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Molybdenum-doped epoxy resins as catalysts for the epoxidation of alkenes

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Abstract

Epoxy resins were polymerised using molybdenum ethoxide and 2-ethylhexanoate as polymerisation initiators. The thermosets thus obtained are useful epoxidation catalysts for a variety of alkenes, including propene with *tert*-butyl hydroperoxide as an oxidant. To investigate the long-term performance of these resins, they were used repeatedly in up to 120 reactions without any reconditioning. Compared with other catalyst systems based on organic polymers, they reveal unprecedented long-term activities over periods of months so that catalyst lifetimes of years can be expected. Di-, tri-, tetra- and oligofunctional epoxy resin monomers were used and compared. The catalytic performance of the thermosets strongly depends on the resin type and the polymerisation initiator. Promising results were obtained with monomers bearing 3 or 4 glycidyl groups in combination with $Mo(OEt)_5$ as an initiator. Metal leaching, determined by sensitive atomic spectroscopic techniques, is extremely low. Inorganic–organic hybrid catalysts can be easily prepared by adding inorganic components such as silicagel to the liquid resins, followed by polymerisation.

Keywords: Epoxidation; Molybdenum; Epoxy resins; Polymer-supported catalysts; Catalyst recycling

1. Introduction

Intensive research into the immobilisation of catalytically active metal species on organic polymers has been carried out over the last several decades [1–4]. In this context, the recent work of Kobayashi et al., who focused on polymer-supported microencapsulated catalysts [5,6], has sparked new interest in this well-established research area. High long-term stabilities of polymer-based catalysts are as desirable as high activities and selectivities and serve as a basic prerequisite for applications in continuously operating processes. A catalyst system that exhibits an excellent initial performance is, from a technological standpoint, worthless if it deactivates after some reaction cycles by either catalyst poisoning or decomposition. Numerous polymer-based catalysts were shown to be recyclable. However, no data on their long-term performance over periods of weeks or months are available, and in most cases mechanistic considerations, such as the distinction between heterogeneous and homogeneous catalysis, came to the fore rather than the evaluation of their long-term applicability.

Since the emergence of the Halcon–Arco process [7,8] for the homogeneously catalysed epoxidation of propene, numerous attempts were made to immobilise molybdenum on various supports to gain heterogeneous epoxidation catalysts. Inorganic supports such as silica [9–14], modified MCM-41 [15–22], SBA-15 [23], zeolites [24], or layered double hydroxides [25] have been used. Sol–gel-derived hybrid organic–inorganic materials were also synthesised [26]. With respect to organic polymers, modified polystyrenes [27–30], modified Merrifield resins [31,32], benzimidazole-functionalised dendrons [33], polyaniline [34], ion-exchange resins [35], poly(thioether-amido-acid) cross-linked resins [36], polymethacrylate-based systems [37], ethylene–propylene rubber, and modified poly(ethylene oxide) [38], as well as modified polyethylene and polypropylene [39], were investigated as supports. Catalyst systems based on polybenzimidazole [40–43] and polyimides [44, 45] reported by Sherrington et al. yielded outstanding results in the liquid-phase epoxidation of alkenes. However, data on their

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long-term performance exceeding periods of some days are not available.

We recently reported on the use of metal-doped epoxy resins as highly stable catalysts for the epoxidation of cyclohexene with *tert*-butyl hydroperoxide (TBHP) as oxidant [46]. The catalysts were obtained in a convenient one-step procedure in which metal complexes act as both initiators for anionic epoxy resin polymerisation and precursors for the catalytically active species in the resulting polymer. The catalysts were characterized, and mechanistic studies revealed a superposition of heterogeneous and homogeneous catalysis. To demonstrate the versatility and applicability of this new type of catalysts, here we report on an extension of this initial study. Several molybdenum-doped epoxy resins built up by different resins and molybdenum compounds are compared. They were tested in the epoxidation of a series of alkenes including propene, focusing on their long-term activities and stabilities for periods up to months.

2. Experimental

2.1. General

The epoxy resins 4,4′-methylene-bis-(N,N-diglycidylaniline) (TGMDA) and N,N-diglycidyl-4-glycidyloxyaniline (TGAP) were purchased from Aldrich, and the diglycidylether of bisphenol A (DGEBA, Bakelite EPR 164) and the epoxy novolac (Bakelite EPR 600) were obtained from Bakelite AG. $Mo(OEt)_5$ and molybdenum 2-ethylhexanoate ($(Mo(EH)_n$, a mixture of compounds $Mo[OOCCH(C_2H_5)C_4H_9]_n$ containing 15 wt% molybdenum), were obtained from Gelest and Strem, respectively. Silicagel type 62 with particle sizes of 75–250 µm (Aldrich) was used for the preparation of silicagel-epoxy hybrid catalysts. Anhydrous TBHP in toluene was prepared by azeotropic drying of TBHP (T-HYDRO solution, Aldrich, 70 wt% TBHP in water) [47]. TBHP concentrations were determined by iodometric titration [48]. Rotilabo syringe filters (PTFE, 0.45 µm pore width) were used for catalyst separation. SEM images were recorded on a Leo 982 digital scanning microscope combined with an Oxford Instruments ISIS 300 EDX unit. DSC data were obtained with a heating rate of 10 °C/min using a Mettler Toledo DSC822^e device. 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 an external standard. Unknown products were identified by GC-MS 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. In the epoxidation of propene, dodecane was added to the reaction mixtures as an internal standard. Propene oxide yields are based on TBHP consumption. The yields were determined by TBHP titration and by GC-FID.

2.2. Preparation of the catalysts

2.2.1. Typical preparation procedure for catalysts of the type resin–$Mo(OEt)_5^{0.75\%Mo}$

The resin (10 g) was heated to 50 °C (100 °C in the case of the epoxy novolac Bakelite EPR 600), and $Mo(OEt)_5$ (0.258 g) was added. The mixture was stirred vigorously for 30 min and transferred to an aluminium mold. A thin (ca. 1 mm) layer was cured in an oven at the following temperatures: 120 °C for 1 h, 180 °C for 3 h, 200 °C for 2 h, and 230 °C for 1 h. The resulting resin plate was cut and ground with an analytical mill, yielding a fine-grained material with particle diameters <800 µm. Subsequently, the polymer was annealed at 230 °C for 4 h and sieved. The catalytic reactions were run using the fractions with particle diameters of 150–300 µm.

2.2.2. Preparation of TGMDA–$Mo(OEt)_5^{1.5\%Mo}$

$Mo(OEt)_5$ (0.534 g, 1.7 mmol) was added to TGMDA (10 g, 23.7 mmol), and the mixture was processed as described above for systems of the type resin–$Mo(OEt)_5^{0.75\%Mo}$.

2.2.3. Typical preparation procedure for catalysts of the type resin–$Mo(EH)_n^{1.5\%Mo}$

Molybdenum 2-ethylhexanoate ($Mo(EH)_n$, 1.111 g) was added to the respective resin (10 g), and the mixture was stirred vigorously at 100 °C for 30 min. The formulation was transferred to an aluminium mold and a thin (ca. 1 mm) layer was cured in an oven by raising the temperature successively from 120 to 230 °C (120 °C for 1 h, 180 °C for 1 h, 200 °C for 1 h, and 230 °C for 4 h). The resin plate thus obtained is cut and milled, yielding a fine-grained polymer with particle diameters <800 µm. The material was annealed for 6 h at 230 °C and sieved. Unless stated otherwise, the catalytic reactions were run using the fractions with particle diameters of 300–500 µm.

2.2.4. Preparation of silicagel/TGMDA–$Mo(OEt)_5^{0.5\%Mo}$

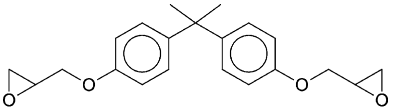
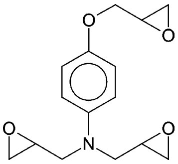
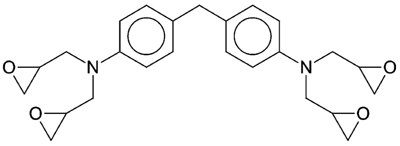
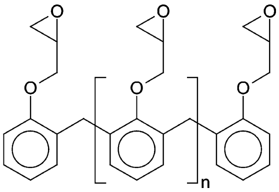
A mixture of silicagel (8.230 g), TGMDA (13.355 g), $Mo(OEt)_5$ (0.343 g), and Et_2O (5 ml) was homogenised and cured in an oven at the following temperatures: 120 °C for 1 h, 180 °C for 3 h, 200 °C for 2 h, and 230 °C for 1 h. The brittle material thus obtained was pulverised and annealed at 230 °C for 8 h.

2.3. Epoxidation procedures

2.3.1. Typical procedure for the epoxidation of liquid alkenes

All reactions were carried out without precautions against moisture and air. In a typical experiment, a mixture of the alkene (10 mmol), a 3.2 M solution of TBHP in toluene (12 or 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, and the solution was diluted with an appropriate volume of water, de-

Table 1
Epoxy resins, polymerisation initiators and catalyst labelling

Epoxy resin	Initiator	Catalyst labelling
	$Mo(OEt)_5$	DGEBA–$Mo(OEt)_5^{0.75\%Mo}$
	$Mo(OEt)_5$ $Mo(EH)_n$[a]	TGAP–$Mo(OEt)_5^{0.75\%Mo}$ TGAP–$Mo(EH)_n^{1.5\%Mo}$
	$Mo(OEt)_5$	TGMDA–$Mo(OEt)_5^{0.75\%Mo}$ TGMDA–$Mo(OEt)_5^{1.5\%Mo}$ Silicagel/TGMDA–$Mo(OEt)_5^{0.5\%Mo}$
	$Mo(OEt)_5$ $Mo(EH)_n$	Novolac–$Mo(OEt)_5^{0.75\%Mo}$ Novolac–$Mo(EH)_n^{1.5\%Mo}$

[a] $Mo(EH)_n$ = molybdenum 2-ethylhexanoate (mixture of compounds $Mo[OOCCH(C_2H_5)C_4H_9]_n$ containing 15 wt% molybdenum).

pending on the metal content, and then analysed by atomic spectroscopy.

2.3.2. *Typical procedure for the epoxidation of propene*

A 80-ml steel autoclave was charged with 50 mmol TBHP (3.6 M solution in toluene), dodecane as an internal standard for GC analysis, and 1 g of catalyst. After replacing the air and saturation of the reaction solution with propene, a pressure of 8 bar was adjusted. The mixture was magnetically stirred for 24 h at 90 °C, and the operating pressure was ca. 25 bar. After cooling to room temperature and expansion of the system, the catalyst was separated by filtration and reused with no reconditioning. TBHP concentrations of the filtrates were determined by iodometric titration. GC and metal analyses were performed as described for reactions with liquid alkenes.

3. Results and discussion

3.1. *Catalyst preparation and characterisation*

Di-, tri-, tetra-, and oligofunctional epoxy resins—namely, the glycidyl derivatives of bisphenol A, 4,4′-methylenedianiline and 4-aminophenol, as well as an epoxy novolac—were polymerised using molybdenum(V) ethoxide or molybdenum 2-ethylhexanoate ($Mo(EH)_n$) as a polymerisation initiator. The metal compounds release ligands on heating, thus initiating epoxy ring opening, followed by anionic polymerisation and crosslinking of the thermosets. The molybdenum compounds act as precursors for the catalytically active species in the resulting polymers so that the catalysts can be obtained in a one-step procedure. A molybdenum content of 0.75 or 1.5 wt%, corresponding to a molybdenum compound content in the resin formulations of 2.5–10%, were adjusted. Thin (ca. 1 mm) layers of the mixtures were polymerised in aluminium molds at 120–230 °C. The resulting resin plates were cut and ground with an analytical mill, yielding granulates with particle diameters <800 µm. The materials were annealed at 230 °C and sieved. Fractions with particle diameters of 150–500 µm were used for the catalytic reactions. Resins, polymerisation initiators, and the resulting catalysts are summarised in Table 1.

The polymerisation reactions were studied by differential scanning calorimetry (DSC). Polymerisation of the TGAP- and TGMDA-based systems started at significantly lower temperatures compared with those of the reactions of DGEBA and the novolac (Fig. 1). The reactions of TGAP and TGMDA initiated by $Mo(OEt)_5$ were strongly exothermic, with reaction enthalpies above 600 $J\,g^{-1}$, indicating a high crosslinkage in the resulting polymers. The corresponding values for DGEBA–$Mo(OEt)_5^{0.75\%Mo}$ and novolac–$Mo(OEt)_5^{0.75\%Mo}$ were 420 and 370 $J\,g^{-1}$, respectively. Doubling the amount of $Mo(OEt)_5$ did not significantly influence the polymerisation of TGMDA; almost the same reaction enthalpy, slightly above 600 $J\,g^{-1}$, was observed [TGMDA–$Mo(OEt)_5^{0.75\%Mo}$ vs TGMDA–$Mo(OEt)_5^{1.5\%Mo}$]. Polymerisations initiated by $Mo(EH)_n$ showed significantly lower reaction enthalpies than those initiated by $Mo(OEt)_5$. Reaction enthalpies for TGAP–$Mo(EH)_n^{1.5\%Mo}$ and novolac–$Mo(EH)_n^{1.5\%Mo}$ were 430 and 320 $J\,g^{-1}$, respectively.

SEM images were recorded, and the polymer surfaces were analysed by energy-dispersive X-ray spectroscopy (SEM-

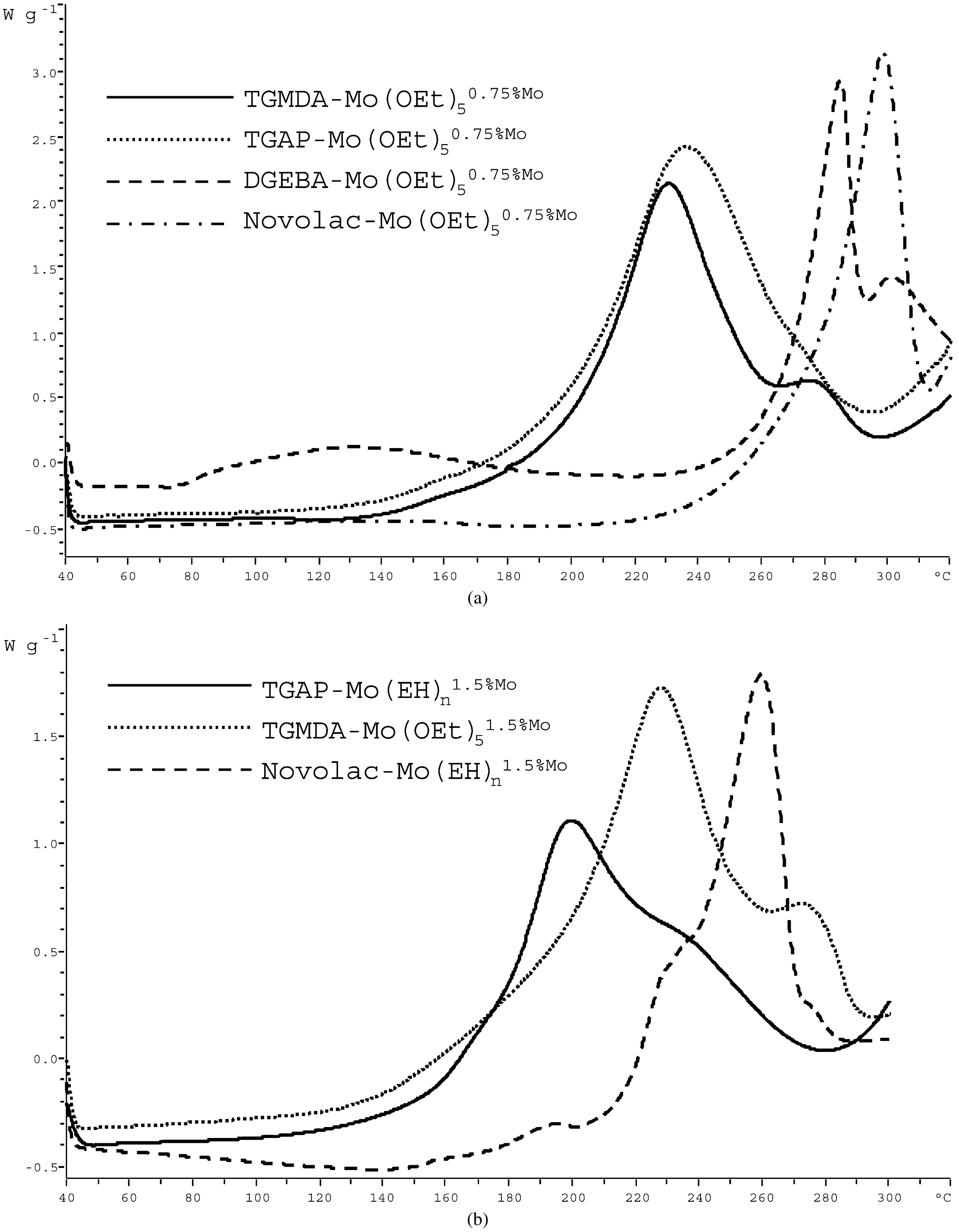


Fig. 1. DSC curves of different resins containing (a) 0.75 and (b) 1.5% of molybdenum.

EDX). Bright spots indicate molybdenum-rich areas consisting of polyoxo complexes with molybdenum content up to 50% [46]. Images of the systems resin–$\text{Mo(OEt)}_5^{0.75\%\text{Mo}}$ reflect the varying solubility of Mo(OEt)_5 in the different resins. Only a few spots are visible in the case of DGEBA–$\text{Mo(OEt)}_5^{0.75\%\text{Mo}}$ and TGAP–$\text{Mo(OEt)}_5^{0.75\%\text{ Mo}}$, due to the good solubility of Mo(OEt)_5 in these resins. Some other agglomerates can be detected at the surface of TGMDA–$\text{Mo(OEt)}_5^{0.75\%\text{Mo}}$, and several are visible at the surface of novolac–$\text{Mo(OEt)}_5^{0.75\%\text{Mo}}$, reflecting the low solubility of Mo(OEt)_5 in the latter resin. Raising the molybdenum content in TGMDA from 0.75 to 1.5% did not increase the number of these spots, and the resins polymerised with the readily soluble Mo(EH)_n exhibited uniform surfaces.

Thin resin plates must be prepared; otherwise, the polymerised thermosets cannot be crushed and milled. Consequently, the amount of catalyst that can be obtained in a single preparation step is limited. To circumvent this constraint, inorganic fillers can be added to the liquid resin. After polymerization, a catalyst powder can be obtained without an additional milling step. The composition of these inorganic–organic hybrid catalysts can be varied over a wide range and

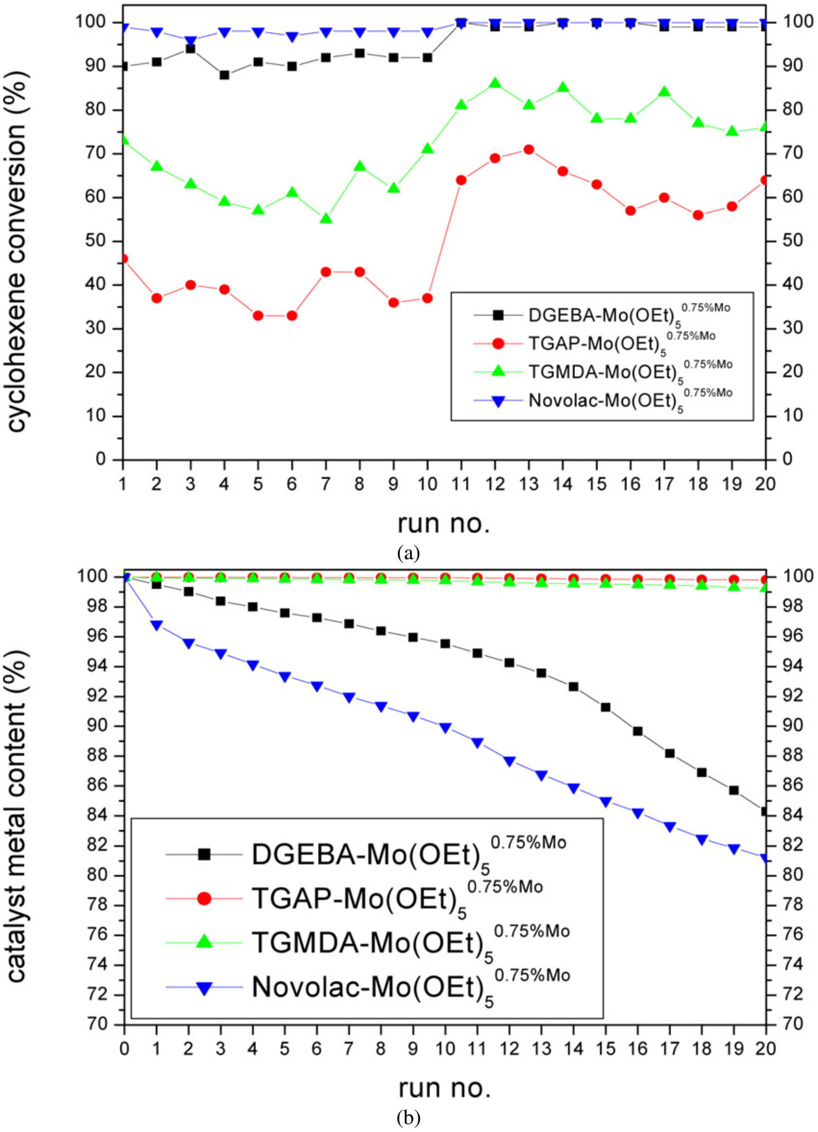


Fig. 2. Catalytic performance of molybdenum-doped epoxy resins in the epoxidation of cyclohexene. (a) Cyclohexene conversions and (b) metal leaching. Reaction conditions: reaction times of 7 h for entries 1–10 and reaction times of 24 h for entries 11–20; 10 mmol cyclohexene, 12 mmol TBHP (3.2 M solution in toluene), 500 mg catalyst, 90 °C; no precautions against moisture and air.

easily adapted to the respective requirements. A catalyst containing 37.5% silicagel was prepared by mixing silicagel with a solution of $Mo(OEt)_5$ and TGMDA in Et_2O, followed by solvent evaporation and polymerisation. The SEM image of the silicagel/TGMDA–$Mo(OEt)_5^{0.5\%Mo}$ thus obtained showed a uniform particle surface, and EDX analysis confirmed a uniform distribution of the components in this composite material.

3.2. *Catalytic performance of molybdenum-doped epoxy resins*

The suitability of different epoxy resins for the development of epoxidation catalysts was evaluated. A series of resins polymerised with $Mo(OEt)_5$ was used, and resins containing 0.75% molybdenum were tested as heterogeneous catalysts in the liquid-phase epoxidation of cyclohexene with anhydrous TBHP as an oxidant. They were initially tested in 10 consecutive reactions with a reaction time of 7 h and also, focusing on the long-term stability of the catalysts, in 10 reactions with a reaction time of 24 h. Catalyst recycling was accomplished by filtering and reusing the resin with no reconditioning. For an accurate study of extremely low amounts of metal in the reaction solutions, removal of volatile components and metal enrichment in the reaction residues, combined with the application of sensitive atomic spectroscopic techniques, is indispensable [46]. Therefore, metal losses of the catalysts were determined by atomic emission spectroscopy (ICP-AES) or, in the case of metal traces in the nanogram range, atomic absorption spectroscopy (AAS) from concentrated solutions of the reaction residues in HNO_3.

Alkene conversions and metal contents of the catalysts are summarised in Fig. 2. Using DGEBA–$Mo(OEt)_5^{0.75\%Mo}$ and novolac–$Mo(OEt)_5^{0.75\%Mo}$, cyclohexene conversions and epoxide selectivities were 90–100%. However, these yields are asso-

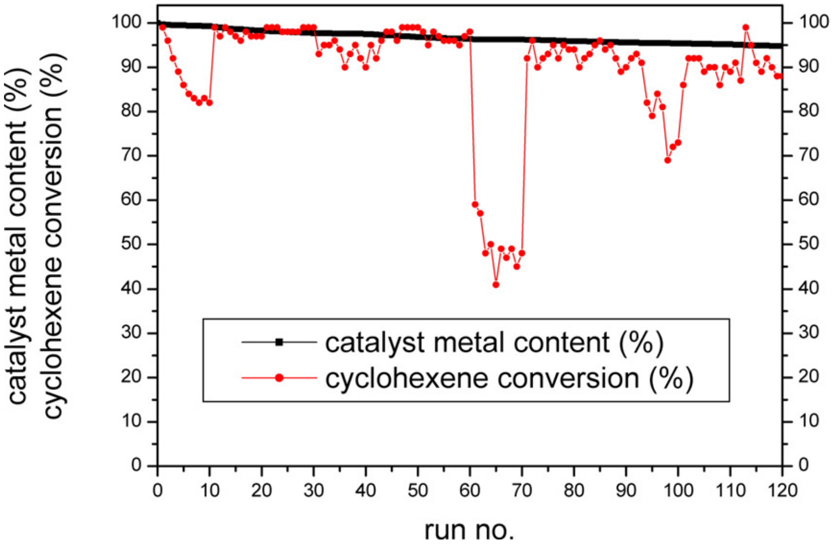


Fig. 3. Catalytic long-term performance of TGMDA–Mo(OEt)$_5^{1.5\%\text{Mo}}$ in the epoxidation of cyclohexene during a period of 105 days. Reaction conditions: reaction times of 7 h for entries 1–10 and 61–70; reaction times of 24 h for entries 11–60 and 71–120; 10 mmol cyclohexene, 16 mmol TBHP (3.2 M solution in toluene), 500 mg catalyst, 90 °C; 1.6 M TBHP solution in runs 94–100; no precautions against moisture and air.

ciated with significant metal leaching; the metal content of the catalysts after 20 reactions was 84% of the molybdenum originally loaded on the polymer for DGEBA–Mo(OEt)$_5^{0.75\%\text{Mo}}$ and 81% for novolac–Mo(OEt)$_5^{0.75\%\text{Mo}}$. In contrast, metal losses were very low for TGAP–Mo(OEt)$_5^{0.75\%\text{Mo}}$ and TGMDA–Mo(OEt)$_5^{0.75\%\text{Mo}}$, and the catalysts still contained 99.82% and 99.25% of the metal, respectively, after 20 reactions. Using TGAP–Mo(OEt)$_5^{0.75\%\text{Mo}}$, cyclohexene conversions were 33–46% in reactions 1–10 with an average epoxide selectivity of 86%. Conversions increased to values of 56–71% with selectivities around 92% in the subsequent 10 reactions. The corresponding values obtained with TGMDA–Mo(OEt)$_5^{0.75\%\text{Mo}}$ were conversions of 55–73% with selectivities of around 93% in runs 1–10 and conversions of 75–86% in reactions 11–20 with selectivities around 95%. All reactions were carried out without precautions against moisture and air, and blank conversions without catalyst of around 5% with low epoxide selectivities of around 20% were observed after reaction times of 24 h. The major byproducts in all reactions were cyclohexenol and cyclohexenone due to allylic oxidation, as well as cyclohexanediol arising from epoxide ring-opening. TBHP consumption was monitored by iodometric titration, and nonproductive TBHP decomposition was negligible ($<1.5\%\,\text{run}^{-1}$).

Based on leaching data, catalyst lifetimes of approximately 80 and 100 days can be estimated under the chosen reaction conditions for DGEBA–Mo(OEt)$_5^{0.75\%\text{Mo}}$ and novolac–Mo(OEt)$_5^{0.75\%\text{Mo}}$, respectively. The high metal loss of the DGEBA-based catalyst can be explained by the lower degree of cross-linking in this polymer compared with the other resins. The resin has only two glycidyl groups per monomer and naturally yields materials with lower thermal and chemical resistance. Regarding novolac–Mo(OEt)$_5^{0.75\%\text{Mo}}$, the comparatively high metal leaching is probably due to the low solubility of Mo(OEt)$_5$ in the resin. Assuming that the catalytic performance does not change, catalyst lifetimes of some years can be expected for TGAP–Mo(OEt)$_5^{0.75\%\text{Mo}}$ and TGMDA–Mo(OEt)$_5^{0.75\%\text{Mo}}$. However, activities of these catalysts are moderate, and cyclohexene conversions reach values of around 80%.

To gain a highly stable catalyst with increased activity, the molybdenum content in TGMDA was doubled, and rigorous long-term testing of TGMDA–Mo(OEt)$_5^{1.5\%\text{Mo}}$ was carried out. The catalyst was used in 120 consecutive reactions corresponding to an application period of approximately 105 days. Its catalytic performance is shown in Fig. 3. Focusing on the catalyst stability, reaction times of 24 h were chosen except for reactions 1–10 and 61–70 with reaction times of 7 h. Cyclohexene conversions decreased from 99 to 82% in reactions 1–10, and the average conversion from reactions 11–30 was 98%. Selectivities in these initial reactions were >96%. The catalyst was not used during a period of 3 months between run 30 and run 31, entailing a slight decrease in conversion and selectivity to values around 93%. After further application, an increase in activity was observed, resulting in conversions and selectivities >95% (reactions 45–60). The average conversion of runs 61–70 was 49%, with an average selectivity of 95%. The lower conversions compared with those of reactions 1–10 are probably due to a 3-month interruption between run 60 and run 61. Conversions in reactions 71–93 with reaction times of 24 h were around 93%. The TBHP concentration in reactions 94–100 was reduced from 3.2 to 1.6 M, resulting in lower conversions with an average value of 77%. Readjusting the concentration to 3.2 M increased the conversion, and the average in the subsequent 20 reactions was 90%. Selectivities in reactions 71–120 were 95–100%. Note that the catalyst was used with several interruptions of some days from run 61 on; this explains the significant variation in conversion compared with the preceding reactions.

Molybdenum leaching was very low, and the average metal content of the reaction solutions was 3 µg per run (ca. 0.04% of metal originally present on the resin and ca. 0.6 ppm in the reaction mixture). After an application period of 105 days, the metal

Table 2
Catalytic performance of TGMDA–Mo(OEt)$_5^{1.5\%\mathrm{Mo}}$ in the epoxidation of different alkenes[a]

Run no.	2-Octene			Styrene			(*R*)-(+)-Limonene			1-Octene			1,2-Dihydronaphthalene		
	Alkene conversion (%)	Epoxide selectivity (%)	Mo leached (µg)	Alkene conversion (%)	Epoxide selectivity (%)	Mo leached (µg)	Alkene conversion (%)	Epoxide selectivity (%)	Mo leached (µg)	Alkene conversion (%)	Epoxide selectivity (%)	Mo leached (µg)	Alkene conversion (%)	Epoxide selectivity (%)	Mo leached (µg)
1	92	>99	7 (0.09)[b]	85	>99	< 1[c]	86	90	<1[c]	80	>99	16 (0.21)	70	76	<2[c]
2	96	>99	8 (0.11)	90	>99	<1	78	90	<1	80	>99	16 (0.21)	70	75	<2
3	97	>99	9 (0.12)	88	>99	<1	80	91	<1	75	>99	14 (0.19)	67	77	<2
4	95	>99	8 (0.11)	75	>99	<1	81	90	<1	76	>99	15 (0.20)	57	76	<2
5	89	>99	5 (0.07)	72	>99	<1	77	90	<1	81	>99	16 (0.21)	62	75	<2

[a] The catalyst was preused for 35 h in each case. Reaction conditions: 10 mmol alkene, 12 mmol TBHP (3.2 M solution in toluene), 500 mg catalyst, 90 °C, 24 h; no precautions against moisture and air.

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

[c] Reaction residues could not be completely dissolved in concentrated HNO_3 and were extracted with the acid during one week.

Table 3
Catalytic performance of TGMDA–Mo(OEt)$_5^{1.5\%\mathrm{Mo}}$ in the epoxidation of propene[a]

Run no.	Propene oxide yield[b] (%)	Mo leached (µg)
1	75	34 (0.23)[c]
2	72	12 (0.08)
3	78	21 (0.14)
4	70	14 (0.09)
5	67	5 (0.03)

[a] The catalyst was preused in 5 reactions. Reaction conditions: 80 ml steel autoclave, 8 bar propene, 50 mmol TBHP (3.6 M solution in toluene), 1 g catalyst, 90 °C, 24 h, 25 bar operating pressure.

[b] Yields are based on TBHP consumption.

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

content of the catalyst was still 94.8% of molybdenum initially loaded on the polymer. Based on these results, and provided that the catalytic performance remains unchanged, catalyst lifetimes in the range of some years can be predicted.

Results obtained with TGMDA–Mo(OEt)$_5^{1.5\%\mathrm{Mo}}$ in the epoxidation of various alkenes are summarised in Table 2. In each case, the catalyst was preused for 35 h to reach steady-state performance. Obviously, less reactive alkenes, such as 1-octene and styrene can also be epoxidised, with conversions between 72 and 90%. Selectivity was around 99% in all reactions except the epoxidation of 1,2-dihydronaphthalene and (*R*)-(+)-limonene. The former yielded significant amounts of the diol as a byproduct, with epoxide selectivity of around 76%. The latter was epoxidised predominately at the ring double bond, yielding monoepoxide with a selectivity of 90%. Byproducts were the diepoxide and products arising from isomerisation processes and allylic oxidation. Metal leaching was low in all reactions (<16 µg or, expressed as a percentage of the initial metal content, <0.21% per run), depending on the alkene. Using 1-octene as substrate, metal losses of the catalyst were significantly higher than those seen in reactions with 2-octene. The dependence of metal leaching on the type of alkene corroborates the previously reported contribution of heterogeneous catalysis to the catalytic activity [46]. In the case of styrene, (*R*)-(+)-limonene, and 1,2-dihydronaphthalene, very small amounts of molybdenum (<2 µg) were detected by ICP-AES after extraction of the reaction residues with concentrated HNO_3. The catalyst was also used in the epoxidation of propene (Table 3), and propene oxide yields between 67 and 75% were obtained in five consecutive reactions. No byproducts were observed. Metal leaching varied from 0.03 to 0.23% (5–34 µg per run), with an average value of 0.11% per run, corresponding to a level of ca. 1.3 ppm of molybdenum in the reaction mixture.

Besides Mo(OEt)$_5$, molybdenum 2-ethylhexanoate Mo-(EH)$_n$ was used as a polymerisation initiator and two polymers TGAP–Mo(EH)$_n^{1.5\%\mathrm{Mo}}$ and novolac–Mo(EH)$_n^{1.5\%\mathrm{Mo}}$ were tested as catalysts in the epoxidation of cyclohexene, 1-octene, and styrene (Tables 4 and 5). Their performance in the epoxidation of cyclohexene was very similar, and alkene conversions

Table 4
Catalytic performance of TGAP–Mo(EH)$_n^{1.5\%\mathrm{Mo}}$ in the epoxidation of different alkenes[a]

Run no.	Cyclohexene			1-Octene			Styrene		
	Alkene conversion (%)	Epoxide selectivity (%)	Mo leached (µg)	Alkene conversion (%)	Epoxide selectivity (%)	Mo leached (µg)	Alkene conversion (%)	Epoxide selectivity (%)	Mo leached (µg)
1	92	95	2 (0.03)[b]	57	>99	1 (0.01)	93	>99	n.d.[c]
2	87	97	2 (0.03)	61	>99	1 (0.01)	94	>99	n.d.
3	93	95	3 (0.04)	62	>99	1 (0.01)	90	>99	n.d.
4	93	96	3 (0.04)	66	>99	1 (0.01)	94	>99	n.d.
5	92	95	3 (0.04)	64	>99	1 (0.01)	95	>99	n.d.

[a] The catalyst was preused for 35 h in each case. Reaction conditions: 10 mmol alkene, 12 mmol TBHP (3.6 M solution in toluene), 500 mg catalyst, 90 °C, 24 h; no precautions against moisture and air.

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

[c] n.d. = not determined.

Table 5
Catalytic performance of novolac–Mo(EH)$_n^{1.5\%\text{Mo}}$ in the epoxidation of different alkenes[a]

Run no.	Cyclohexene			1-Octene			Styrene		
	Alkene conversion (%)	Epoxide selectivity (%)	Mo leached (μg)	Alkene conversion (%)	Epoxide selectivity (%)	Mo leached (μg)	Alkene conversion (%)	Epoxide selectivity (%)	Mo leached (μg)
1	92	96	3 (0.04)[b]	74	>99	10 (0.13)	99	>99	n.d.[c]
2	93	95	3 (0.04)	81	>99	12 (0.16)	99	>99	n.d.
3	91	96	4 (0.05)	80	>99	12 (0.16)	99	>99	n.d.
4	93	95	3 (0.04)	82	>99	14 (0.19)	99	>99	n.d.
5	94	95	4 (0.05)	85	>99	17 (0.23)	99	>99	n.d.

[a] The catalyst was preused for 35 h in each case. Reaction conditions: 10 mmol alkene, 12 mmol TBHP (3.6 M solution in toluene), 500 mg catalyst, 90 °C, 24 h; no precautions against moisture and air.

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

[c] n.d. = not determined.

were around 92% with epoxide selectivities of about 95%. Metal losses were in the range of 2–4 μg run, and those of the novolac catalyst were slightly higher than those of the TGAP-based system. 1-Octene conversions were around 62% using TGAP–Mo(EH)$_n^{1.5\%\text{Mo}}$ and around 80% using novolac–Mo(EH)$_n^{1.5\%\text{Mo}}$, with epoxide selectivities >99% in both cases. Metal leaching from the former catalyst was significantly lower (1 μg per run^{-1}) than from the latter (10–17 μg run^{-1}). Conversions of 90–95% were obtained in the epoxidation of styrene with TGAP–Mo(EH)$_n^{1.5\%\text{Mo}}$, whereas conversions of 99% were achieved using novolac–Mo(EH)$_n^{1.5\%\text{Mo}}$. Selectivities were >99% in both cases. The catalysts were also tested in the epoxidation of propene (Table 6); epoxide yields were 61–74% for TGAP–Mo(EH)$_n^{1.5\%\text{Mo}}$. The affect of temperature on propene oxide yields was studied (Fig. 4). The average epoxide yield from 5 consecutive reactions was 17% at 60 °C, 39% at 75 °C, and 67% at 90 °C. Epoxide yields between 55% and 88% were obtained for novolac–Mo(EH)$_n^{1.5\%\text{Mo}}$ at 90 °C. No byproducts were detected in any reaction. Metal losses of TGAP–Mo(EH)$_n^{1.5\%\text{Mo}}$ (3–16 μg per run) were significantly lower than those of the novolac-based catalyst (16–117 μg per run). The average values per run were 0.06% of the molybdenum initially loaded on the polymer for the TGAP catalyst and 0.28% for the novolac catalyst.

Table 6
Catalytic performance of TGAP–Mo(EH)$_n^{1.5\%\text{Mo}}$ and novolac–Mo(EH)$_n^{1.5\%\text{Mo}}$ in the epoxidation of propene[a]

Run no.	TGAP–Mo(EH)$_n^{1.5\%\text{Mo}}$		Novolac–Mo(EH)$_n^{1.5\%\text{Mo}}$	
	Propene oxide yield[b] (%)	Mo leached (μg)	Propene oxide yield[b] (%)	Mo leached (μg)
1	74	16 (0.11)[c]	88	117 (0.78)
2	71	7 (0.05)	63	29 (0.19)
3	67	13 (0.09)	72	23 (0.15)
4	62	6 (0.04)	55	16 (0.11)
5	61	3 (0.02)	64	24 (0.16)

[a] Reaction conditions: 80 ml steel autoclave, 8 bar propene, 50 mmol TBHP (3.6 M solution in toluene), 1 g catalyst, 90 °C, 24 h, 25 bar operating pressure; particle size of TGAP–Mo(EH)$_n^{1.5\%\text{Mo}}$: 150–300 μm.

[b] Yields are based on TBHP consumption.

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

Up to now, only a few catalyst systems based on organic polymers had been tested in the epoxidation of propene.

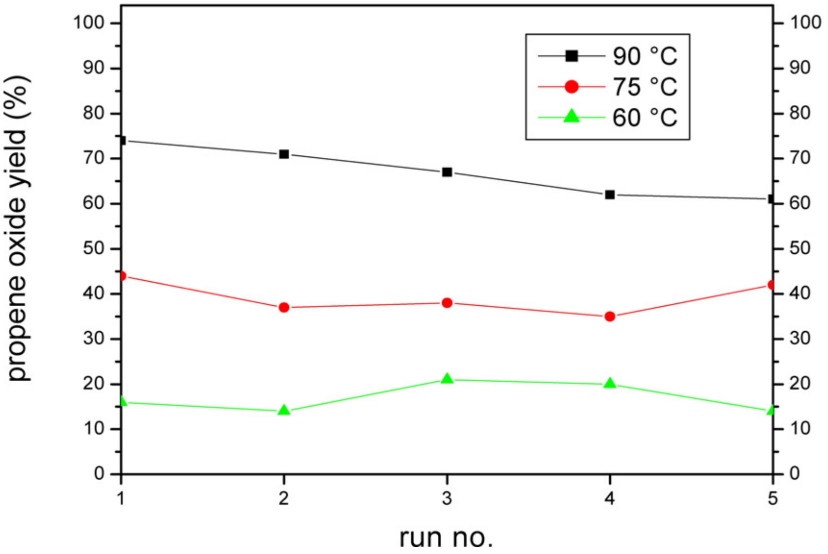


Fig. 4. Epoxidation of propene catalysed by TGAP–Mo(EH)$_n^{1.5\%\text{Mo}}$: influence of the temperature on the epoxide yield. Reaction conditions: see Table 6.

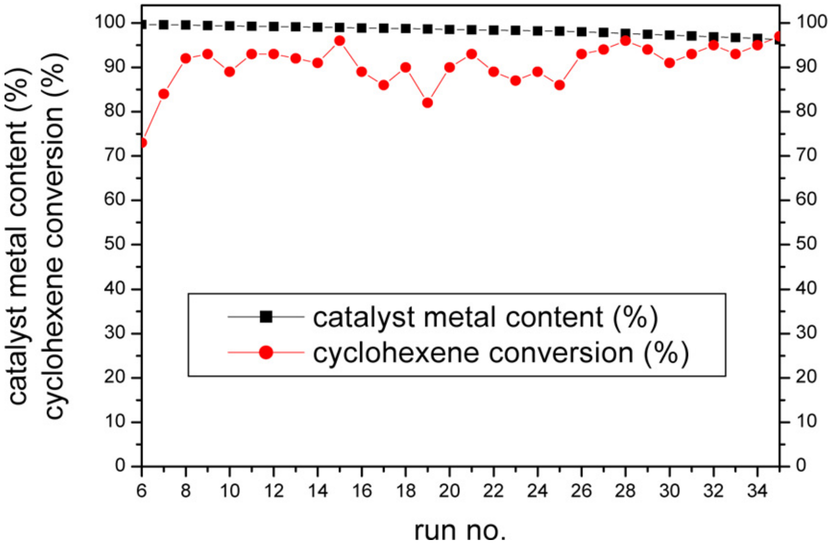


Fig. 5. Catalytic long-term performance of TGAP–Mo$(EH)_n^{1.5\%Mo}$ in the epoxidation of cyclohexene during a period of 30 days. Reaction conditions: see Table 4.

Micelle-incorporated manganese porphyrin catalysts were used [49], but no data on their long-term performance are available. High propene oxide yields from 59.0 to 99.8% were reported using molybdenum supported on benzimidazole [50]. However, the catalyst was tested only during 10 h, and, with respect to molybdenum leaching, a high AAS detection limit expressed as a percentage of molybdenum originally loaded on the polymer (0.2%), corresponding to 23 μg of metal, was reported.

The long-term performance of TGAP–Mo$(EH)_n^{1.5\%Mo}$ in the epoxidation of cyclohexene was studied. The catalyst was used in 30 additional reactions, extending its application time to about 36 days (Fig. 5). Neglecting the low cyclohexene conversion in run 6, which likely was due to an interruption in catalyst testing lasting for some weeks between runs 5 and 6, conversions were between 82 and 97% (average conversion, 91%), with selectivities of around 96%. The metal content after about 36 days was 96.2%. Using TGMDA–Mo$(OEt)_5^{1.5\%Mo}$ this value was reached after 72 reactions, that is, after an application period of 58 days (Fig. 3). The higher metal leaching in the long-term testing of TGAP–Mo$(EH)_n^{1.5\%Mo}$ could be due to the somewhat higher TBHP concentration (3.6 M) compared with the reactions catalysed by TGMDA–Mo$(OEt)_5^{1.5\%Mo}$, for which a 3.2 M solution was used. However, this did not result in higher alkene conversions. In contrast, conversions obtained with TGMDA–Mo$(OEt)_5^{1.5\%Mo}$ were higher than those in reactions catalysed by TGAP–Mo$(EH)_n^{1.5\%Mo}$. The lower performance of systems polymerised with Mo$(EH)_n$ compared with systems polymerised with Mo$(OEt)_5$ could be due to the lower molybdenum content in the initiator [15% in Mo$(EH)_n$ vs 30% in Mo$(OEt)_5$], so that significantly higher amounts are needed to adjust a molybdenum content of 1.5%, which could interfere with the polymerisation and cross-linking of the resins.

The catalytic performance of the inorganic–organic hybrid system silicagel/TGMDA–Mo$(OEt)_5^{0.5\%Mo}$ was also investigated, and the composite material was tested in 5 consecutive reactions as catalyst in the epoxidation of styrene (Table 7). Metal leaching was extremely low (average metal loss of 0.07% per run) and could be measured accurately only by AAS. Alkene conversions ranged from 75 to 83%, and epoxide selectivities were >99%. Although the molybdenum content was much lower in the hybrid system, the results were similar to those obtained with TGMDA–Mo$(OEt)_5^{1.5\%Mo}$.

Table 7
Catalytic performance of silicagel/TGMDA–Mo$(OEt)_5^{0.5\%Mo}$ in the epoxidation of styrene[a]

Run no.	Alkene conversion (%)	Epoxide selectivity (%)	Mo leached (μg)
1	83	>99	3.55 (0.142)[b]
2	80	>99	1.68 (0.067)
3	80	>99	1.20 (0.048)
4	78	>99	1.52 (0.061)
5	75	>99	0.85 (0.034)

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

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

4. Conclusion

We report for the first time on catalyst systems based on organic polymers that can operate over periods of months. The catalysts can be prepared in a convenient time- and cost-saving one-step procedure, and a series of commercially available epoxy resins and metal compounds facilitates their optimisation. Their catalytic performance in epoxidation reactions strongly depends on the type of resin, the polymerisation initiator, and the alkene. Promising epoxide yields have been obtained in the epoxidation of propene. Good resin solubilities of the initiators and a homogeneous distribution of the active components in the resin matrix, as well as a high degree of polymer cross-linking, are prerequisites for leaching-resistant catalyst systems. Metal leaching depends on the alkene, and the substrate dependence corroborates the contribution of heterogeneous catalysis to the catalytic activity. It is possible to prepare catalysts that exhibit extremely low metal losses even after application periods of months under thermo-oxidatively demanding reaction conditions, so that catalysts with lifetimes in the range of years can be obtained. The liquid resins can be easily modified before polymerisation through the addition of various compounds, and the systems thus can be adjusted to the respective requirements. In combination with inorganic components such as silicagel, inorganic–organic hybrid catalysts can be obtained even on a large scale. Because epoxy resins are typically used as coatings, reactor surfaces and/or packing materials could be coated with catalytically active resin layers.

Currently the catalysts are optimized, and some systems are being tested in a continuously operating setup. The concept is being extended to other metals, such as palladium and rhodium. Combinations of different metals also can be used, and metal-doped epoxy resins have been successfully tested as catalysts in various reactions, including hydrogenations, hydroformylations, and carbon–carbon bond coupling reactions.

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