) and 500 mg of catalyst was magnetically stirred at 90 °C for 24 h. The reaction solution was allowed to cool down to room temperature, filtered through a PTFE filter (0.45 μm pore width) and analysed by GC. The catalyst was subjected immediately to the next run without any reconditioning. A sample of 2 g was taken from the filtrate and the volatile components were allowed to evaporate at room temperature. The reaction residue was dissolved in 2 g of concentrated $HNO_3$ and then analysed by ICP-AES. Control experiments were carried out where one half of the reaction mixture was filtered at 90 °C immediately after the reaction and the other half was filtered after cooling down to room temperature. A sample of 1 g was taken, respectively, and analysed separately by ICP-AES. In another type of control experiment 1 g of the filtrate was filtered again through aluminium oxide filters with a pore width of 0.02 μm and analysed again by atomic spectroscopy. Filtration experiments were performed from run nos. 31 to 40 and from run nos. 55 to 60 where the reaction mixtures were filtered at 90 °C through PTFE filters and cyclohexene as well as TBHP were added to the filtrate, readjusting the initial amount of 10 mmol of cyclohexene and 16 mmol of TBHP. The reactions were run again under exactly the same reaction conditions as mentioned above. Conversions were determined from GC samples taken immediately before and after the reactions. After GC analysis and removal of liquid components the reaction residues were analysed by ICP-AES.

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