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Metal-doped epoxy resins: Easily accessible, durable, and highly versatile catalysts

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Abstract

Thermosetting epoxy resins, such as the triglycidyl derivative of 4-aminophenol, can be polymerized using molybdenum, palladium, or rhodium complexes as initiators. The resulting metal-doped materials proved to be efficient catalysts for epoxidation, carbon–carbon coupling, hydrogenation, and hydroformylation reactions. Propylene oxide yields of around 50% were obtained in the epoxidation of propylene with *tert*-butyl hydroperoxide as the oxidant, and biphenyl yields of $\geqslant 98\%$ were observed in the Suzuki coupling of iodobenzene with phenylboronic acid. Almost quantitative conversions were accomplished in the hydrogenation of ethyl crotonate, ethyl cinnamate, and croton aldehyde, whereas aldehyde yields of around 16% were obtained in the hydroformylation of 1-octene. Organic–inorganic hybrid catalysts can be obtained in a convenient one-step procedure by the addition of inorganic components to the liquid resins and subsequent polymerization. Different metal species can be combined in one thermoset matrix, affording multifunctional catalysts that can be us in various catalytic liquid-phase transformations. Quantification of metal traces in the reaction mixtures by metal enrichment and atomic spectroscopy demonstrated very low metal losses of the catalysts. The catalysts can be simply recovered by filtration and reused without reconditioning while maintaining stability, activity, and selectivity.

Keywords: Epoxidation; Carbon–carbon coupling; Hydrogenation; Hydroformylation; Molybdenum; Palladium; Rhodium; Epoxy resins; Polymer-supported catalysts; Catalyst recycling

1. Introduction

Modification of organic polymers with catalytically active species represents one of the most versatile strategies for the development of efficient catalyst systems that can be easily separated from reaction mixtures, thus facilitating recycling. Catalysts can be obtained by attachment of metal species to already polymerized materials via several established immobilization techniques [1]. Catalytically active species also can be incorporated in polymer matrices during polymer growth by, for example, (co)polymerization of metal complexes bearing ligands with polymerizable moieties [2] or polycondensation in the presence of metal complexes [3]. In a recent approach, metal complexes were used as polymerization initiators serving simultaneously as precursors for catalytically active species in the resulting polymers [4]. Innumerable monomers and a series of polymerization techniques afford a wide variety of catalyst systems applicable in a series of catalytic transformations, and current research focuses on enantioselective catalysis using polymer-bound catalysts [5–7], soluble supports [8], microencapsulated catalysts [9–11], or hybrid organic–inorganic catalysts [12].

But academic research frequently concentrates on mechanistic investigations, such as the question of metal leaching, the distinction between heterogeneous and homogeneous catalysis, and the development of "truly heterogeneous catalysts" [13], neglecting technological, ecological, and economic criteria, such as costs or long-term applicability (e.g., in continuously operating processes). In fact, almost no data on the long-term performance of polymer-based catalysts exceeding hours or a few days are available. Keep in mind that a "truly heterogeneous catalyst" that exhibits a perfect initial performance can

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deactivate after a few reaction cycles by poisoning, leaching, or decomposition, whereas a catalyst that exhibits high initial metal leaching can reach a steady-state performance after several cycles with negligible metal loss while maintaining high catalytic activity. Furthermore, heterogeneous and homogeneous catalysis can proceed simultaneously, interfering with each other, and leached metal traces in the nanogram range, detectable only by accurate metal enrichment techniques, can contribute significantly to the catalytic activity.

Epoxy resins are widely used high-performance thermosets with numerous applications such as coatings, composites, or adhesives [14–17]. Monomeric epoxy resins can be polymerized using metal complexes as polymerization initiators [18–22]. The complexes release ligands (i.e., Lewis bases) on heating, thus initiating epoxy ring opening, followed by anionic polymerization. According to this concept, a wide variety of metal species can be incorporated in the network of crosslinked epoxy resins.

Recently, we reported on the use of metal-doped epoxy resins as catalysts [4,23] obtainable in a convenient time- and cost-savings one-step procedure using metal complexes as polymerization initiators and precursors for catalytically active species in the polymerized materials. Molybdenum-doped resins were used as epoxidation catalysts, and mechanistic studies revealed a superposition of heterogeneous and homogeneous catalysis. Compared with other metal catalysts based on organic polymers [1,10,24–33], unprecedented long-term activities over periods of months were observed. To demonstrate the versatility and applicability of this new type of catalyst, we report on a broad extension of this concept. Epoxy resins doped with molybdenum, palladium, or rhodium species were prepared and used as recyclable catalysts for epoxidation, carbon–carbon coupling, hydrogenation, and hydroformylation reactions.

2. Experimental

2.1. General

The epoxy resin N,N-diglycidyl-4-glycidyloxyaniline (TGAP) was purchased from Aldrich. $Mo(OEt)_5$ and $Pd(PPh_3)_4$ were obtained from Gelest and Strem, respectively. The rhodium complex $Rh(C_8H_{12})[(i\mathrm{Pr})_2PC_6H_4CH(OMe)_2]Cl$ was prepared as described previously [34]. Silicagel type 62 with particle sizes of 75–250 µm (Aldrich) was used for the preparation of the resin–silicagel hybrid catalysts. Propylene 2.5, synthesis gas (CO 4.7, H_2 6.0, 49.6 vol% CO), and hydrogen 5.0 were obtained from Messer Griesheim, Air Liquide, and Basi, respectively. Anhydrous *tert*-butyl hydroperoxide (TBHP) in toluene was prepared by azeotropic drying of TBHP (T-HYDRO® solution from Aldrich, 70 wt% TBHP in water) [35] and TBHP concentrations were determined by iodometric titration [36]. All other substrates, reagents, and solvents were purchased from Aldrich and used as received.

SEM images were recorded on a Leo 982 digital scanning microscope combined with an Oxford Instruments ISIS 300 energy-dispersive X-ray (EDX) unit. Differential scanning calorimetry (DSC) data for the polymerization reactions were recorded using a Mettler Toledo DSC822^e device with a heating rate of $10\,^\circ\mathrm{C\,min^{-1}}$. Measurements were carried out under nitrogen atmosphere typically using 3–10 mg resin samples. Polymerized resins were pulverized in a cryogenic grinding mill at liquid nitrogen temperature. Surface areas were determined using a Quantachrome NOVA 2000 gas sorption analyzer by adsorption–desorption of nitrogen at 77 K. Thermogravimetric analyses (TGA) of the catalysts were carried out using a Mettler Toledo TGA/SDTA851^e instrument with a heating rate of $10\,^\circ\mathrm{C\,min^{-1}}$ under air and nitrogen flow. Catalyst samples of 2–6 mg were used.

Conversions and selectivities were analyzed 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 propylene, dodecane was added as internal standard to the reaction mixtures. Propylene oxide yields were based on TBHP consumption. Yields were determined by TBHP titration and GC-FID.

Quantifications of metal traces in the reaction solutions were carried out by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy (AAS) analyses on a Varian Liberty 150 and a Varian SpectrAA 800 instrument, respectively. Metals were concentrated before analysis by evaporation of the solvents and dissolving of the reaction residues in concentrated HNO_3. In the case of C–C-coupling reactions, the palladium content of aqueous and organic phases was determined after metal enrichment in the reaction residues.

Rotilabo® syringe filters (PTFE, 0.45 µm pore width) were used for catalyst separation. In the case of C–C-coupling reactions, the catalyst was recovered by filtration of the reaction mixtures through Whatman GF/C glass fiber paper. In recycling tests, the catalysts were reused without any reconditioning unless stated otherwise.

2.2. Catalyst preparation

2.2.1. Preparation of $TGAP^{62.0\%}/SiO_2{}^{36.4\%}$–$Mo^{0.5\%}$

The epoxy resin TGAP (9.998 g), the initiator $Mo(OEt)_5$ (0.265 g), and silicagel (5.860 g) were mixed vigorously at 50 °C for 15 min. The formulation was transferred to an aluminum mold and polymerized in an oven by raising the temperature successively from 120 to 230 °C (120 °C for 1 h, 180 °C for 3 h, 200 °C for 2 h and 230 °C for 1 h). The resulting brittle material was pulverized manually in a mortar and annealed at 230 °C for 4 h. The powder was sieved, and two fractions with particle diameters of 20–150 and 150–500 µm were obtained.

2.2.2. *Preparation of* $TGAP^{48.3\%}/SiO_2^{50.0\%}$–$Mo^{0.5\%}$

A mixture of TGAP (10.000 g), $Mo(OEt)_5$ (0.347 g), and silicagel (10.347 g) was stirred vigorously at 50 °C for 15 min. The resulting powder was transferred to an aluminum mold, and polymerization was carried out in an oven by raising the temperature successively from 120 to 220 °C (120 °C for 1 h, 140 °C for 30 min, 160 °C for 30 min, 180 °C for 30 min, 200 °C for 30 min, and 220 °C for 1 h). The powder was annealed at 220 °C for 4 h and sieved. Two fractions with particle diameters of 20–150 and 150–300 μm were obtained.

2.2.3. *Preparation of* $TGAP^{46.7\%}/SiO_2^{50.0\%}$–$Mo^{1.0\%}$

A mixture of TGAP (10.000 g), $Mo(OEt)_5$ (0.718 g), and silicagel (10.718 g) was homogenized and processed as described above for the system $TGAP^{48.3\%}/SiO_2^{50.0\%}$–$Mo^{0.5\%}$.

2.2.4. *Preparation of TGAP–*$Pd^{1.0\%}$

The epoxy resin TGAP (8.2 g) was heated to 50 °C, and $Pd(PPh_3)_4$ (1.0 g) was added under vigorous stirring. After 30 min, the temperature was raised, and the mixture was stirred for another 10 min at 80 °C. The resin was cast into an aluminum mold, and a thin (ca. 1 mm) layer was polymerized in an oven by raising the temperature successively from 120 to 200 °C (120 °C for 1 h, 180 °C for 1 h and 200 °C for 4 h). The polymer was cut, milled, sieved, and annealed for 4 h at 200 °C. Fractions with particle diameters of 20–150, 150–300, and 300–500 μm were obtained.

2.2.5. *Preparation of TGAP–*$Rh^{1.0\%}$

The rhodium complex $Rh(C_8H_{12})[(i\text{Pr})_2PC_6H_4CH(OMe)_2]$-Cl (0.537 g) was dissolved at 50 °C in TGAP (10.214 g), and a thin (ca. 1 mm) layer of the formulation was polymerized in an aluminum mold at 100 °C for 1 h, 120 °C for 1 h, 140 °C for 1 h, 160 °C for 1 h, and 180 °C for 1 h. After demolding, the resin plate was crushed and milled. Particle sizes were adjusted to 20–150 μm by sieving the polymer powder.

2.2.6. *Preparation of TGAP–*$Mo^{1.4\%}/Pd^{0.5\%}$

A mixture of $Mo(OEt)_5$ (0.427 g), $Pd(PPh_3)_4$ (0.488 g), and TGAP (8.070 g) was homogenized by ultrasonic treatment and transferred to an aluminum mold. The formulation was cured by raising the temperature successively from 120 to 200 °C (120 °C for 1 h, 140 °C for 1 h, 160 °C for 3 h, 180 °C for 1 h, and 200 °C for 1 h). The resulting resin plate (thickness of approximately 1 mm) was crushed and milled, and the polymer powder was heated to 200 °C for 2 h. Particle diameters of 20–150, 150–300, and 300–500 μm were adjusted by sieving.

2.3. *Catalytic procedures*

2.3.1. *Epoxidation of propylene*

A 80-ml steel autoclave was charged with TBHP (anhydrous solution in toluene), dodecane as an internal standard for GC analysis and the catalyst. Reaction conditions for $TGAP^{62.0\%}/SiO_2^{36.4\%}$–$Mo^{0.5\%}$: TBHP (50 mmol, 31 wt% in toluene/dodecane corresponding to ca. 16 ml) and catalyst (1 g; particle sizes: 20–150 μm); reaction conditions for $TGAP^{48.3\%}/SiO_2^{50.0\%}$–$Mo^{0.5\%}$ and $TGAP^{46.7\%}/SiO_2^{50.0\%}$–$Mo^{1.0\%}$: TBHP (50 mmol, 34 wt% in toluene/dodecane corresponding to ca. 15 ml), and catalyst (2 g; particle sizes: 150–300 μm); reaction conditions for TGAP–$Mo^{1.4\%}/Pd^{0.5\%}$: TBHP (50 mmol, 36 wt% in toluene/dodecane corresponding to ca. 14 ml), and catalyst (1 g; particle sizes: 150–300 μm). After replacing the air and saturating the reaction solution with propylene, a pressure of 8 bar was adjusted. The mixture was magnetically stirred for 24 h at 90 °C, with an operating pressure of ca. 25 bar. Cylindrical 20 × 6 mm stirring bars were used at 200 rpm. After cooling to room temperature and expansion of the system, the catalyst was separated by filtration and reused without reconditioning.

2.3.2. *Suzuki coupling of iodobenzenes with phenylboronic acid*

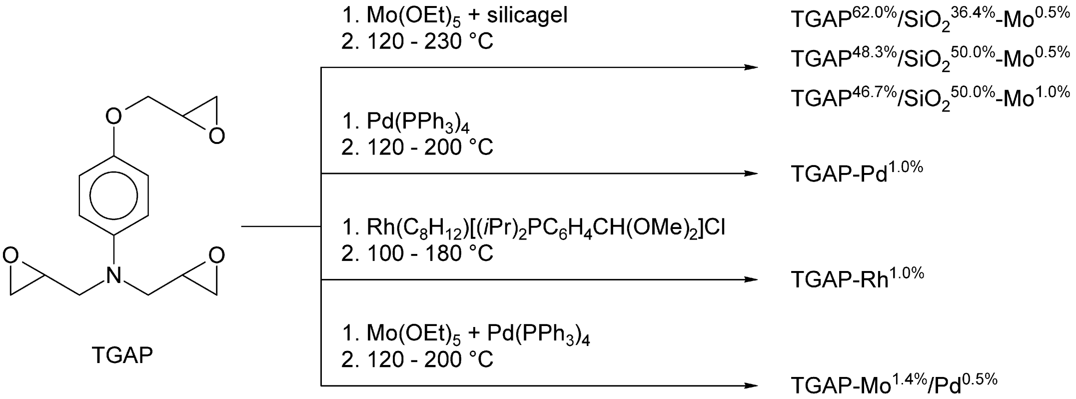
Iodobenzene (5 mmol), phenylboronic acid (6 mmol), and K_2CO_3 (20 mmol) were dissolved in a mixture of dioxane (10 ml) and water (10 ml). The catalyst (0.5 g; TGAP–$Pd^{1.0\%}$ with particle sizes of 150–300 μm or TGAP–$Mo^{1.4\%}/Pd^{0.5\%}$ with particle sizes of 20–150 μm) was added, and the mixture was magnetically stirred for 24 h at 90 °C. After cooling to room temperature, Et_2O (10 ml) was added. The catalyst was recovered by filtration and reused in the following reactions without reconditioning. The two phases of the filtrate were separated, and samples for ICP-AES, AAS, and GC analysis were taken.

2.3.3. *Hydrogenation reactions*

A 250-ml glass autoclave was charged with the substrate (10 mmol), 20 ml of solvent (MeOH in the case of ethyl crotonate and ethyl cinnamate; toluene in the case of crotonaldehyde and cinnamaldehyde), and the catalyst (0.5 g; TGAP–$Pd^{1.0\%}$ or TGAP–$Mo^{1.4\%}/Pd^{0.5\%}$ with particle sizes of 150–300 μm). After replacing the air and saturating the reaction solution with hydrogen, the pressure was raised to 2.5 bar. The mixture was heated to 60 °C and magnetically stirred for 4 h (for ethyl crotonate and ethyl cinnamate) or 24 h (for crotonaldehyde and cinnamaldehyde). After cooling to room temperature and expansion of the system, the catalyst was separated by filtration and reused without reconditioning.

2.3.4. *Hydroformylation of 1-octene*

A 300-ml steel autoclave with an integrated gas injection stirrer and a thermocouple was charged with 1-octene (0.624 mol) and the catalyst TGAP–$Rh^{1.0\%}$ (5 g with particle sizes of 20–150 μm). After replacing the air and saturating the reaction mixture with synthesis gas, the temperature of 110 °C was adjusted, and the pressure was raised to 50 bar. The reaction was run for 8 h with the impeller operating at 580 rpm, and the pressure was kept constant at 50 bar by an automated gas doser (Brooks 5866 pressure controller and Bronkhorst F-231C-FD-33-V flow regulator). After cooling to room temperature, the system was purged with nitrogen and the catalyst recovered by filtration. The catalyst was heated to 160 °C for 2 h and used in a second reaction under the same reaction conditions. In the



Scheme 1. Preparation of metal-doped epoxy resins by polymerization of TGAP.

subsequent reactions, the catalyst was reused without thermal treatment.

2.3.5. Heck coupling of iodobenzene with ethyl acrylate

Iodobenzene (50 mmol), ethyl acrylate (75 mmol), and K_2CO_3 (100 mmol) were dissolved in N-methylpyrrolidone (50 ml). The catalyst TGAP–$Mo^{1.4\%}$/$Pd^{0.5\%}$ (0.5 g with particle size 150–300 μm) was added, and the mixture was magnetically stirred for 24 h at 120 °C. After cooling to room temperature, the solids were removed by filtration. The catalyst was recovered by washing the solids with H_2O and Et_2O and reused in the subsequent reactions without reconditioning. Volatile components of the filtrate were removed under reduced pressure, and the residue was extracted with 100 ml of Et_2O three times. The combined organic layers were washed with 100 ml of H_2O three times and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the purity of ethyl cinnamate was controlled by NMR.

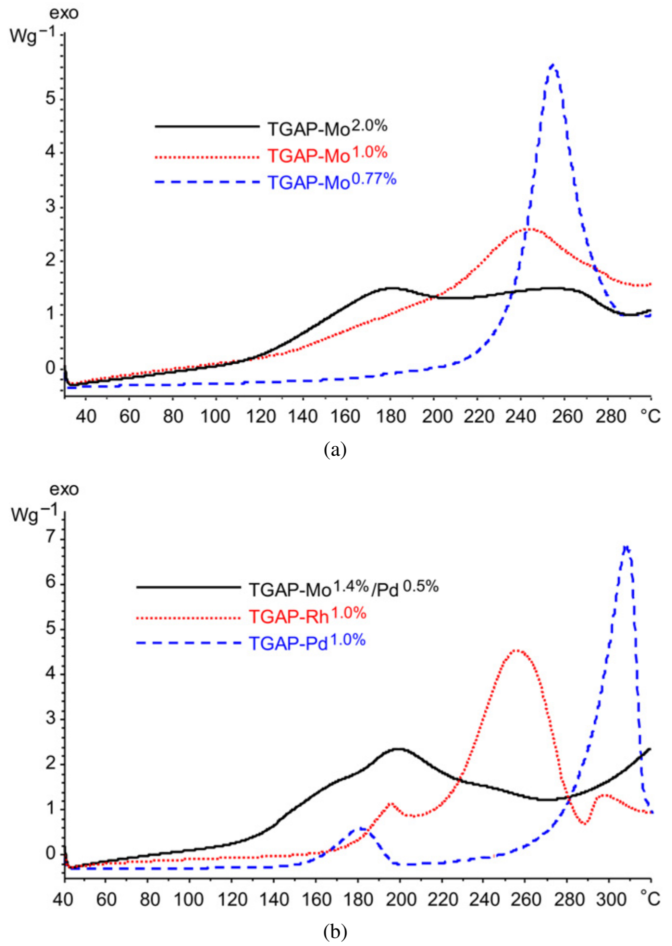
3. Results and discussion

3.1. Catalyst preparation and characterization

Several metal-doped resins based on the triglycidyl derivative of 4-aminophenol (TGAP) were prepared in a one-step procedure using $Mo(OEt)_5$, $Pd(PPh_3)_4$ and $Rh(C_8H_{12})[(i\mathrm{Pr})_2P$-$C_6H_4CH(OMe)_2]Cl$ as polymerization initiators (Scheme 1). Metal contents of 0.5, 1.0, or 1.4% were adjusted, and the mixtures were polymerized at temperatures between 100 and 230 °C. The resulting resin plates were milled and sieved. Fractions with particle diameters of 20–300 μm were used for the catalytic reactions. As shown previously [4,23], catalytic performances depend significantly on catalyst particle sizes, and catalysts with particle diameters in this range exhibit an optimum balance between low metal leaching and high catalytic activity. Organic–inorganic hybrid catalysts containing 0.5 and 1.0% of molybdenum and designated $TGAP^{62.0\%}/SiO_2{}^{36.4\%}$–$Mo^{0.5\%}$, $TGAP^{48.3\%}/SiO_2{}^{50.0\%}$–$Mo^{0.5\%}$, and $TGAP^{46.7\%}/SiO_2{}^{50.0\%}$–$Mo^{1.0\%}$ were prepared by modification of molybdenum-doped TGAP with 36.4 and 50.0% of silicagel, respectively. In the case of $TGAP^{62.0\%}/SiO_2{}^{36.4\%}$–$Mo^{0.5\%}$, a brittle material was obtained that could be easily pulverized. Increasing the silicagel content to 50%, catalyst powders were obtained directly after polymerization, and milling of the thermosets could be circumvented. A bimetallic system comprising molybdenum and palladium labeled as TGAP–$Mo^{1.4\%}$/$Pd^{0.5\%}$ was also prepared using a mixture of $Mo(OEt)_5$ and $Pd(PPh_3)_4$ as an initiator.

Polymerization reactions were investigated by differential scanning calorimetry (DSC); strongly exothermic reactions with enthalpies $>560\ \mathrm{J\,g^{-1}}$ indicate a high cross-linkage in the polymers (Fig. 1 and Table 1). In the case of molybdenum catalysts, neat resins without silicagel were investigated to ensure comparability to other catalysts. Thus, TGAP–$Mo^{0.77\%}$, TGAP–$Mo^{1.0\%}$, and TGAP–$Mo^{2.0\%}$ were the resin components of the corresponding hybrid catalysts $TGAP^{62.0\%}/SiO_2{}^{36.4\%}$–$Mo^{0.5\%}$, $TGAP^{48.3\%}/SiO_2{}^{50.0\%}$–$Mo^{0.5\%}$, and $TGAP^{46.7\%}/SiO_2{}^{50.0\%}$–$Mo^{1.0\%}$. The onset and peak temperatures of the polymerization reactions depend on the amount of $Mo(OEt)_5$ in the mixture and decrease with increasing amounts of the metal compound (Fig. 1a and entries 1–3 in Table 1). Two separated peaks were observed for TGAP–$Pd^{1.0\%}$ (Fig. 1b and entry 4 in Table 1); the less intense peak at 182 °C is likely due to decomposition of $Pd(PPh_3)_4$ and/or reaction with the resin before initiation of polymerization. The reaction of TGAP–$Rh^{1.0\%}$ (Fig. 1b and entry 5 in Table 1) shows three overlapping processes. It is strongly exothermic with a high onset temperature of 177 °C. A comparison of the bimetallic system TGAP–$Mo^{1.4\%}$/$Pd^{0.5\%}$ (Fig. 1b and entry 6 in Table 1) with TGAP–$Mo^{1.0\%}$, TGAP–$Mo^{2.0\%}$, and TGAP–$Pd^{1.0\%}$ shows that the polymerization was initiated by $Mo(OEt)_5$ and an onset temperature similar to that seen for TGAP–$Mo^{1.0\%}$ was detected.

Catalyst surfaces were investigated by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX). The surfaces of TGAP–$Pd^{1.0\%}$ and TGAP–$Rh^{1.0\%}$ appear to be homogeneous (Figs. 2a and 2b), with the latter showing a uniform metal distribution in the resin matrix with the expected rhodium content of around 1.0 wt%. In the case of the palladium catalyst, a few palladium conglomerates with metal content up to 61 wt% were detected along with homogeneously dispersed palladium, reflecting the significantly lower resin solubility of the palladium complex compared with the rhodium complex. Bright areas and spots



(a)

(b)

Fig. 1. DSC curves of TGAP containing (a) different amounts of $Mo(OEt)_5$ (2.0, 1.0 and 0.77% of molybdenum) and (b) TGAP containing a mixture of $Mo(OEt)_5$ and $Pd(PPh_3)_4$, $Rh(C_8H_{12})[(i Pr)_2PC_6H_4CH(OMe)_2]Cl$ and $Pd(PPh_3)_4$.

Table 1
DSC-data of metal-doped resins

Entry	Metal-doped resin	T_{Onset}[a] (°C)	T_{Peak}[b] (°C)	ΔH[c] ($J\,g^{-1}$)
1	TGAP–$Mo^{0.77\%}$	237	257	756
2	TGAP–$Mo^{1.0\%}$	136	242	567
3	TGAP–$Mo^{2.0\%}$	122	179, 262	638
4	TGAP–$Pd^{1.0\%}$	159, 289	182, 311	116, 881
5	TGAP–$Rh^{1.0\%}$	177	196, 258, 297	1074
6	TGAP–$Mo^{1.4\%}$/$Pd^{0.5\%}$	134	199	656

[a] Onset temperature of reaction peak.
[b] Peak temperature.
[c] Polymerization enthalpy.

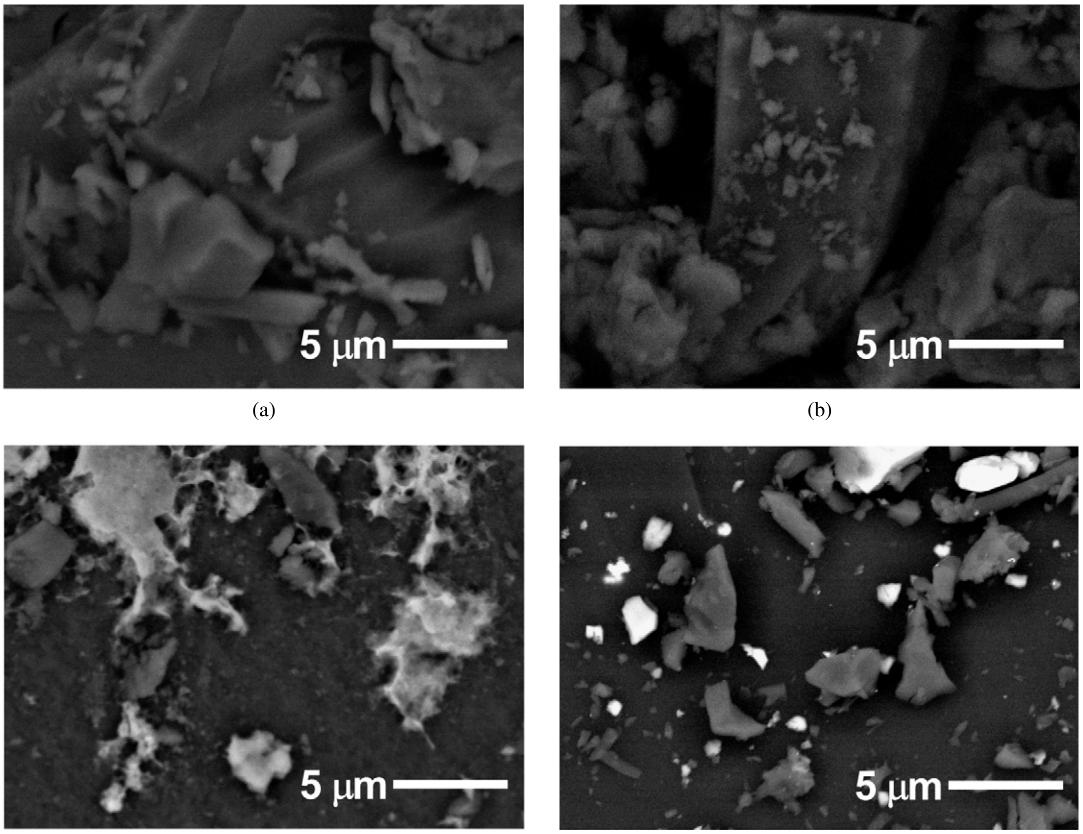
were visible in the case of the molybdenum-containing catalysts $TGAP^{46.7\%}/SiO_2{}^{50.0\%}–Mo^{1.0\%}$ and TGAP–$Mo^{1.4\%}/Pd^{0.5\%}$ (Figs. 2c and 2d), respectively. Molybdenum contents up to 42% were determined in these areas by EDX, as described previously for similar catalyst systems and these agglomerates are due to the formation of molybdenum oxo clusters [4, 23]. Variable palladium contents between 0 and 1.0 wt% were detected in the resin matrix of the bimetallic catalyst TGAP–$Mo^{1.4\%}/Pd^{0.5\%}$ with the expected average palladium content of around 0.5 wt%.

The catalysts are highly cross-linked, nonporous thermosets that swell slightly in the presence of organic solvents, resulting in a weight increase of a few percent. Surface area analysis by nitrogen adsorption–desorption at 77 K revealed low surface areas (around 1 $m^2\,g^{-1}$) for catalysts based on neat TGAP. But the surface areas could be increased significantly by the addition of silicagel; a surface area of 87 $m^2\,g^{-1}$ was found for the organic–inorganic hybrid system $TGAP^{46.7\%}/SiO_2{}^{50.0\%}–Mo^{1.0\%}$. Thermogravimetric analyses (TGA) of the catalyst systems demonstrated high thermal stability and decomposition starting at around 300 °C regardless of whether the measurement was carried out under air or nitrogen flow. An initial weight loss of around 2% was observed up to 150 °C, likely due to the release of adsorbed water. The silica-modified catalysts $TGAP^{62.0\%}/SiO_2{}^{36.4\%}–Mo^{0.5\%}$ and $TGAP^{46.7\%}/SiO_2{}^{50.0\%}–Mo^{1.0\%}$ exhibited significantly higher initial weight loss of around 4% and 5%, respectively.

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

The hybrid catalysts $TGAP^{62.0\%}/SiO_2{}^{36.4\%}–Mo^{0.5\%}$, $TGAP^{48.3\%}/SiO_2{}^{50.0\%}–Mo^{0.5\%}$, and $TGAP^{46.7\%}/SiO_2{}^{50.0\%}–Mo^{1.0\%}$ were tested in the epoxidation of propylene with *tert*-butyl hydroperoxide (TBHP) as an oxidant (Fig. 3). The catalysts were used in 10 consecutive reactions with no reconditioning. Catalyst recycling was carried out by filtration, and metal leaching was determined using highly sensitive atomic emission and atomic absorption spectroscopic techniques after removal of volatile compounds and metal enrichment in the reaction residues. Using $TGAP^{62.0\%}/SiO_2{}^{36.4\%}–Mo^{0.5\%}$, propylene oxide yield increased from 35% in the first run to 62% in the second run; however, yields decreased in the subsequent reactions to values of around 25% from run 8 on. Metal leaching was very low, and the average value per run was 0.02% of molybdenum initially loaded on the polymer corresponding to 0.1 ppm in the reaction mixture. Using $TGAP^{48.3\%}/SiO_2{}^{50.0\%}–Mo^{0.5\%}$, a catalyst with the same molybdenum loading of 0.5% but a higher silicagel content, a comparatively constant performance was observed throughout the 10 reactions. Metal leaching was around 0.06% run^{-1} (0.5 ppm), and epoxide yields of around 28% were obtained. Using the catalyst with a double molybdenum loading of 1.0%, a steady-state performance with epoxide yields of around 50% was observed from run 3 on after catalyst activation in the first two reactions. Metal leaching was slightly higher with an average metal loss of 0.11% run^{-1} (1.7 ppm). No byproducts were observed in any of the reactions, and nonproductive TBHP decomposition, monitored by iodometric titration, was negligible (<1.5% run^{-1}). Blank experiments with metal-free $TGAP/SiO_2$ materials under the same reaction conditions gave no propylene conversions, and thus a contribution of the catalyst matrix to the catalytic activity can be excluded.

So far, only a few catalysts based on organic polymers, such as molybdenum compounds supported on benzimidazole, polystyrene, or poly(glycidyl methacrylate) [37] and micelle-



(a) (b) (c) (d)

Fig. 2. SEM images of (a) TGAP–Pd$^{1.0\%}$, (b) TGAP–Rh$^{1.0\%}$, (c) TGAP$^{46.7\%}$/SiO$_2$$^{50.0\%}$–Mo$^{1.0\%}$, and (d) TGAP–Mo$^{1.4\%}$/Pd$^{0.5\%}$.

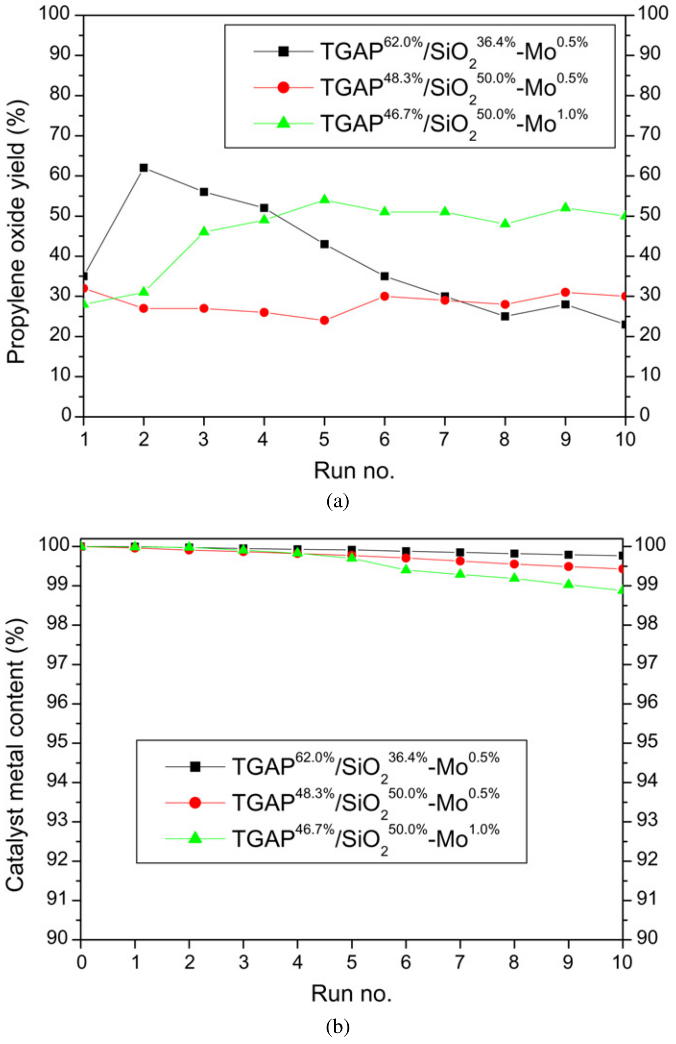
incorporated manganese porphyrin catalysts [38], have been tested in the epoxidation of propylene. The former afforded remarkably high propylene oxide yields up to 99.8%, but were tested for a few hours only.

Using the palladium-doped system TGAP–Pd$^{1.0\%}$ as a catalyst for the Suzuki coupling of iodobenzene with phenylboronic acid (Table 2), biphenyl yields of $\geqslant$98% with very low palladium leaching ($<$0.4 ppm in the reaction mixture) were obtained. Metal loss decreased significantly, from 0.21% in the first to 0.08% in the fifth run, while catalytic activity remained unchanged. Control experiments under the same reaction conditions with substituted iodobenzenes, such as 2- and 4-iodoanisole, 4-iodotoluene, and 4-iodoacetophenone, confirmed cross-coupling, and no homocoupling was observed. Quantitative conversions were obtained using these substrates. Significantly lower yields of 32 and 22% were observed using bromobenzene and chlorobenzene as substrates.

Much research has been devoted to elucidating the nature of the active species in palladium-catalyzed coupling reactions [39–41]; recent developments have been highlighted previously [42]. In this context, several control experiments have been discussed to distinguish between homogeneous catalysis due to leached metal species and heterogeneous catalysis. With respect to TGAP–Pd$^{1.0\%}$, hot filtration tests, mercury and poly(vinyl pyridine) poisoning tests, and redeposition tests have strongly suggested that catalysis is to a large extent due to leached metal species exhibiting a distinctive tendency to redeposit on catalyst particles on termination of the reaction and cooling of the reaction mixture to ambient temperature [43].

Considering polymer-supported catalysts for Suzuki coupling, significant progress has been made recently through microencapsulation of catalytically active metal species. Microencapsulated palladium catalysts, so-called "polymer-incarcerated palladium" catalysts, were prepared using glycidyl-functionalized copolymers as a matrix [44]. The catalysts demonstrated high activity in the coupling of bromobenzenes with boronic acids and could be recycled [45]. However, they had to be synthesized in a multistep procedure, including polymer preparation by radical copolymerization, and, in most cases, a high catalyst loading of 5 mol% was employed in the coupling reactions. In another approach, a polyurea–encapsulated palladium catalyst, designated PdEnCat™, has been successfully tested as a catalyst for Suzuki cross-coupling reactions [11], and high yields were achieved in reactions of bromobenzenes with boronic acids under batch and continuous flow conditions [46].

Quantitative conversions of ethyl crotonate from run 4 on were observed using TGAP–Pd$^{1.0\%}$ as the hydrogenation catalyst (Table 3). Almost the same results were obtained with ethyl cinnamate and crotonaldehyde as substrates; the latter was selectively reduced at the C–C-double bond. Significantly lower yields of around 83% were obtained using this catalyst in the hydrogenation of cinnamaldehyde, and selectivities to 3-phenyl propionaldehyde were 100%. Palladium leaching was very low ($<$0.007% run^{-1}, corresponding to values $<$0.02 ppm in the re-



(a)

(b)

Fig. 3. Catalytic performance of different molybdenum hybrid catalysts in the epoxidation of propylene. (a) Propylene oxide yields and (b) metal leaching. Reaction conditions for TGAP$^{62.0\%}$/SiO$_2$$^{36.4\%}$–Mo$^{0.5\%}$: propylene (8 bar), TBHP (50 mmol, 31 wt% in toluene/dodecane), and catalyst (1 g; particle sizes: 20–150 µm); reaction conditions for TGAP$^{48.3\%}$/SiO$_2$$^{50.0\%}$–Mo$^{0.5\%}$ and TGAP$^{46.7\%}$/SiO$_2$$^{50.0\%}$–Mo$^{1.0\%}$: propylene (8 bar), TBHP (50 mmol, 34 wt% in toluene/dodecane), and catalyst (2 g; particle sizes: 150–300 µm), 90 °C, 24 h. Yields are based on TBHP consumption (determined by iodometric titration and GC analysis).

action mixtures) even after reaction times of 24 h, and metal traces could not be quantified even after metal enrichment and application of highly sensitive AES and AAS techniques.

With respect to polymer-supported hydrogenation catalysts, the aforementioned polymer-incarcerated palladium catalysts exhibited high activity in the hydrogenation of various olefins and could be recycled [47,48]. Recently, this concept was significantly improved by the use of polysilane-supported palladium [49]. Almost quantitative conversions within a few hours were observed in the hydrogenation of numerous substrates at room temperature. The polyurea-encapsulated palladium catalyst PdEnCat™ (see above) also has been tested successfully as hydrogenation catalyst [50]. Metal leaching was extremely low, and the catalyst could be recovered and recycled 20 times in the hydrogenation of cyclohexene with no significant loss of activity. A comparatively high catalyst loading of 5 mol% was used, however.

Table 2
Catalytic performance of TGAP–Pd$^{1.0\%}$ in the Suzuki coupling of iodobenzene with phenylboronic acid[a]

Run no.	Biphenyl yield[b] (%)	Pd leached (%)
1	98	0.21
2	99	0.14
3	99	0.17
4	98	0.09
5	98	0.08

[a] Iodobenzene (5 mmol), phenylboronic acid (6 mmol), dioxane (10 ml), water (10 ml), K$_2$CO$_3$ (20 mmol), and catalyst (0.5 g; particle sizes: 150–300 µm), 90 °C, 24 h.

[b] Determined by GC analysis.

The rhodium-doped resin TGAP–Rh$^{1.0\%}$ was tested as catalyst in the hydroformylation of 1-octene (Table 4), with the reaction carried out in the neat alkene with a reaction time of 8 h. Metal leaching was high in the first run (4.18%) and decreased drastically to around 0.09% (0.6 ppm) in the subsequent reactions. The aldehyde yield was 59% in the first reaction, and the product mixture comprised nonanal (43%), 2-methyloctanal (36%), 2-ethylheptanal (12%), and 2-propylhexanal (9%). Isomerization products of 1-octene, namely 2- and 3-octene, also were observed. Selectivities were significantly higher in runs 2 to 5, and aldehyde mixtures of nonanal, 2-methyloctanal, and 2-ethylheptanal in a molar ratio of 72:27:1 were obtained. Aldehyde yields in these reactions were around 16%.

Recent developments in the field of polymer-supported hydroformylation catalysts include rhodium complexes attached to phosphine-functionalized acetals of polyvinyl alcohol [34,51] or phosphine-functionalized polystyrene [52]. Almost quantitative conversions of 1-octene or 4-vinylanisole were reported using a significantly higher catalyst loading compared with the TGAP–Rh$^{1.0\%}$-catalyzed hydroformylation of 1-octene. Rhodium catalysts bound to polystyrene [53] or a fluoroacrylate copolymer [54] through phosphine ligands and their use in supercritical carbon dioxide also have been described. High activities with up to quantitative conversions of 1-hexene or styrene were observed. Additional promising approaches include dendrimeric phosphine ligands and their rhodium complexes [55–57], asymmetric hydroformylation using highly cross-linked polystyrene-supported BINAPHOS-Rh(I) complexes [58], and rhodium catalysts supported on amphiphilic polymers for hydroformylations in water [59,60]. Outstanding results were obtained using the dendrimer-supported catalysts in the hydroformylation of aryl olefins and vinylesters, with almost quantitative conversions reached at room temperature [56]. Some of these catalysts could be used in up to 10 consecutive reactions, but data on metal leaching are limited. Compared with TGAP–Rh$^{1.0\%}$, preparation of these catalysts is much more elaborate, starting with polymer modification by coordinating moieties or even *ab initio* synthesis of appropriate polymers or linkers between polymer and catalyst species.

The bimetallic system TGAP–Mo$^{1.4\%}$/Pd$^{0.5\%}$ was tested as an epoxidation, C–C-coupling, and hydrogenation catalyst (Table 5). Epoxide yields between 48 and 73% were observed

Table 3
Catalytic performance of TGAP–Pd$^{1.0\%}$ in hydrogenation reactions[a]

Run no.	Ethyl crotonate		Ethyl cinnamate		Crotonaldehyde		Cinnamaldehyde	
	Yield[b] (%)	Pd leached (%)	Yield[b] (%)	Pd leached (%)	Yield[b] (%)	Pd leached (%)	Yield[b] (%)	Pd leached (%)
1	96	<0.004	95	<0.004	>99	<0.006	88	<0.006
2	98	<0.004	99	<0.004	>99	<0.006	81	<0.006
3	98	<0.004	97	<0.004	>99	<0.006	85	<0.006
4	>99	<0.003	>99	<0.004	>99	<0.006	79	<0.006
5	>99	<0.004	>99	<0.004	>99	<0.006	81	<0.007

[a] Hydrogenation of ethyl crotonate and ethyl cinnamate: alkene (10 mmol), H_2 (2.5 bar), MeOH (20 ml), and catalyst (0.5 g; particle sizes: 150–300 µm), 60 °C, 4 h; hydrogenation of crotonaldehyde and cinnamaldehyde: alkene (10 mmol), H_2 (2.5 bar), toluene (20 ml), and catalyst (0.5 g; particle sizes: 150–300 µm), 60 °C, 24 h.

[b] Determined by GC analysis.

Table 4
Catalytic performance of TGAP–Rh$^{1.0\%}$ in the hydroformylation of 1-octene[a]

Run no.	Aldehyde yield[b] (%)	Selectivity[b] (%)				Rh leached (%)
		Nonanal	2-Methyl-octanal	2-Ethyl-heptanal	2-Propyl-hexanal	
1	59	43	36	12	9	4.18
2	16	72	27	1	0	0.11
3	19	73	26	1	0	0.11
4	12	73	26	1	0	0.04
5	18	71	28	1	0	0.09

[a] 1-Octene (624 mmol), H_2/CO (50 bar), and catalyst (5.0 g; particle sizes: 20–150 µm), 110 °C, 8 h.

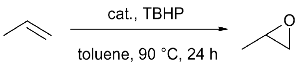
[b] Determined by GC analysis.

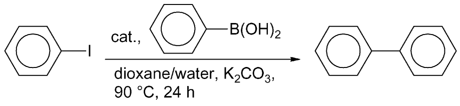
in the epoxidation of propylene, with an epoxide selectivity of 100%. Molybdenum leaching was very low and decreased from 0.14% (1.6 ppm) in the initial reaction to 0.02% (0.2 ppm) in the fourth and fifth runs. The material also demonstrated catalytic activity in the Suzuki coupling of iodobenzene with phenyl boronic acid. The catalyst exhibited an initial activation period, and the yield of coupling product increased from 89% in the first run to around 97% in the subsequent reactions. Palladium leaching decreased significantly from 0.70% (0.7 ppm) in the initial reaction to around 0.17% (0.2 ppm) from the third run on. Ethyl cinnamate yields up to 82% were isolated using this polymer as a catalyst for the Heck coupling of iodobenzene with ethyl acrylate. The reactions were carried out at 120 °C with NMP as the solvent; significant metal leaching of around 2.2% run^{-1} (0.7 ppm) was observed after a metal loss of 10% (3.0 ppm) in the first run. This finding suggests that the resin matrix was affected by the solvent and/or the base at a comparatively high temperature of 120 °C. In addition, the material was tested as a hydrogenation catalyst using ethyl crotonate as the test substrate. The alkene was quantitatively converted to ethyl butyrate from run 4 on; palladium leaching was very low (<0.008%, corresponding to values <0.01 ppm in the reaction mixtures). Similar catalytic behavior was observed using ethyl cinnamate as the substrate.

4. Conclusion

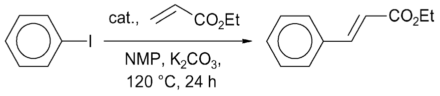
We have described a convenient solvent-free, time- and cost-saving, one-step procedure for the preparation of a wide variety of catalysts based on thermosetting epoxy resins. Using metal compounds as polymerization initiators, catalytically active metal species can be incorporated in the thermoset matrices with no additional modification of the organic polymer. Thus, catalysts for epoxidation, carbon–carbon coupling, hydrogenation, or hydroformylation reactions can be prepared. Various resin monomers and metal compounds can be combined, affording promising potential for optimization. Multifunctional catalysts for different catalytic reactions can be obtained by combining several catalytically active components in one thermoset matrix. The catalysts demonstrated superior long-term activity and stability compared with other systems based on organic polymers and could be recovered and reused with no reconditioning. Based on previously reported long-term tests, catalyst lifetimes of months up to years can be expected. Metal leaching is extremely low and can be controlled by choice of the resin composition. The liquid resin systems can be easily modified by, for example, adding inorganic components, thus yielding organic–inorganic hybrid catalysts after polymerization with tunable surface properties. This also makes catalyst preparation possible on a kg scale. Reactor surfaces and porous reactor filling materials could be coated with metal-doped resin layers and integrated in catalytic processes after polymerization. The applicability of the catalysts may be limited depending on the required thermal, mechanical, and chemical resistance of the materials. Another constraint is that the catalyst performance is only somewhat predictable and tunable, because the complexes decompose at least partially under the somewhat harsh polymerization and catalyst preparation conditions. Further work, particularly in the characterization and optimization of the catalyst systems, are needed.

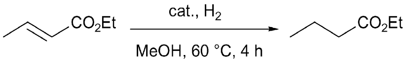
Table 5
Catalytic performance of TGAP–$Mo^{1.4\%}/Pd^{0.5\%}$ in epoxidation, C–C-coupling and hydrogenation reactions[a]





Run no.	Yield[b] (%)	Mo leached (%)	Yield[c] (%)	Pd leached (%)
1	73	0.14	89	0.70
2	62	0.10	97	0.31
3	69	0.06	97	0.18
4	55	0.02	97	0.15
5	48	0.02	96	0.19





Run no.	Yield[d] (%)	Pd leached (%)	Yield[c] (%)	Pd leached (%)
1	80	9.96	97	<0.007
2	78	2.52	96	<0.007
3	82	2.00	98	<0.007
4	64	2.20	>99	<0.008
5	70	2.20	>99	<0.008

[a] Epoxidation of propylene: propylene (8 bar), TBHP (50 mmol, 36 wt% in toluene/dodecane), and catalyst (1 g; particle sizes: 150–300 µm), 80 ml steel autoclave, 25 bar operating pressure; Suzuki coupling of iodobenzene: iodobenzene (5 mmol), phenylboronic acid (6 mmol), dioxane (10 ml), water (10 ml), K_2CO_3 (20 mmol), and catalyst (0.5 g; particle sizes: 20–150 µm); Heck coupling of iodobenzene: iodobenzene (50 mmol), ethyl acrylate (75 mmol), NMP (50 ml), K_2CO_3 (100 mmol), and catalyst (0.5 g; particle sizes: 150–300 µm); hydrogenation of ethyl crotonate: ethyl crotonate (10 mmol), H_2 (2.5 bar), MeOH (20 ml), and catalyst (0.5 g; particle sizes: 150–300 µm).

[b] Yields are based on TBHP consumption (determined by iodometric titration and GC analysis).

[c] Determined by GC analysis.

[d] Isolated yields.

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References

[1] B.M.L. Dioos, I.F.J. Vankelecom, P.A. Jacobs, Adv. Synth. Catal. 348 (2006) 1413.
[2] P. Mastrorilli, C.F. Nobile, Coord. Chem. Rev. 248 (2004) 377.
[3] M. Nielsen, A.H. Thomsen, T.R. Jensen, H.J. Jakobsen, J. Skibsted, K.V. Gothelf, Eur. J. Org. Chem. (2005) 342.
[4] U. Arnold, W. Habicht, M. Döring, Adv. Synth. Catal. 348 (2006) 142.
[5] Q.H. Xia, H.Q. Ge, C.P. Ye, Z.M. Liu, K.X. Su, Chem. Rev. 105 (2005) 1603.
[6] S. Bräse, F. Lauterwasser, R.E. Ziegert, Adv. Synth. Catal. 345 (2003) 869.
[7] Q.H. Fan, Y.M. Li, A.S.C. Chan, Chem. Rev. 102 (2002) 3385.
[8] D.E. Bergbreiter, Top. Curr. Chem. 242 (2004) 113.
[9] D.A. Pears, S.C. Smith, Aldrichim. Acta 38 (2005) 23.
[10] S. Kobayashi, R. Akiyama, Chem. Commun. (2003) 449.
[11] C. Ramarao, S.V. Ley, S.C. Smith, I.M. Shirley, N. DeAlmeida, Chem. Commun. (2002) 1132.
[12] M.H. Valkenberg, W.F. Hölderich, Catal. Rev. Sci. Eng. 44 (2002) 321.
[13] R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U. Schuchardt, Acc. Chem. Res. 31 (1998) 485.
[14] B. Ellis (Ed.), Chemistry and Technology of Epoxy Resins, Blackie Academic & Professional, London, 1993.
[15] C.A. May (Ed.), Epoxy Resins, Chemistry and Technology, Marcel Dekker, New York, 1988.
[16] J.W. Muskopf, S.B. McCollister, in: W. Gerhartz, Y.S. Yamamoto, L. Kaudy, J.F. Rounsaville, G. Schulz (Eds.), Ullmann’s Encyclopedia of Industrial Chemistry, vol. A9, VCH, Weinheim, 1987, p. 547.
[17] H. Lee, K. Neville (Eds.), Handbook of Epoxy Resins, McGraw–Hill, New York, 1967.
[18] I. Hamerton, B.J. Howlin, P. Jepson, Coord. Chem. Rev. 224 (2002) 67.
[19] Z. Zhang, C.P. Wong, J. Appl. Polym. Sci. 86 (2002) 1572.
[20] A. Palinsky, M. Döring, H. Dey, J. Wuckelt, EP 0995766 (2000), to Bakelite AG.
[21] J. Brown, I. Hamerton, B.J. Howlin, J. Appl. Polym. Sci. 75 (2000) 201.
[22] M. Döring, W. Ludwig, E. Uhlig, S. Wocadlo, U. Müller, Z. Anorg. Allg. Chem. 611 (1992) 61.
[23] U. Arnold, F. Fan, W. Habicht, M. Döring, J. Catal. 245 (2007) 55.
[24] A.D. Pomogailo, Kinet. Catal. 45 (2004) 67.
[25] R. Haag, S. Roller, Top. Curr. Chem. 242 (2004) 1.
[26] N.E. Leadbeater, M. Marco, Chem. Rev. 102 (2002) 3217.
[27] B. Clapham, T.S. Reger, K.D. Janda, Tetrahedron 57 (2001) 4637.
[28] D.C. Sherrington, J. Polym. Sci. Part A Polym. Chem. 39 (2001) 2364.
[29] Y.R. de Miguel, E. Brulé, R.G. Margue, J. Chem. Soc. Perkin Trans. 1 (2001) 3085.
[30] Y.R. de Miguel, J. Chem. Soc. Perkin Trans. 1 (2000) 4213.
[31] D.C. Sherrington, Catal. Today 57 (2000) 87.
[32] S.V. Ley, I.R. Baxendale, R.N. Bream, P.S. Jackson, A.G. Leach, D.A. Longbottom, M. Nesi, J.S. Scott, I. Storer, S.J. Taylor, J. Chem. Soc. Perkin Trans. 1 (2000) 3815.
[33] S.J. Shuttleworth, S.M. Allin, R.D. Wilson, D. Nasturica, Synthesis 8 (2000) 1035.
[34] M. Ahlmann, O. Walter, M. Frank, W. Habicht, J. Mol. Catal. A 249 (2006) 80.
[35] J.G. Hill, B.E. Rossiter, K.B. Sharpless, J. Org. Chem. 48 (1983) 3607.
[36] K.B. Sharpless, T.R. Verhoeven, Aldrichim. Acta 12 (1979) 63.
[37] D.C. Sherrington, Catal. Today 57 (2000) 87.
[38] J.H.M. Heijnen, V.G. de Bruijn, L.J.P. van den Broeke, J.T.F. Keurentjes, Chem. Eng. Process. 42 (2003) 223.
[39] V. Farina, Adv. Synth. Catal. 346 (2004) 1553.
[40] R.B. Bedford, C.S.J. Cazin, D. Holder, Coord. Chem. Rev. 248 (2004) 2283.

[41] A.F. Littke, G.C. Fu, Angew. Chem. Int. Ed. 41 (2002) 4176.

[42] N.T.S. Phan, M. Van Der Sluys, C.W. Jones, Adv. Synth. Catal. 348 (2006) 609.

[43] F. Fan, Ph.D. thesis, University of Heidelberg, 2007.

[44] K. Okamoto, R. Akiyama, S. Kobayashi, Org. Lett. 6 (2004) 1987.

[45] H. Hagio, M. Sugiura, S. Kobayashi, Org. Lett. 8 (2006) 375.

[46] C.K.Y. Lee, A.B. Holmes, S.V. Ley, I.F. McConvey, B. Al-Duri, G.A. Leeke, R.C.D. Santos, J.P.K. Seville, Chem. Commun. (2005) 2175.

[47] R. Akiyama, S. Kobayashi, J. Am. Chem. Soc. 125 (2003) 3412.

[48] K. Okamoto, R. Akiyama, S. Kobayashi, J. Org. Chem. 69 (2004) 2871.

[49] H. Oyamada, R. Akiyama, H. Hagio, T. Naito, S. Kobayashi, Chem. Commun. (2006) 4297.

[50] N. Bremeyer, S.V. Ley, C. Ramarao, I.M. Shirley, S.C. Smith, Synlett (2002) 1843.

[51] M. Ahlmann, O. Walter, J. Organomet. Chem. 689 (2004) 3117.

[52] T.-J. Yoon, J.I. Kim, J.-K. Lee, Inorg. Chim. Acta 345 (2003) 228.

[53] S.-I. Fujita, S. Akihara, S. Fujisawa, M. Arai, J. Mol. Catal. A 268 (2007) 244.

[54] I. Kani, R. Flores, J.P. Fackler Jr., A. Akgerman, J. Supercrit. Fluids 31 (2004) 287.

[55] S. Ricken, P.W. Osinski, P. Eilbracht, R. Haag, J. Mol. Catal. A 257 (2006) 78.

[56] S.-M. Lu, H. Alper, J. Am. Chem. Soc. 125 (2003) 13126.

[57] G.E. Oosterom, S. Steffens, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Top. Catal. 19 (2002) 61.

[58] F. Shibahara, K. Nozaki, T. Matsuo, T. Hiyama, Bioorg. Med. Chem. Lett. 12 (2002) 1825.

[59] M.T. Zarka, M. Bortenschlager, K. Wurst, O. Nuyken, R. Weberskirch, Organometallics 23 (2004) 4817.

[60] Y. Uozumi, M. Nakazono, Adv. Synth. Catal. 344 (2002) 274.