Katalytische Eigenschaften von Übergangsmetallspezies enthaltenden Epoxidharzen

INAUGURAL-DISSERTATION

zur Erlangung der Doktorwürde

der Naturwissenschaftlich-Mathematischen Gesamtfakultät

der Ruprecht-Karls-Universität

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vorgelegt von

M. Sc. Fengwen Fan

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Catalytic properties of epoxy resins containing transition metal species

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Ich erkläre hiermit an Eides statt, dass ich die vorliegende Arbeit selbständig und ohne unerlaubte Hilfsmittel durchgeführt habe.

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Zusammenfassung

Um eine einfache und verlässliche Vorgehensweise für die Immobilisierung von katalytisch aktiven Metallverbindungen zu entwickeln, wurden übergangsmetall-dotierte Epoxidharze via Polyaddition oder Homopolymerisation quervernetzt, wobei verschiedene Metallkomplexe des *d*-Blocks als Polymerisationsinitiatoren oder Reaktionsbeschleuniger verwendet wurden. Die Katalyse-eigenschaften der so erhaltenen Polymere wurden anhand einiger wichtiger Reaktionen, wie z.B. der Epoxidierung von Alkenen, C-C-Kopplungsreaktionen und Hydrierung von ungesättigten Verbindungen charakterisiert. Bei der Epoxidierung von flüssigen Alkenen und Propen, unter Einsatz von *tert*-Butylhydroperoxid oder Cumolhydroperoxid als Oxidationsmittel, wurden Epoxidharzmaterialien basierend auf TGMDA, TGAP, Novolak, ERL4221 oder Harzmischungen, wie z.B. TGAP/PT30 untersucht, die unter Zugabe von Titan-, Molybdän-, Vanadium- oder Wolframkomplexen wie z.B. $Ti(EH)_4$, $Mo(OEt)_5$, $Mo(EH)_n$, $H_3Mo_{12}O_{40}P{\bullet}xH_2O$, $MoO_2(TMHD)_2$, $VO(OPr)_3$, $V(NAPH)_n$ oder $W(OEt)_5$ gehärtet wurden. Diese Arbeiten umfassen gewonnene Erkenntnisse zu den beiden verschiedenen Härtungsmethoden von Epoxidharzen, die Abhängigkeit zwischen der katalytischen Aktivität und dem Auslaugen der aktiven Metallspezies, sowie zur Natur der aktiven Spezies. Unter Berücksichtigung der möglichen technischen Anwendbarkeit der vorgestellten Katalysatorsysteme wurden Langzeitstudien, ihre Aktivität und Stabilität betreffend, durchgeführt. Auf dem Gebiet der C-C-Verknüpfungsreaktionen, wie z.B. der Suzuki- oder Heck-Kopplung, kam TGAP zum Einsatz, welches unter Verwendung von $Pd(PPh_3)_4$ als Initiator gehärtet wurde. Um diese Reaktionen zu optimieren, wurde sowohl der Einfluss des Lösungsmittels, wie auch der eingesetzten Base untersucht. Die weiterführenden Überlegungen führten zu einem umfassenden Vergleich zwischen Oberflächenkatalyse und homogener Katalyse gelöster und adsorbierter aktiver Spezies mittels Heißfiltration, Löslichkeitstests und Katalysatorvergiftungsversuchen. Konkurrenzreaktionen bei Suzuki-Kopplungen zwischen verschieden substituierten Substraten mit Phenylboronsäure wurden ebenfalls untersucht. Auf dem Gebiet der Hydrierungsreaktionen wurde mittels $Pd(PPh_3)_4$ bzw. $Nb(OEt)_5$ gehärtetes TGAP als Katalysator eingesetzt. Unter Verwendung des besten Katalysators konnten ungesättigte Ester und Aldehyde unter milden Bedingungen quantitativ in die hydrierten Produkte überführt werden. Die Metallverluste der Katalysatoren waren dabei sehr niedrig und eine Anwendung über längere Zeiträume ist möglich. Verschiedene magnetisch aktive Katalysatoren wurden ebenfalls synthetisiert und in Hydrierungs-, Epoxidierungs- und C-C-Kopplungsreaktionen getestet.

Abstract

In order to develop a simple and reliable protocol for the immobilization of catalytically active metal species, epoxy resins containing *d*-block metal species were prepared via polyaddition or homopolymerization of the resins using metal complexes as initiators and evaluated in the epoxidation of alkenes, C-C coupling reactions and hydrogenation of unsaturated substrates.

The resins TGMDA, TGAP, Novolac, ERL4221, or TGAP/PT30 were cured in the presence of $Mo(OEt)_5$, $Mo(EH)_n$, $H_3Mo_{12}O_{40}P\bullet xH_2O$, $MoO_2(TMHD)_2$, $W(OEt)_5$, $Ti(EH)_4$, $VO(OPr)_3$ or $V(NAPH)_n$ and the catalytic activities of the resulting materials were evaluated in the epoxidation of liquid alkenes and propene with organic hydroperoxides as oxidants. This part represents investigations on different curing methods, the relation between catalytic activity and metal species leaching, and the nature of true active species. Insights into long-term activities and stabilities of the catalysts were also taken into account. In the Suzuki and Heck coupling reactions, TGAP cured by using $Pd(PPh_3)_4$ as polymerization initiator was investigated. In order to optimize the reaction conditions, the influences of different solvents, bases and other factors were considered. Hot filtration, dissolving/redeposition and poisoning tests were also carried out to distinguish the true active species in these C-C coupling reactions. In addition, competition reactions were performed in the Suzuki coupling of different substituted substrates with phenylboronic acid to compare the influence of substituents. In the hydrogenation reactions, TGAP containing palladium or niobium species prepared by using $Pd(PPh_3)_4$ or $Nb(OEt)_5$ as initiators was investigated. Unsaturated esters and aldehydes can be quantitatively converted to the corresponding hydrogenation products under mild reaction conditions. Metal species leaching is extremely low and a long-term application is possible. Different magnetic catalysts were also prepared via homopolymerization by inclusion of magnetic particles and evaluated in the epoxidation of cyclohexene, Suzuki coupling and hydrogenation reactions. The approach for the immobilization of *d*-block metal compounds via homopolymerization of epoxy resins seems to allow the use of further metal compounds and extension of the concept to other catalytic reactions.

Publications:

‘‘Molybdenum-doped epoxy resins as catalysts for the epoxidation of alkenes’’,
U. Arnold, F. Fan, W. Habicht, M. Döring, *J. Catal.* **2007**, *245*, 55.

‘‘Metal-doped epoxy resins – easily accessible, durable and highly versatile catalysts’’,
U. Arnold, J. Artner, H. Bautz, F. Fan, O. Walter, M. Döring, submitted.

Conference contributions:

U. Arnold, F. Fan, M. Döring, ‘‘Metalldotierte Epoxidharze – eine neue Klasse leicht zugänglicher, langlebiger und vielseitiger Katalysatoren’’, Proceedings of the XXXIX. Jahrestreffen Deutscher Katalytiker, Weimar, Germany, 2006.

U. Arnold, J. Artner, F. Fan, M. Döring, ‘‘Anorganisch-organische Hybridkatalysatoren auf Basis metalldotierter Epoxidharze’’, Proceedings of the XXXX. Jahrestreffen Deutscher Katalytiker, Weimar, Germany, 2007.

Abbreviations

AAS	atomic adsorption spectroscopy
2-ABA	2-aminobenzylamine
AcAc	acetylacetonate (acac)
AMP	2-aminomethyl pyridine
CHP	cumyl hydroperoxide
bipy	2,2’-bipyridine
5BzCO2	5-benzimidazole carboxylate
dba	dibenzylideneacetone
DEDC	diethyldithiocarbamate
DHNT	1,2-dihydronaphthalene
DGEBA	diglycidyl ether of bisphenol A
DMA	dimethylacetamide
DMF	dimethylformamide
dppf	1,1’-bis(diphenylphosphino)ferrocene
DSC	differential scanning calorimetry
DVB	1,4-divinylbenzene
EBHP	ethylbenzene hydroperoxide
EDX	energy – dispersive X-ray spectroscopy
EH	2-ethylhexanoate
en	ethylenediamine
ERL4221	3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate
GC-FID	gas chromatography – flame ionization detector
GC-MS	gas chromatography – mass selective detector
HHPA	hexahydrophthalic anhydride
HMPA	hexahydro-4-methylphthalic anhydride
HPP	(2-hydroxypropyl)-aminomethyl-2-pyridine
ICP-AES	inductively coupled plasma – atomic emission spectroscopy
MC	microencapsulated

MTBE	methyl-*tert*-butyl ether
NAPH	naphthenate
NMP	N-methyl-2-pyrrolidone
Novolac	epoxy phenol novolac (Bakelite® EPR600)
OPD	*o*-phenylendiamine
PBI-Mo	polybenzimidazole supported Mo(VI) compounds
PCy_3	tricyclohexylphosphine
PGMA	poly(glycidylmethacrylate)
PEG	polyethyleneglycol
Ps	polystyrene
PVPy	poly(vinylpyridine)
PT30	cyanate ester based on phenol novolac (Lonza: Primaset PT30)
PyIm	2-pyridyl-2-imidazole
SEM	scanning electron microscopy
SPPS	solid-phase peptide synthesis
TBA	*tert*-butyl alcohol
TBAB	tetrabutylammonium bromide
TBHP	*tert*-butylhydroperoxide
TEA	triethylamine
TEOS	tetraethoxysilane
TGA	thermogravimetric analysis
TGAP	N,N’-diglycidyl-4-glycidyloxyaniline
TGMDA	4,4’-methylene-bis-(N,N-diglycidylaniline)
TMHD	2,2,6,6-tetramethyl-3,5-heptanedionate
TPMTGE	triphenylolmethane triglycidyl ether
TS-1	titanium silicalite 1
XRD	X-ray diffraction

Table of contents

1 Introduction and motivation

1.1 Epoxy resins and curing of epoxy resins

Epoxy resins are widely used as electrical and electronic insulation materials, protective coatings, and composite materials due to their excellent strength, toughness, chemical and thermal resistance, adhesive and electrical properties. Despite strong competition from other thermosets and thermoplastics, their consumption is still growing. Nowadays, global production capacity of epoxy resins is around 5 million tons per year. Most commercially important epoxy resins are prepared by coupling epichlorohydrin with compounds that possess at least two reactive hydrogen atoms[1]. The preparation process of the most important epoxy resin, the diglycidyl ether of bisphenol A (DGEBA), is depicted in Figure 1.

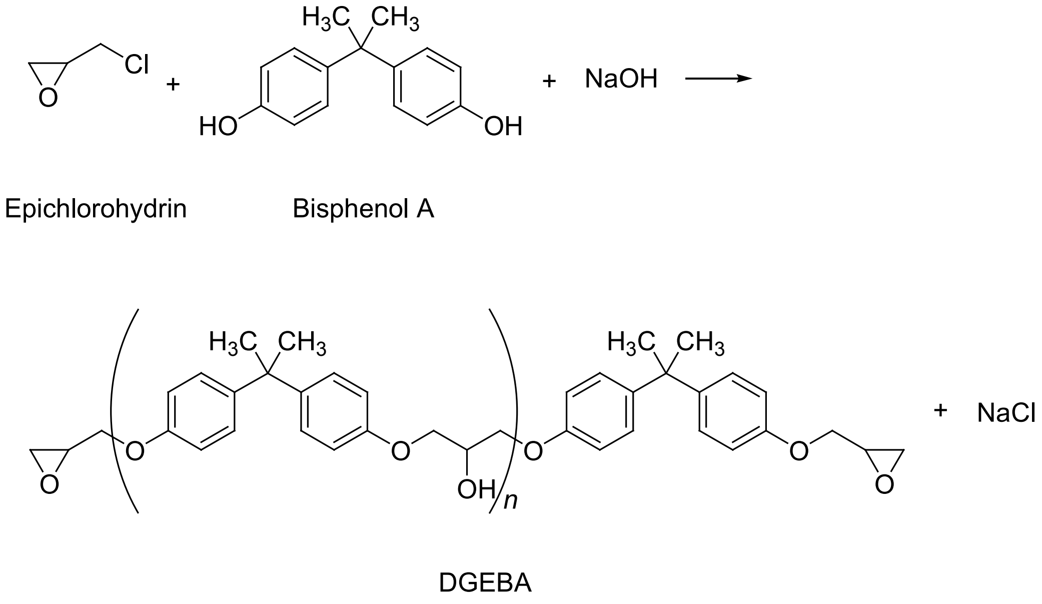
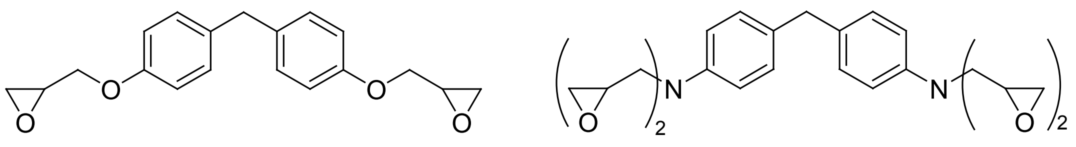
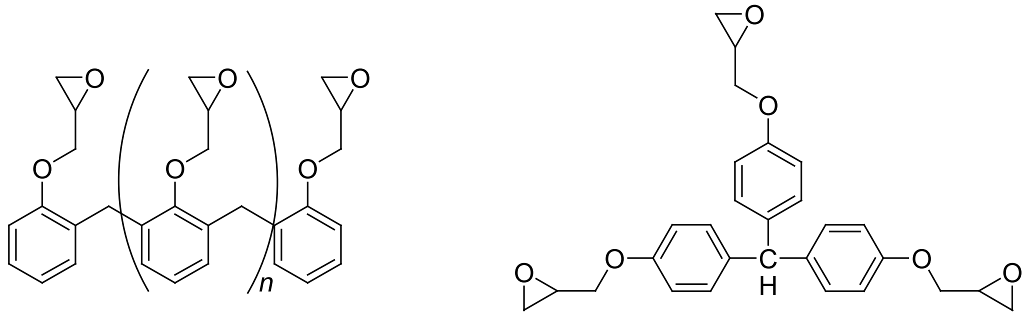


Figure 1: The preparation process of the diglycidyl ether of bisphenol A (DGEBA).

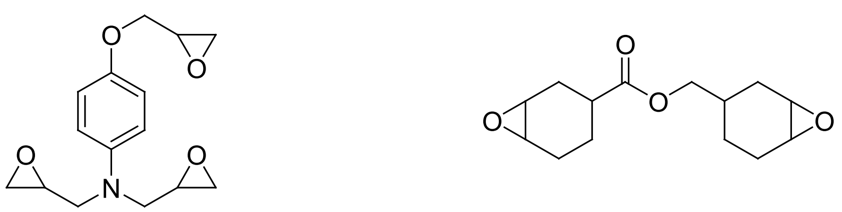
About 75% of the epoxy resins currently used worldwide are derived from the diglycidyl ether of bisphenol A (DGEBA). Some other glycidyl-based epoxy resins including diglycidyl ether of bisphenol F (DGEBF), tetraglycidyl methylenedianiline (TGMDA), epoxy phenol novolac, triphenylolmethane triglycidyl ether (TPMTGE) and triglycidyl *p*-aminophenol (TGAP) are also very important. Epoxy resins based on epoxidized aliphatic and cycloaliphatic dienes such as 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (ERL4221) are also commercially available. These resins were developed as alternatives to glycidyl-based resins because of their improved electrical properties and weatherability[2]. The structures of some epoxy resins are shown in Figure 2.



Diglycidyl ether of bisphenol F (DGEBF) Tetraglycidyl methylenedianiline (TGMDA)



Epoxy phenol novolac Triphenylolmethane triglycidyl ether (TPMTGE)



Triglycidyl-*p*-aminophenol (TGAP) 3,4-Epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (ERL4221)

Figure 2: The structures of commercially important epoxy resins.

Epoxy resins are cured mainly by polyaddition with multifunctional curing agents such as polyamines or acid anhydrides. An alternative curing method is cationic or anionic homopolymerization initiated by Lewis acids or bases. In order to improve physical, chemical, mechanical and electrical properties of the thermosets, many studies have been carried out. Mixing or hybridization with inorganic compounds, especially with silica[3-6], has been widely investigated, and most attempts focus on the utilization of sol-gel methods using tetraethoxysilane (TEOS) as silica source and hexahydrophthalic anhydride (HHPA) as a curing agent of epoxy resin and condensation agent of alkoxysilane[6]. Kurnoskin[7,8] has reported the curing of epoxy oligomers with metal chelates of the general formula $[M(R)_n(X)_p]$ where M is the cation of the transition metal; R, a nitrogen-containing ligand; X, the anion of an organic acid. Recently, the development of controllable curing agents based on metal chelates for epoxy resins has been addressed by Hamerton[9-11] et al.. In many cases, Ni(II)[10-14] and Cu(II)[10,11,15] were used as transition metals, and imidazole[9,16], *o*-phenylendiamine (OPD)[10,11,13], acetylacetonate (AcAc)[17,18], ethylenediamine (en)[12,14,19] and 2-aminobenzylamine (2-ABA)[10,11] were used as ligands. In addition, in order to enhance epoxy resin/metal heterojunction, further attempts such as the introduction of sulfur-containing polymers have been taken into account[20]. These investigations showed that curing of epoxy resins with metal complexes can improve some properties of resulting materials such as mechanical and electrical properties, as well as thermo-oxidative and chemical resistance.

According to the above-mentioned work, metal complexes can be used as initiators for the curing of epoxy resins via homopolymerization due to the potential of releasing free ligands, i.e. Lewis bases such as ethylenediamine or acetylacetonate etc. by heating, which promote polymerization reactions. The curing mechanism is depicted in Figure 3. A major drawback is the poor solubility of some metal complexes while mixing with epoxy resins [9]. Organic solvents can be used to increase the solubility of metal complexes in epoxy resins, but influence the final properties of the resulting materials[12-14]. Therefore, how to find suitable metal complexes with improved solubilities in epoxy resins is very important to improve the thermal stability, chemical resistance and electrical properties of resulting materials.

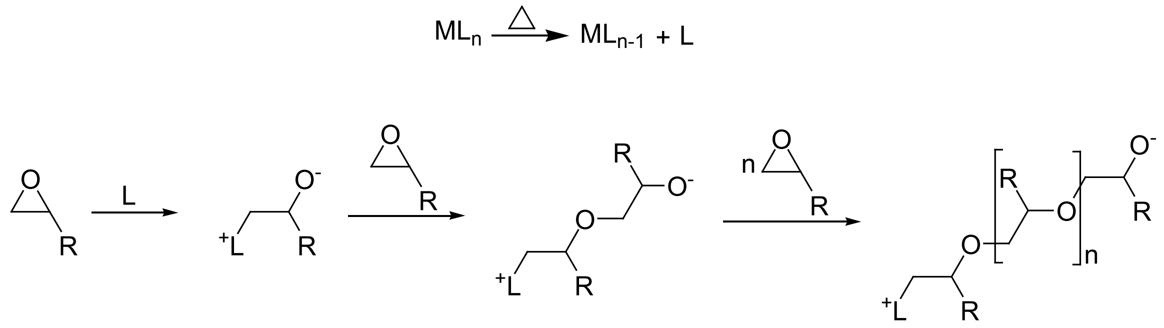


Figure 3: Curing of epoxy resins using metal complexes as thermally latent polymerization initiators.

1.2 Developments and applications of polymer-supported metal catalysts

Polymer supported metal catalysts had not attracted much interest until the introduction of solid-phase peptide synthesis (SPPS) by Merrifield in 1963[21]. Recent interest in the development of environmentally benign synthesis has evoked a renewed interest in developing polymer-supported metal catalysts for organic synthesis that maintain high activity and selectivity[22]. The immobilization of transition metal species on the polymeric supports offers a number of advantages over homogeneous catalysts. The main benefits are due to the ease of physical separation of the polymer and its bound component from the reaction mixture, the ease of recycling (especially with expensive catalysts and ligands), and the simplification of handling a range of toxic or odorous materials. Such immobilization also enables the use of high concentrations of reagents to drive reactions to completion, as byproducts or excess reagents can be easily removed by filtration, often eradicating the need for time-consuming, laborious purification steps such as chromatography, distillation, or crystallization. Another advantage is due to the unique microenvironment created for the reactants within the polymeric support, improved catalyst stability within the polymer matrix and increased selectivity for intramolecular reactions. In addition, the recognition that all industrial chemical processes need to meet appropriate environmental standards has focused attention on the use of heterogenized reactive species as a potentially important technology for achieving the greening of chemistry.

Numerous polymer supported metal catalysts have been developed. Polystyrene is one of the most popular polymeric materials used[23]. The methods used for catalyst immobilization have ranged from co-polymerization of functionalised monomers to the more commonly used approach of covalent or ionic anchoring of the ligand onto a preformed support[24]. Over the past years, much progress has been made in the development of heterogeneous catalysts with comparable activities and selectivities to their homogeneous counterparts. To this aim, novel polymeric supports have been explored, often incorporating the metal complexes in the rigid polymer backbones such as dendrimers[25]. New types of polymer-supported catalysts, microencapsulated catalysts, have also been developed based on a microencapsulation technique for binding catalysts to polymers utilizing physical envelopment by polymer backbones and interaction between π electrons of benzene rings of the polystyrene used as polymer backbones and vacant orbitals of the catalysts[26]. The authors claimed, in all cases, no leaching of the catalysts occurred, and the immobilized catalysts were recovered quantitatively by simple filtration and reused without loss of activity. It is noted that this method enables direct immobilization of metals onto polymers, and that normally unstable species such as $Pd(PPh_3)_4$ can be kept stable by this immobilization technique.

Polymer supported metal catalysts have been widely used in a number of classes of organic transformations including oxidation, reduction, addition, cycloaddition, and transition metal-catalyzed carbon-carbon bond-forming reactions[25,27,28]. There are however a number of disadvantages[22] including the fact that often there is metal species leaching during the course of a reaction. This is a particular problem when they are being used in applications such as synthesis of fine chemicals where contamination of the product with heavy metals is highly undesirable. Leaching still proves to be a weakness of supported metal catalysis, and the development of new ligands that hold the metal complex firmly during the course of a reaction proves an exciting avenue for future research. In practical applications, a high catalyst lifetime is also very important. 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. As a result, much recent work has been focused on developing and screening new polymer supports for attachment of metal species and on developing new preparative methods for increasing long-term activity and selectivity.

1.3 Motivation

Epoxy resins are excellent materials possessing high thermal and chemical resistance[1,2]. Transition metal complexes can be used as initiators for anionic epoxy resin homopolymerization and precursors of catalytically active species during the catalysis reactions. The immobilization of active metal species on epoxy matrices via homopolymerization or polyaddition using *d*-block metal complexes as initiators is feasible, facile and timesaving and presents a promising alternative for the preparation of catalysts preventing agglomeration and possessing high thermal and chemical resistance during the reactions while providing the inherent advantages of heterogeneous catalysts such as ease of product separation and catalyst recycling. For this reason, it is interesting to investigate the curing of epoxy resins using transition metal complexes as initiators. In this work, numerous transition metal complexes were investigated for the curing of epoxy resins and epoxy resins containing transition metal species were prepared via homopolymerization or polyaddition. In addition, in order to investigate the catalytic performance of resulting materials, obtained polymers were evaluated in some important reactions such as the epoxidation of alkenes, C-C coupling and hydrogenation reactions.

2 Results and discussions

2.1 Preparation of epoxy resins containing *d*-block metal species

2.1.1 DSC analyses of epoxy resins mixed with *d*-block metal complexes

A variety of experimental techniques has been developed to follow the curing reaction of thermosetting systems. Of the many used techniques, the differential scanning calorimetry (DSC) technique is commonly used for the determination of glass transition temperatures, reaction kinetics and material purity of the polymers. It is also a very convenient tool to study the curing reaction of epoxy resins by measuring the heat flow of the reaction systems. It was shown that the final properties of cured epoxy resins can be controlled by the change of composition of the curing agents[7,8]. Therefore, in this work, the influences of epoxy resin monomer, transition metal such as Mo, W or Nb, the solubility of transition metal complexes in epoxy resin, the concentration of transition metal complex in the resin mixture and the ligands on the curing of epoxy resins have been investigated.

2.1.1.1 Influence of epoxy resin monomer on the curing of epoxy resins

Table 1 shows DSC data of the curing of different epoxy resins using the same metal complex as initiator. These data include the epoxy resin type, the concentration of metal complex in the resin mixture, the solubility of metal complex in the epoxy resin, the onset temperature of curing reaction, the peak temperature of curing reaction and reaction enthalpy. Molybdenum 2-ethylhexanoate containing 15% Mo named as $Mo(EH)_n$ was used as initiator for the curing of different epoxy resins. This precursor possesses some advantages such as low price and high solubility etc.. Metal carboxylates have been used previously as initiators for the curing of epoxy resins by Ghaemy et al.[15]. They suggest that the curing mechanism is anionic homopolymerization due to the attack of carboxylate anions to open the epoxy ring and the concentration of anions in the resin mixtures determines the rate of curing reactions. From Table 1, it can be seen that the epoxy resin type has a significant influence on the curing reactions. Of the used epoxy resins with $Mo(EH)_n$ as initiator, TGAP has a lower onset curing temperature than Novolac and TGMDA. The distances between onset curing temperature and peak curing temperature increase with the order: Novolac < TGAP < TGMDA and vary between 27 and 43 ^oC. TGMDA shows a higher reaction enthalpy than other epoxy resins with $Mo(EH)_n$ as initiator maybe due to more glycidyl groups. Higher curing temperatures and lower reaction enthalpies were observed using epoxy blends such as TGAP/Novolac and Novolac/TPMTGE. In addition, other metal complexes such as CrO_2Cl_2, $Nb(OEt)_5$, $V(NAPH)_n$ and $VO(OPr)_3$ were also investigated and they show a different behavior in different resins. For example, using CrO_2Cl_2 and $V(NAPH)_n$ as initiators, the onset curing temperature and reaction enthalpy of TGAP are higher than the onset curing temperature and reaction enthalpy of TGMDA; using $Nb(OEt)_5$ as initiator, the onest curing temperature and reaction enthalpy of TGAP are lower than the onset curing temperature and reaction enthalpy of TGMDA; using $VO(OPr)_3$ as initiator, the onset curing temperature of TGAP is lower than the onset curing temperature of TGMDA, but reaction enthalpy of TGAP is higher than reaction enthalpy of TGMDA.

Table 1: DSC data of the curing of different epoxy resins using transition metal complexes[a].

Epoxy resin	Metal complex (%)	Solubility[b]	T_o[c] (°C)	T_{max}[c] (°C)	△H[c] (J/g)
Novolac	$Mo(EH)_n$(10.00)	++	233	260	320
TGAP	$Mo(EH)_n$(9.12)	+	171	200	430
TGMDA	$Mo(EH)_n$(9.44)	-	183	226	643
TGAP+Novolac (50:50)	$Mo(EH)_n$(13.83)	+	197	237	396
Novolac+TPMTGE (50:50)	$Mo(EH)_n$(10.28)	+	215	254	253
TGAP	CrO_2Cl_2 (3.03)	-	253	290	772
TGMDA	CrO_2Cl_2 (2.55)	-	241	277	702
TGAP	$Nb(OEt)_5$ (2.90)	++	158	188	332
TGMDA	$Nb(OEt)_5$ (3.16)	++	200	225	534
TGAP	$V(NAPH)_n$ (50.74)	++	192	222	212
Novolac	$V(NAPH)_n$ (47.09)	-	126	163	53
TGAP	$VO(OPr)_3$ (8.68)	-	231	247	604
TGMDA	$VO(OPr)_3$ (6.88)	-	236	252	308

[a]Heating rate: 10 °C/min. [b]++: excellent solubility; +: good solubility; -: low solubility. [c]T_o: onset of polymerization peak; T_{max}: peak maximum; ΔH: reaction enthalpy.

2.1.1.2 Influence of the transition metal type on the curing of epoxy resins

Many nickel and copper complexes are often used in the curing of epoxy resins because of their latent curing properties and good solubilities in epoxy resins[20]. Table 2 shows the DSC data of the curing of TGMDA using $Mo(OEt)_5$, $W(OEt)_5$, a mixture of $Mo(OEt)_5$ and $W(OEt)_5$, and $Nb(OEt)_5$ as initiators. For the first time they were used as initiators for the curing of epoxy resins due to their high solubility in epoxy resins. It is supposed that alkoxide groups are released at elevated temperatures that initiate homopolymerization of TGMDA. From Table 2, it can be seen that using $Mo(OEt)_5$, $W(OEt)_5$ and $Nb(OEt)_5$ as initiators, the onset curing temperatures of TGMDA are different and increase with the order: $Mo(OEt)_5$ < $Nb(OEt)_5$ < $Mo(OEt)_5$/$W(OEt)_5$ < $W(OEt)_5$. Reaction enthalpy of TGMDA using $Mo(OEt)_5$ and $W(OEt)_5$ together as initiators is higher than reaction enthalpy of TGMDA using $Mo(OEt)_5$ or $W(OEt)_5$. The distances between onset curing temperature and peak curing temperature of TGMDA vary between 20 and 39 °C. Thus, different metals in combination with the same coordination sphere also have an influence on the curing of the same epoxy resin.

Table 2: DSC data of the curing of TGMDA using $Mo(OEt)_5$, $W(OEt)_5$ and $Nb(OEt)_5$[a]

Epoxy resin	Metal complex (%)	Solubility[b]	T_o[c] (°C)	T_{max}[c] (°C)	△H[c] (J/g)
TGMDA	$Mo(OEt)_5$(4.89)	++	190	229	604
TGMDA	$W(OEt)_5$(3.38)	++	264	294	614
TGMDA	$Mo(OEt)_5$(1.62)+$W(OEt)_5$(1.13)	++	246	266	691
TGMDA	$Nb(OEt)_5$ (3.16)	++	200	225	534

[a]Heating rate: 10 °C/min. [b]++: excellent solubility. [c]T_o: onset of polymerization peak; T_{max}: peak maximum; ΔH: reaction enthalpy.

2.1.1.3 Influence of the solubility of transition metal complexes in epoxy resin on the curing of epoxy resins

The solubility of transition metal complexes in the epoxy resins is very important for the final properties of resulting thermosets[9,20]. If the transition metal complex has a low solubility in the epoxy resin, the metal complex can not be dispersed in the epoxy resin uniformly and the mechanical, physical and electrical properties of the materials will be affected severely. In order to increase the solubility of transition metal complexes in epoxy resins, acetone has been used to achieve this goal by Ghaemy[12-15,19]. Besides the addition of organic solvents such as DMF and methanol, the addition of some anhydrides can also increase the solubility of transition metal complexes in epoxy resins and epoxy resins were cured by polyaddition. The solubility of different metal complexes in epoxy resins is given in Table 3. $V(NAPH)_n$ has an excellent solubility in TGAP, but a low solubility in Novolac. In the curing of ERL4221 using $Mo(EH)_n$ as initiator, HMPA was added to increase the solubility of $Mo(EH)_n$ in ERL4221. Methanol was used to make solid $H_3Mo_{12}O_{40}P\cdot xH_2O$ dissolved in TGMDA. In many cases, the solubility of metal complex in epoxy resin can be increased at elevated temperatures. For example, $Pd(PPh_3)_4$ can be dissolved well in TGAP at 200 °C, but the compound precipitates from the mixture after cooling. The solubility of transition metal complex in epoxy resin has a significant influence on the curing of epoxy resins.

It is noted that many metal complexes can be dissolved in epoxy resins at elevated temperatures and the decomposition of metal complexes can occur during the dissolving process. Usually, in order to increase the solubility of metal complexes in epoxy resins, solvents and anhydrides are added. Solvents should be removed quantitatively during crosslinking by evaporating. Otherwise material parameters are negatively influenced. The addition of anhydrides results in the curing of epoxy resins by polyaddition and also affects the final properties of resulting materials.

Table 3: DSC data of the curing of epoxy resins using different transition metal complexes[a].

Epoxy resin	Metal complex (%)	Solubility[b]	T_o[c] (^oC)	T_{max}[c] (^oC)	△H[c] (J/g)
TGMDA	$MoO_2(TMHD)_2$(1.95)	+	211	236	661
TGMDA	$MoO_2(DEDC)_2$(2.79)	-	205	236	658
TGMDA	$Mo(OEt)_5$(4.89)	++	190	229	604
TGMDA	$Mo(EH)_n$(9.44)	-	183	226	643
TGAP+TGMDA (50:50)	$Mo(OEt)_5$(3.52)	++	198	241	535
TGAP+TGMDA (50:50)	$Mo(OEt)_5$(0.89)+$W(OEt)_5$(1.13)	++	256	285	627
TGAP	$Nb(OEt)_5$(2.90)	++	158	188	332
TGMDA	$Nb(OEt)_5$(3.16)	++	200	225	534
TGAP	$V(NAPH)_n$(50.74)	++	192	222	212
Novolac	$V(NAPH)_n$(47.09)	-	126	163	53
TGMDA	$Ti(EH)_4$(17.80)	++	220	283	543
TGAP	$Pd(PPh_3)_4$(11.02)	+	293	308	832
TGAP+Fe (44:50)	$Pd(PPh_3)_4$(5.42)	+	308	320	654
TGAP	CrO_2Cl_2(3.03)	-	253	290	772
TGMDA	CrO_2Cl_2(2.55)	-	241	277	702
TGMDA	$H_3Mo_{12}O_{40}P{\bullet}xH_2O$(0.67)+$CH_3OH$	+	235	251	692
ERL4221	HMPA+$Mo(EH)_n$(9.01)	++	156	179	72

[a]Heating rate: 10 ^oC/min. [b]++: excellent solubility; +: good solubility; -: low solubility. [c]T_o: onset of polymerization peak; T_{max}: peak maximum; ΔH: reaction enthalpy.

2.1.1.4 Influence of the concentration of transition metal complex in epoxy resin on the curing of epoxy resins

The influence of the concentration of transition metal complex in epoxy resin has been investigated widely[7,11,15,19]. Table 4 shows DSC data of the curing of epoxy resins using different amounts of $Mo(EH)_n$ or $Nb(OEt)_5$ as initiators. From Table 4 it can be seen that the concentration of $Mo(EH)_n$ or $Nb(OEt)_5$ in the resin mixtures has a significant effect on the curing of TGMDA and Novolac. The higher the concentration of $Mo(EH)_n$ or $Nb(OEt)_5$ in the resin mixtures, the lower the onset curing temperature and reaction enthalpy of

TGMDA and Novolac. This coincides with the results of other groups investigating the concentrations of transition metal complexes in epoxy resins[7,11,15,19]. In Table 4, the onset curing temperatures and reaction enthalpies of the resins decrease with increasing concentrations of $Mo(EH)_n$ or $Nb(OEt)_5$. Thus, it can be concluded that the concentration of transition metal complex in the resin mixture has a significant effect on the curing of epoxy resins, and in most cases, higher concentration of transition metal complex in epoxy resin accelerates the curing of epoxy resin.

Table 4: DSC data of the curing of epoxy resins using different amounts of $Mo(EH)_n$ or $Nb(OEt)_5$[a].

Epoxy resin	Metal complex (%)	Solubility[b]	T_o[c] (°C)	T_{max}[c] (°C)	△H[c] (J/g)
TGMDA	$Mo(EH)_n$(9.44)	-	183	226	643
TGMDA	$Mo(EH)_n$(9.48)	-	171	217	605
TGMDA	$Mo(EH)_n$(18.77)	-	139	194	480
Novolac+Fe (64:29)	$Mo(EH)_n$(6.69)	-	233	262	251
Novolac+Fe (64:29)	$Mo(EH)_n$(10.14)	+	210	249	171
TGMDA	$Nb(OEt)_5$ (3.16)	++	200	225	534
TGMDA	$Nb(OEt)_5$ (9.87)	++	138	165	268

[a]Heating rate: 10 °C/min. [b]++: excellent solubility; +: good solubility. [c]T_o: onset of polymerization peak; T_{max}: peak maximum; ΔH: reaction enthalpy.

2.1.1.5 Influence of the ligands on the curing of epoxy resins

The influence of the ligand on the curing of epoxy resins has been investigated widely[9-19]. Zhang and Wong studied the curing behavior of the epoxy/anhydride/metal AcAc systems using a series of different metal acetylacetonates[17]. They suggested that the decomposition products of the metal AcAc complexes might be the active species responsible for initiating polymerization in the epoxy/anhydride resin systems. Of the many ligands used often, the ligands based on AcAcs are especially attractive because they offer not only a wide range of curing latency but also a wide range of curing temperatures. However, many transition metal complexes based on the two ligands have a drawback because of their low solubility in epoxy resins. Table 5 shows DSC data for the curing of TGMDA using different molybdenum complexes as initiators. From Table 5 it can be seen that the curing reaction enthalpy of TGMDA is beyond 600 J/g using different molybdenum complexes. This shows that there is a high crosslinkage in the obtained solid materials. In the curing of TGMDA using four molybdenum complexes as initiators, the onset curing temperature of TGMDA decreases in the order: $MoO_2(TMHD)_2$ > $MoO_2(DEDC)_2$ > $Mo(OEt)_5$ > $Mo(EH)_n$. Usually, the curing of epoxy resins is followed with the dissociation of transition metal complexes in epoxy resins[9,10,14]. The chelated molybdenum complexes are more stable than $Mo(OEt)_5$ and $Mo(EH)_n$, and therefore the reaction temperatures are higher. Another important parameter is the different solubility of molybdenum complexes in TGMDA. Therefore, it can be concluded the ligands have a significant effect on the curing of epoxy resins.

Table 5: DSC data of the curing of TGMDA using different molybdenum complexes[a].

Epoxy resin	Metal complex (%)	Solubility[b]	T_o[c] (°C)	T_{max}[c] (°C)	△H[c] (J/g)
TGMDA	$MoO_2(TMHD)_2$(1.95)	+	211	236	661
TGMDA	$MoO_2(DEDC)_2$(2.79)	-	205	236	658
TGMDA	$Mo(OEt)_5$(4.89)	++	190	229	604
TGMDA	$Mo(EH)_n$(9.44)	-	183	226	643

[a]Heating rate: 10 °C/min. [b]++: excellent solubility; +: good solubility; -: low solubility. [c]T_o: onset of polymerization peak; T_{max}: peak maximum; ΔH: reaction enthalpy.

From these investigations, it can be concluded that epoxy resin monomers, the transition metal type, the solubility of transition metal complexes in epoxy resin, the concentration of transition metal complex in the resin mixture and the ligands all have a significant influence on the curing of epoxy resins.

2.1.2 Preparation of epoxy resins containing *d*-block metal species

In a typical preparation procedure, the transition metal complex was added to the epoxy resin monomer and the obtained mixture was stirred for 4 h, then transferred to aluminum molds to form a thin layer of around 1 mm thickness. The mixture was heated successively and obtained solid plate was cut and ground with an analytic mill. Obtained grains were annealed and sieved.

It is noted that, metal complex should be dissolved in the epoxy resin completely. If the metal complex has a low solubility in the epoxy resin like $H_3Mo_{12}O_{40}P{\bullet}xH_2O$ and $Pd(PPh_3)_4$, solvents such as DMF or methanol were added or the mixture was heated at elevated temperatures so that a homogeneous dispersion of metal complex in epoxy resin was achieved. In the case of other metal complexes such as $Mo(EH)_n$ and $V(NAPH)_n$, the solubility is also high because some free ligands are already present prior to heating. During the stirring procedure, in order to achieve the homogeneous dispersion of metal complexes in epoxy resins possibly, the operation was undergone for a long time or by using an ultrasonic bath. During the curing of epoxy resins, the temperatures were increased successively with an interval of 20 °C. After the curing of epoxy resins, the obtained polymers were crushed and annealing at higher temperatures.

2.2 Characterization of epoxy resins containing *d*-block metal species

Obtained epoxy resins containing *d*-block metal species were characterized by thermogravimetric analysis (TGA) and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) for their thermal stabilities and metal species dispersions in polymer matrices.

2.2.1 Thermogravimetric analyses of epoxy resins containing *d*-block metal species

With the goal to examine the catalytic performance of epoxy resins containing transition metals, and to demonstrate their advantages with respect to activity and reusability, it is important to study the thermal stabilities of the obtained thermosets. TGA is the most common tool to investigate the thermal stabilities of materials. TGA data recorded from [*]TGMDA-$Mo(OEt)_5^{1.50\%Mo}$, TGAP-$Mo(EH)_n^{1.50\%Mo}$, Novolac-$Mo(EH)_n^{1.50\%Mo}$ and TGAP-$Pd(PPh_3)_4^{1.00\%Pd}$ are shown in Figure 4, 5, 6 and 7.

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[*] The catalysts are labeled as follows: for example, TGMDA-$Mo(OEt)_5^{1.50\%Mo}$ means solid particle catalyst obtained after curing of the epoxy resin TGMDA via homopolymerization using $Mo(OEt)_5$ as polymerization initiator. The molybdenum loading is 1.50%. All of the catalysts throughout this work are expressed in this mode.

In Figure 4, the small weight loss in the temperature range of 30-300 °C could be attributed to desorption of water and/or low molecular weight compounds from the catalyst (The catalyst was kept under air prior to analysis). In the temperature interval of 30-340 °C, a weight loss of 24% in TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$ is observed. The catalyst starts to decompose at 300 °C and decomposition is complete at 600 °C. This shows that TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$ could be used up to 300 °C and a high thermal stability can be expected.

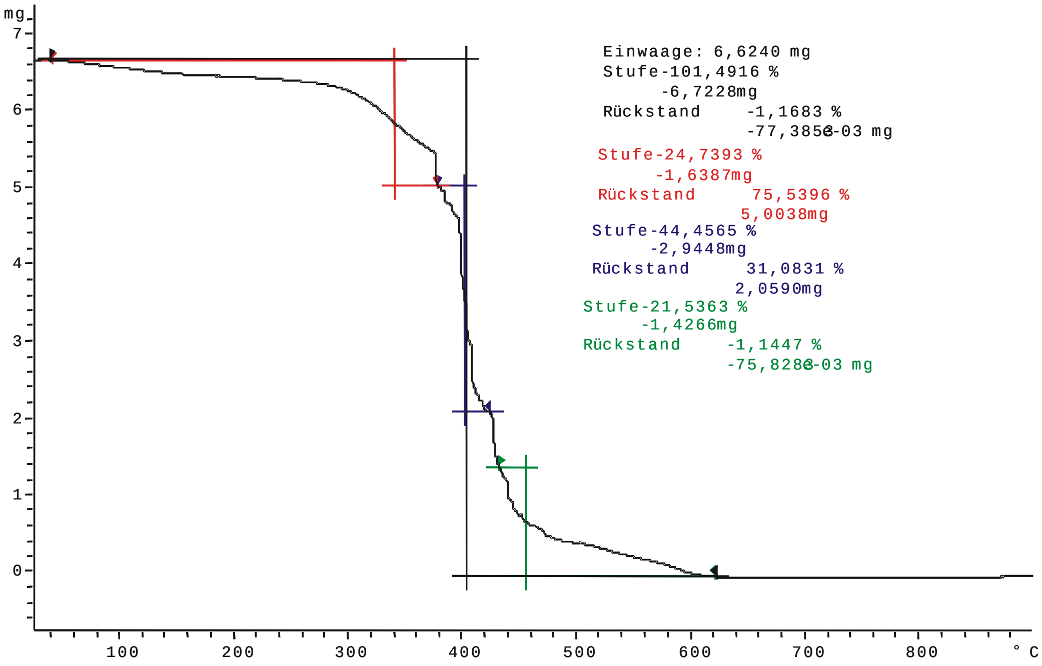


Figure 4: TGA data recorded from TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$.

In Figure 5, the weight loss in the temperature range of 30-300 °C could be attributed to desorption of water and/or low molecular weight compounds from the catalyst. In the temperature interval of 30-320 °C, a weight loss of 12% in TGAP-Mo(EH)$_n$$^{1.50\%Mo}$ is observed. The decomposition of the catalyst occurs at 300 °C and is complete at 540 °C. This shows that TGAP-Mo(EH)$_n$$^{1.50\%Mo}$ is highly thermal stable and could be used up to 300 °C.

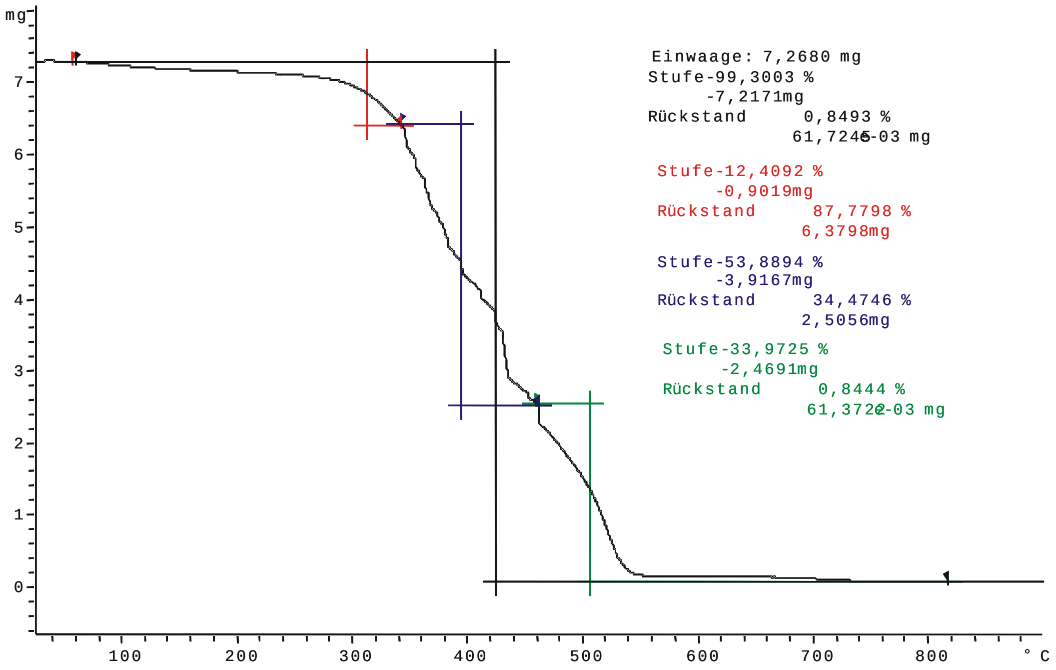


Figure 5: TGA data recorded from TGAP-Mo(EH)$_n$$^{1.50\%Mo}$.

In Figure 6, the weight loss in the temperature range of 30-300 °C could be attributed to desorption of water and/or low molecular weight compounds from the catalyst. In the temperature interval of 30-360 °C, a weight loss of 22% in Novolac-Mo(EH)$_n$$^{1.50\%Mo}$ is observed. The decomposition of the catalyst starts at 300 °C and ends at 600 °C. This shows that Novolac-Mo(EH)$_n$$^{1.50\%Mo}$ possesses high thermal stability and could be used up to 300 °C. In comparison with TGAP-Mo(EH)$_n$$^{1.50\%Mo}$, the complete decomposition of Novolac-Mo(EH)$_n$$^{1.50\%Mo}$ appears at higher temperatures.

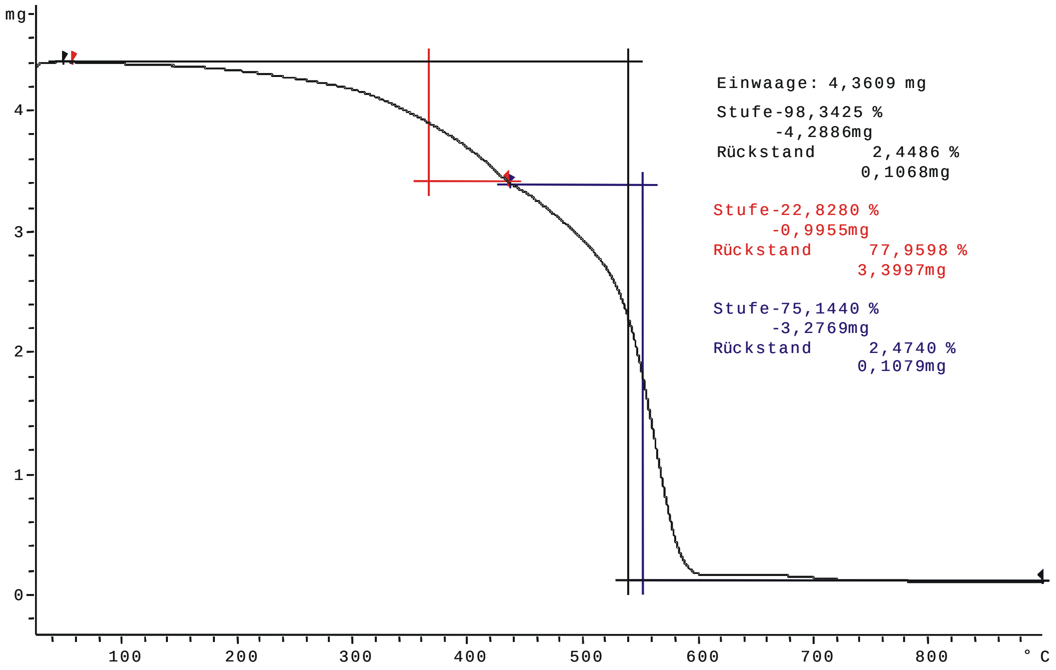


Figure 6: TGA data recorded from Novolac-Mo(EH)$_n^{1.50\%Mo}$.

In Figure 7, the weight loss in the temperature range of 30-300 °C could arise from the desorption of water and/or low molecular weight compounds from the catalyst. In the temperature interval of 30-330 °C, a weight loss of 16% in TGAP-Pd(PPh$_3$)$_4^{1.00\%Pd}$ is observed. The decomposition of the catalyst is complete at 620 °C. This shows that TGAP-Pd(PPh$_3$)$_4^{1.00\%Pd}$ is highly thermal stable and could be used up to 300 °C.

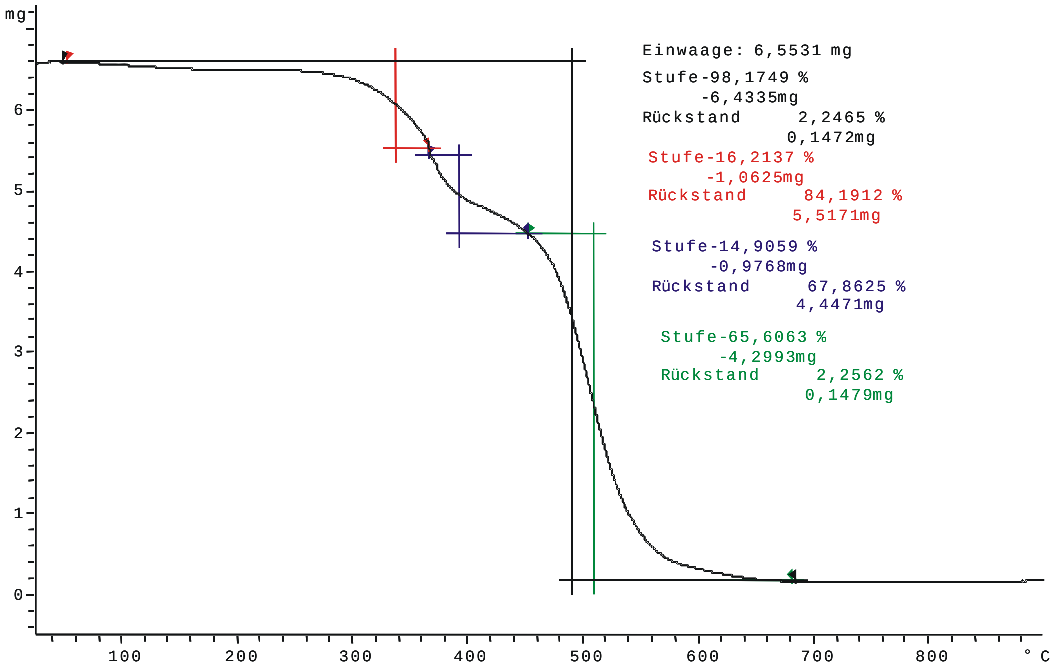


Figure 7: TGA data recorded from TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$.

In summary, four epoxy resins containing transition metal species, TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$, TGAP-Mo(EH)$_n$$^{1.50\%Mo}$, Novolac-Mo(EH)$_n$$^{1.50\%Mo}$ and TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$ were investigated by TGA. All of the investigated catalysts show a high thermal stability and could be used up to 300 ^{o}C. This suggests that epoxy resins are promising materials for the immobilization of transition metal species and the preparation of catalysts with high lifetime.

2.2.2 SEM-EDX analyses of epoxy resins containing *d*-block metal species

The polymer surfaces were analyzed by SEM-EDX. Figure 8a, 8b, 8c and 8d show SEM images of TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$, TGAP-Mo(EH)$_n$$^{1.50\%Mo}$, Novolac-Mo(EH)$_n$$^{1.50\%Mo}$, and TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$, respectively. In these images, some agglomerates are always observed, especially in the case of TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$ and TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$, reflecting the low solubility of Mo(OEt)$_5$ and Pd(PPh$_3$)$_4$ in TGMDA and TGAP, respectively. Different resolutions (from 250 to 3000) were used to examine the polymer surface.

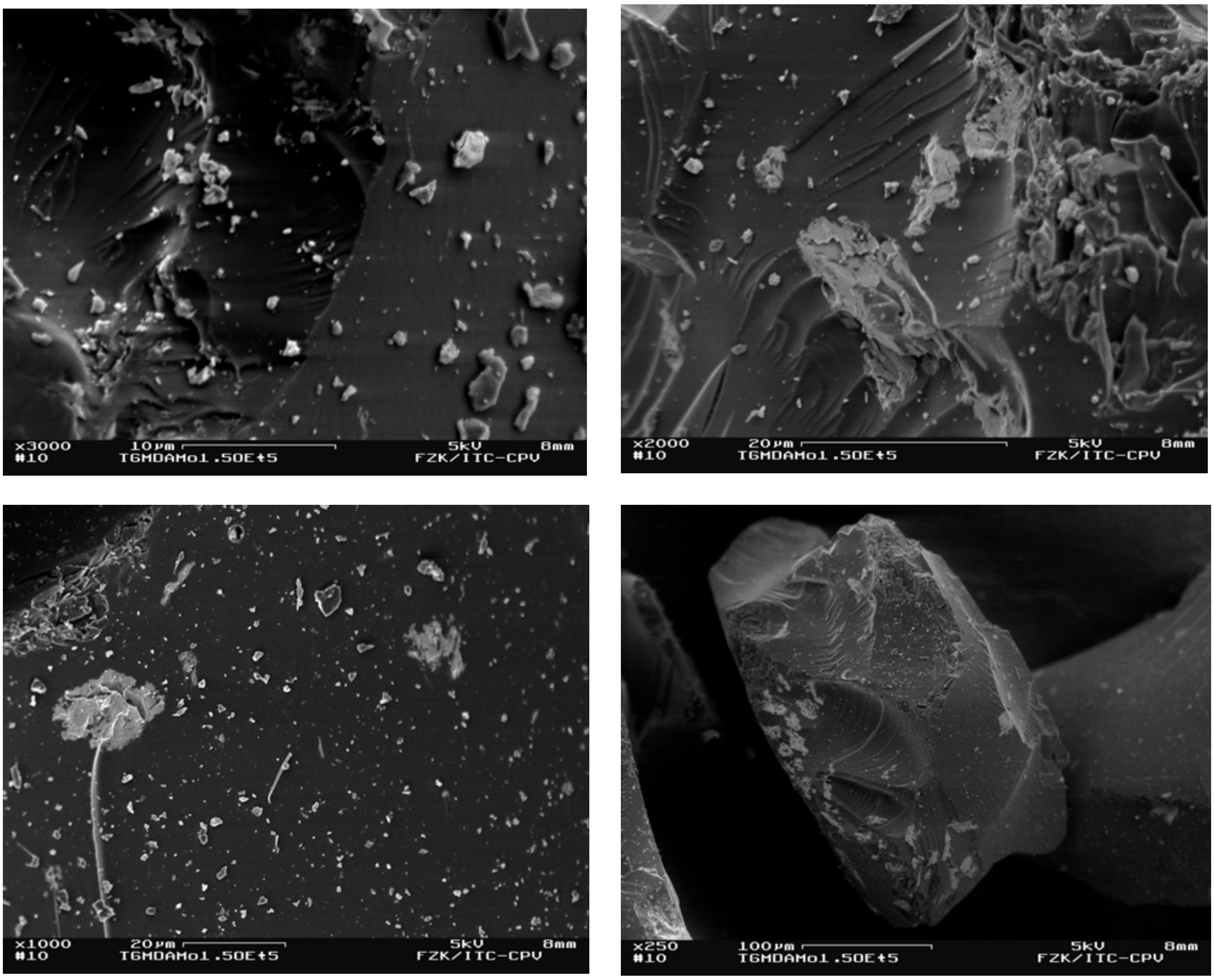


Figure 8a: SEM images of TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$.

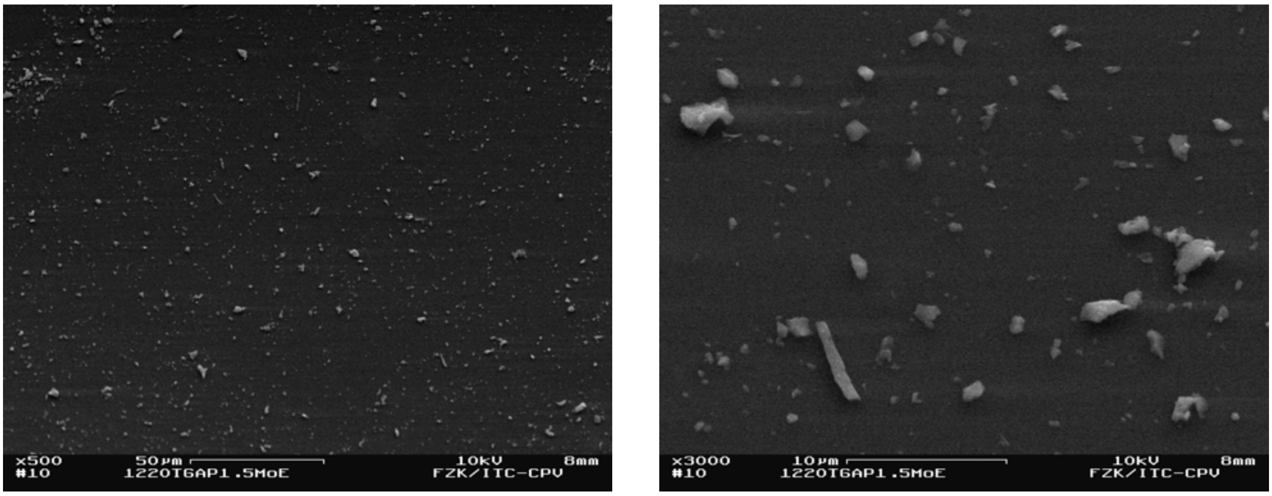


Figure 8b: SEM images of TGAP-Mo(EH)$_n$$^{1.50\%Mo}$.

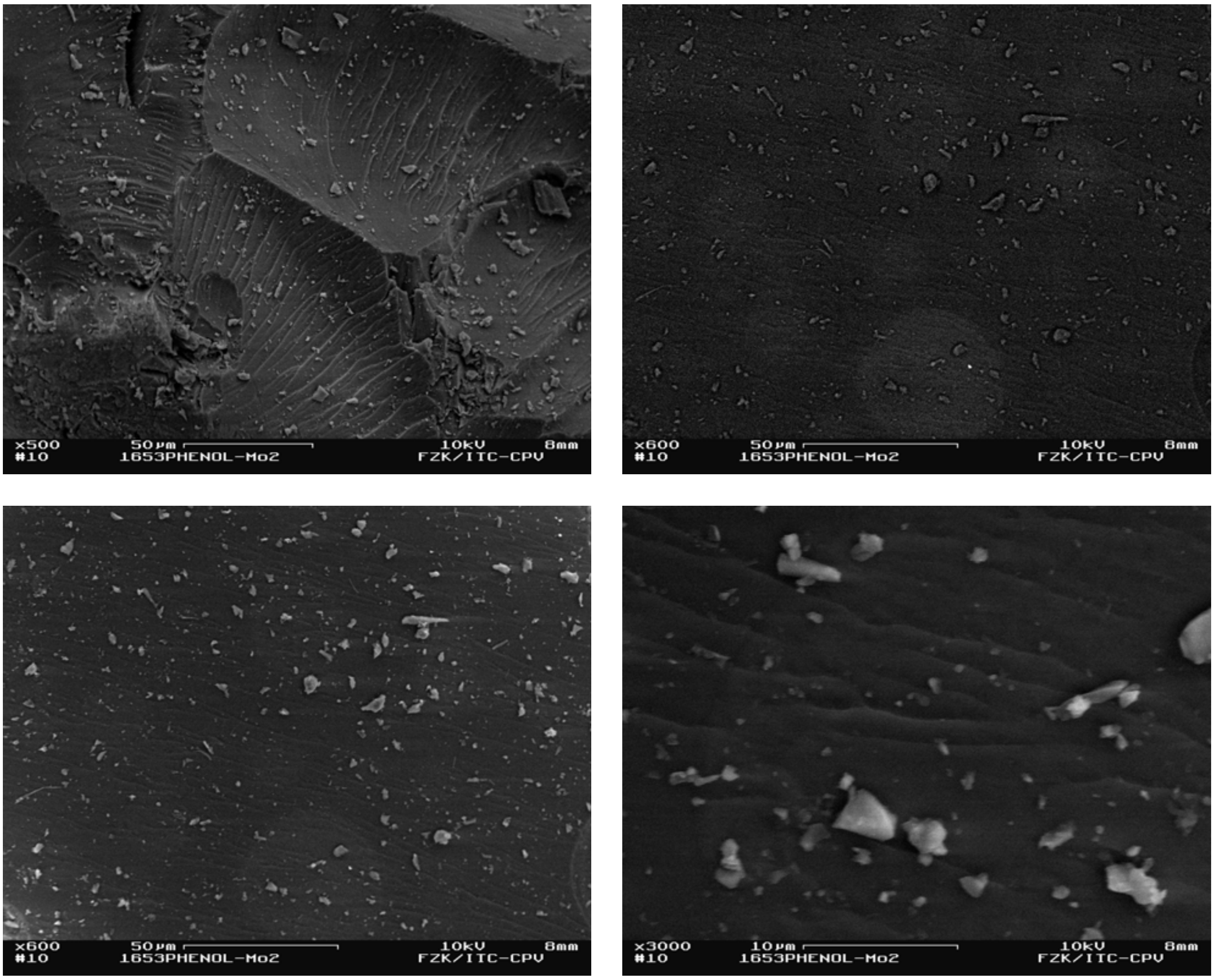


Figure 8c: SEM images of Novolac-Mo(EH)$_n$$^{1.50\%Mo}$.

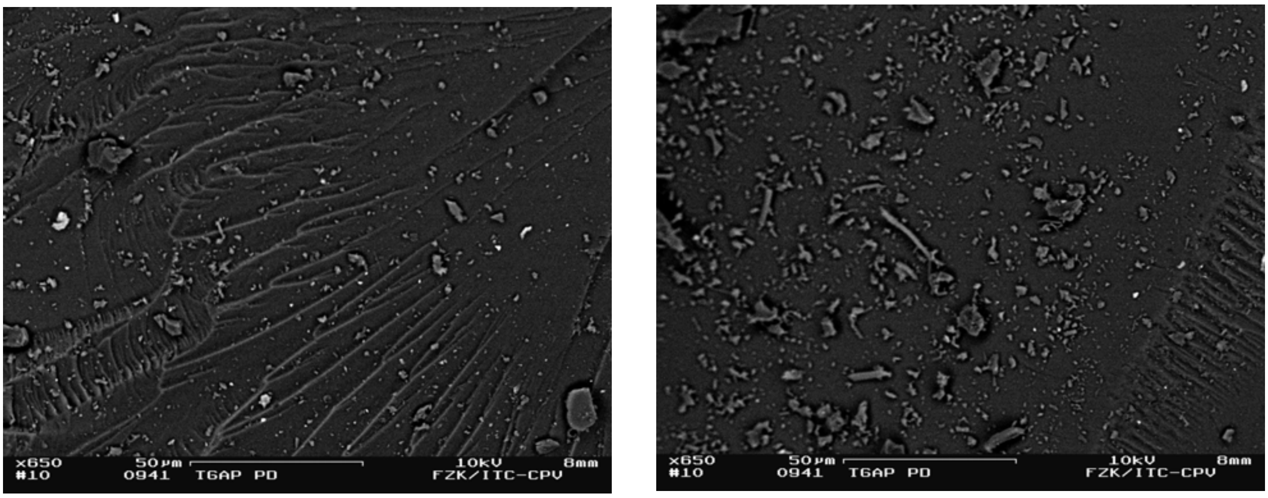


Figure 8d: SEM images of TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$.

In Figure 8e, three spots at the surface of TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$ were analyzed by EDX elemental analysis. The molybdenum contents are 48.61, 41.39 and 1.23% in spot 1, 2 and 3, respectively. It is obvious that the bright spots 1 and 2 show agglomerates of molybdenum species. Spot 3 represents molybdenum species homogeneously dispersed in the resin matrix. Difference of molybdenum contents in different positions and many agglomerates show that Mo(OEt)$_5$ has a low solubility in TGMDA.

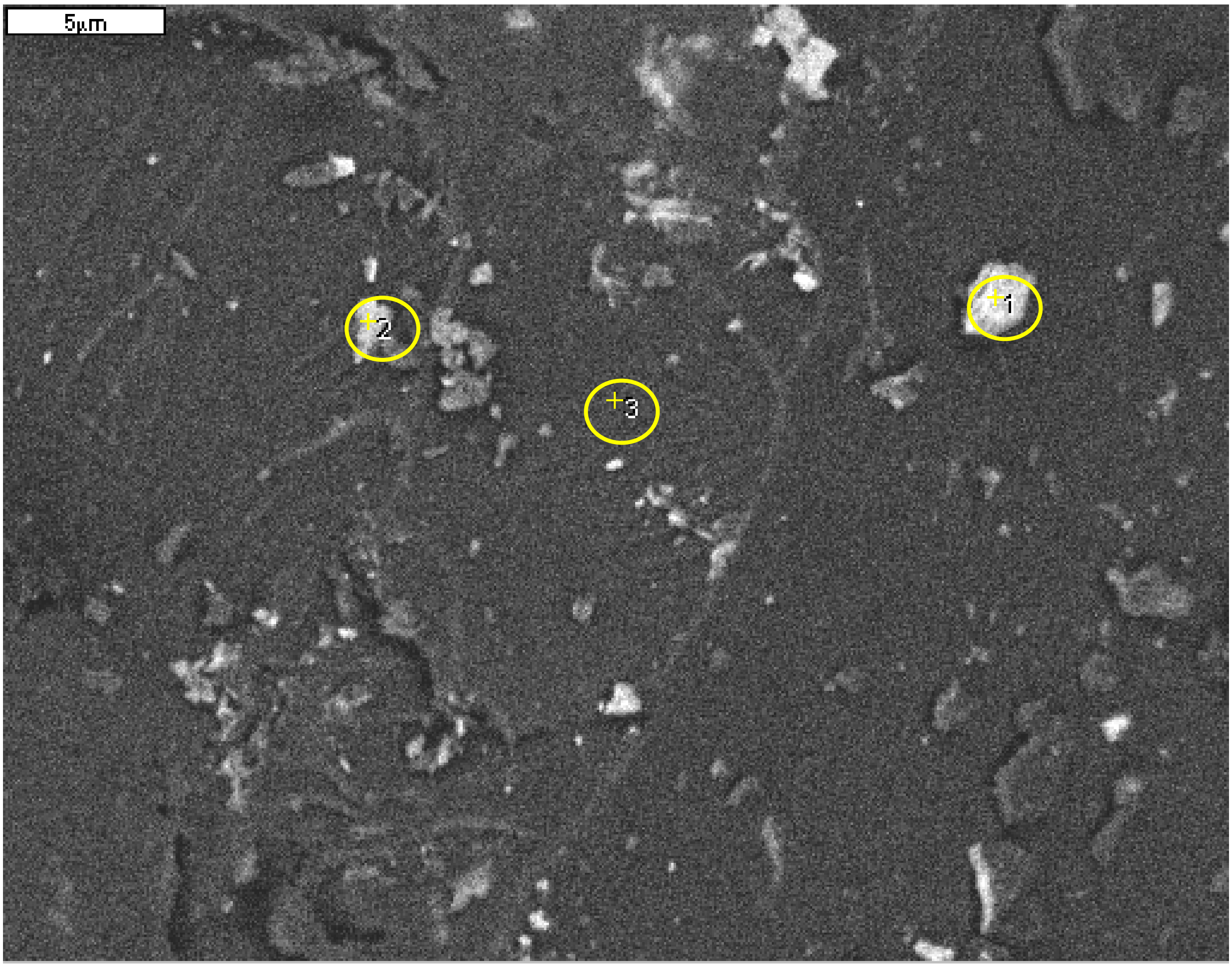


Figure 8e: SEM images of TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$ (EDX elemental analyses).

In Figure 8f, five surface spots were analyzed by EDX elemental analysis using TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$. The palladium contents are 0.02, 0.51, 0.89, 0.32 and 1.58% in spot 1, 2, 3, 4 and 5, respectively. The results show a non-uniform distribution of palladium species in the polymer matrix. However, the metal content in bright spots 1, 2, 3 and 4 is much lower than spot 5. This is different from the molybdenum catalyst (Figure 8e).

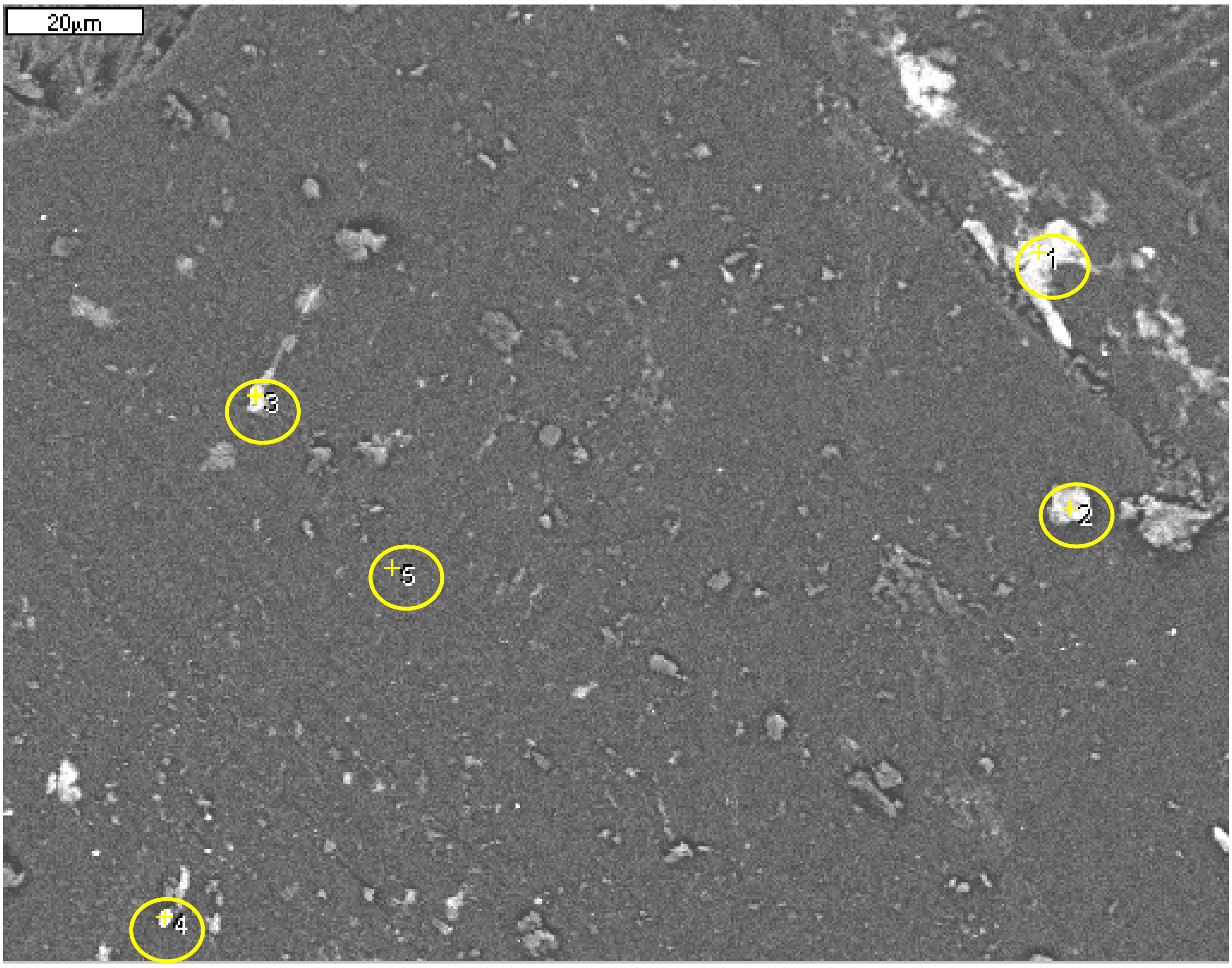


Figure 8f: SEM images of TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$ (EDX elemental analyses).

In order to obtain some information about the component and structure of these agglomerates (bright spots), $MoO_2(acac)_2$ and $Mo(OEt)_5$ were reacted with stoichiometric amounts of TGMDA, TGAP or diglycidylaniline using DMF as solvent at 80 °C, molybdenum polyoxo complexes such as $[Mo_8O_{26}]^{4-}$ were formed and characterized by X-ray diffraction (XRD) and the cluster is shown in Figure 8g. This suggests that the surface agglomerates could comprise polyoxo compounds[29,30].

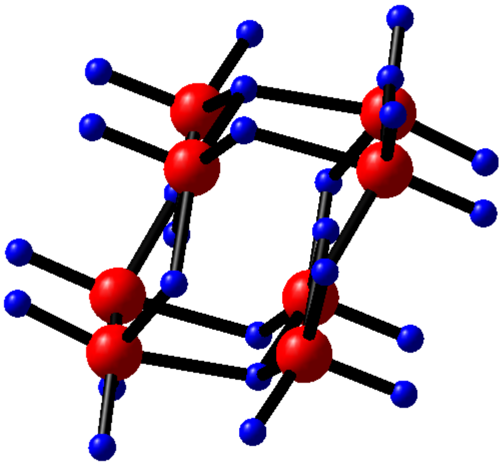
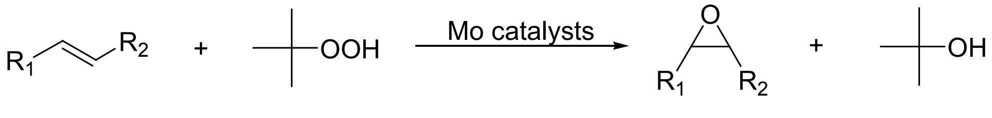


Figure 8g: The structure of molybdenum polyoxo cluster $[Mo_8O_{26}]^{4-}$.

2.3 Epoxy resins containing Mo, W, Ti or V species for the epoxidation of liquid alkenes

2.3.1 Developments of liquid alkene epoxidation catalysts

Oxiranes are a class of commodity chemicals of enormous importance in the chemical industry. The oxidation of alkenes to the corresponding oxiranes in liquid phase with organic hydroperoxides (TBHP or EBHP) in the presence of a catalyst is well known[31]. Many transition metals in particular such as Au[32], Ti[33-35] have been investigated for this transformation using organic hydroperoxides as oxidants. Molybdenum complexes are particularly effective homogeneous catalysts and are used in the ARCO process[31] in combination with organic hydroperoxides. Numerous molybdenum complexes, ranging from monomeric molybdenum complexes such as $Mo(CO)_6$ and $MoO_2(acac)_2$ to molybdenum clusters such as ammonium molybdate [$(NH_4)_6Mo_7O_{24}$•$4H_2O$], catalyze the epoxidation of many different alkenes with different peroxides as oxygen donors. Recently, a variety of molybdenum complexes has been synthesized and tested in the epoxidation of alkenes[36-40]. Despite successes in homogeneous catalysis, there is a clear demand for solid materials that catalyze epoxidations with easily available organic hydroperoxides or H_2O_2 for the ease of products separation and catalysts recycling[41]. In order to realize the heterogenization of homogeneous molybdenum catalysts, various supports have been used. Inorganic supports such as TiO_2[42], α-Al_2O_3[43], layered double hydroxide[44], silica[45], mesoporous molecular sieves (MCM-41 or MCM-48)[46-51], modified mesoporous molecular sieves (MCM-41 or MCM-48)[52-54] are the most widely investigated for the immobilization of molybdenum species. Polymer such as 1,4-divinylbenzene (DVB) crosslinked polystyrene[56,57], benzimidazole-functionalized dendrons[58], functional polyimide particulates[59], polybenzimidazole (PBI)[60,61], chelating ion-exchange polyampholites[62], spherical particulate polysiloxanes[63], imidazole-containing polymers[64,65], poly(ethylene oxide)[66], polymer-bound piperazine[67], and polymer-bound phosphines[68] supported molybdenum catalysts have also been developed for the epoxidation of alkenes[55]. In these polymer-supported molybdenum catalysts, $MoO_2(acac)_2$ and $Mo(CO)_6$ are commonly chosen as the precursors. In addition, polymer-supported[69] and microencapsulated[70] homogeneous vanadium catalysts such as $VO(acac)_2$ have also been investigated because of better catalytic performance in the epoxidation of allyl alcohol. The epoxidation of alkenes catalyzed by molybdenum catalysts with *tert*-butyl hydroperoxide (TBHP) is depicted in Figure 9.



R_1, R_2: H, alkyl, Ph

Figure 9: Epoxidation of alkenes catalyzed by molybdenum catalysts with TBHP.

2.3.2 Suggested reaction mechanism of liquid alkene epoxidations catalyzed by molybdenum catalysts with organic hydroperoxides

Despite a long history and industrial relevance of the Mo(VI)-catalyzed epoxidation of alkenes with alkyl hydroperoxides, the reaction mechanism remains a subject of debate. There is general agreement that it involves rate-controlling oxygen transfer from an electrophilic alkylperoxometal complex to the olefinic double bond. However, it remains a point of contention whether the reaction proceeds by direct oxygen atom transfer or via the formation of a Mo(VI)-alkene complex. A mechanism, as shown in Figure 10, was proposed by Sheldon in 1973[71].

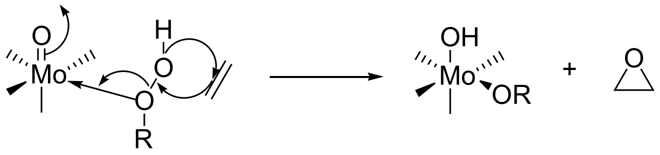


Figure 10: The mechanism of oxygen transfer in the epoxidation of alkenes catalyzed by molybdenum complexes proposed by Sheldon[71].

Subsequently, Sharpless reasoned[72], on the basis of steric arguments, that the mechanism according to Figure 11, involving coordination of alkylperoxo ligand through the distal rather than the proximal oxygen, was more likely.

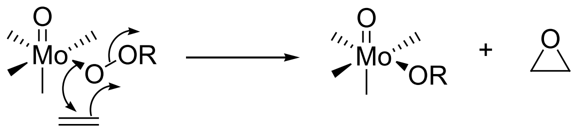


Figure 11: The mechanism of oxygen transfer in the epoxidation of alkenes catalyzed by molybdenum complexes proposed by Sharpless[72].

The mechanism according to Figure 12 is a slight variation of that outlined in Figure 11 and closely resembles the mechanism proposed for analogous epoxidations with H_2O_2[73].

The difference between Figure 11 and Figure 12 is in the molybdenum centre before and after the reactions.

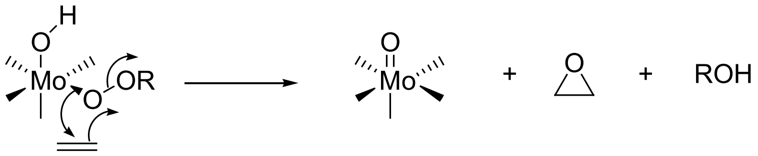


Figure 12: The mechanism of oxygen transfer in the epoxidation of alkenes catalyzed by molybdenum complexes proposed by Sharpless[73].

An alternative mechanism for oxygen transfer was proposed by Mimoun[74]. In this mechanism (Figure 13) initial coordination of the olefin to the metal is followed by its rate-limiting insertion into the metal-oxygen bond giving a pseudocyclic dioxometallocyclopentane. The latter decomposes to the epoxide and the metal alkoxide.

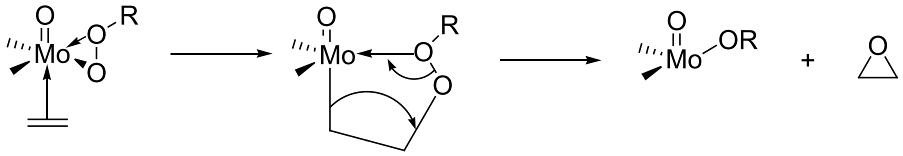


Figure 13: The mechanism of oxygen transfer in the epoxidation of alkenes catalyzed by molybdenum complexes proposed by Mimoun[74].

Recently, Mitchell et al. reported a new mechanism of oxygen atom transfer in the epoxidation of alkenes using their molybdenum catalysts and TBHP[40]. Two important features distinguish these catalysts from those previously reported. First, their coordination environment remains well-defined during the epoxidation reaction. Second, the ligand design does not permit simultaneous coordination of olefin and alkylhydroperoxide. Therefore, an epoxidation mechanism involving direct oxygen atom transfer to olefin was suggested.

In summary, the conflicting mechanisms are summarized in Figure 10, 11, 12 and 13. The direct oxygen atom transfer mechanism (Figure 10, 11 and 12) involves a concerted single-step process in which an olefin nucleophile attacks a Mo(VI)-coordinated alkyl hydroperoxide electrophile, producing epoxide and metal alkoxide. The alternative mechanism (Figure 13) involves reversible binding of the olefin to a Mo(VI) alkyl hydroperoxide complex. In the most commonly discussed variation, a rearrangement occurs to form peroxymetallacycle, which fragments into epoxide and metal alkoxide.

2.3.3 Epoxy resins containing Mo, W, Ti or V species for the epoxidation of liquid alkenes

In order to investigate the catalytic performance of Mo, W, Ti or V catalysts based on epoxy resins, a series of epoxy resins containing Mo, W Ti or V species have been prepared via homopolymerization of the resins such as TGMDA, TGAP and Novolac or polyaddition of ERL4221 and HMPA using different Mo, W, Ti or V complexes as initiators and evaluated in the epoxidation of liquid alkenes including cyclohexene, 1-octene, *trans*-2-octene, styrene, 1,2-dihydronaphthalene (DHNT), (R)-(+)-limonene, 3-butene-2-ol and allyl alcohol using *tert*-butyl hydroperoxide (TBHP) or cumyl hydroperoxide (CHP) as oxidant.

2.3.3.1 Blank reactions of liquid alkene epoxidations using TBHP as oxidant without catalysts

For comparison with the epoxidation of liquid alkenes using TBHP and the catalysts, blank reactions using TBHP as oxidant without catalysts were carried out using 12 mmol TBHP (36 wt.% TBHP/toluene) (prepared according to literature method[75] and measured by iodometric titration[76]) as oxidant and 10 mmol of substrate at 90 ^{o}C with a reaction time of 24 h. The results are given in Table 6. 1-Octene can not be converted to the corresponding oxirane under these reaction conditions. Cyclohexene can be converted to cyclohexene epoxide (13%) with a low selectivity (20%), but styrene (13%) and *trans*-2-octene (28%) can be converted to their corresponding oxiranes with a high selectivity.

Table 6: Blank reactions of liquid alkene epoxidations using TBHP as oxidant without catalysts[a].

Alkene	Conversion[b] (%)	Selectivity[c] (%)
Cyclohexene	13	20[d]
1-Octene	0	-
trans-2-Octene	13	>99
Styrene	28	>99

[a] Reaction conditions: 10 mmol substrate, 12 mmol TBHP (36 wt.% TBHP in toluene), 90 °C, 24 h. [b] Determined by GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [c] Determined by GC-MS. [d] Byproducts are mainly cyclohexenol, cyclohexenone and diol.

2.3.3.2 Epoxidation of liquid alkenes using TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$ and TBHP

TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$ was used as heterogeneous catalyst in the epoxidation of liquid alkenes with anhydrous TBHP as oxidant. In each case the catalyst was used in five consecutive reactions with a reaction time of 7 h and additional 5 runs with a reaction time of 24 h. The catalyst can be separated by filtration and reused in the next run without any treatments. Metal contents of the filtrates were determined by ICP-AES analysis by evaporating the liquid components before adding 65% concentrated HNO_3. Obtained results are summarized in Table 7.

When TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$ was used as catalyst to transform liquid alkenes to the corresponding oxiranes, the alkene conversions depend on the nature of liquid alkenes. In five consecutive runs with a reaction time of 7 h, the conversion of cyclohexene is higher than the conversion of other liquid alkenes under identical reaction conditions. Conversions decrease in the following order: cyclohexene (77-91%) > *trans*-2-octene (55-76%) > (R)-(+)-limonene (61-71%) > styrene (41-49%), 1,2-dihydronaphthalene (40-43%), 1-octene (15-48%). 1-Octene is the most difficult alkene to be epoxidized with TBHP, but the selectivity to its oxirane is high, almost 100%. In five consecutive runs with a reaction time of 24 h, conversions decrease in the following order: cyclohexene (95-100%) > *trans*-2-octene (89-97%) > (R)-(+)-limonene (77-86%), styrene (72-90%), 1-octene (75-81%) > 1,2-dihydronaphthalene (57-70%).

In general, alkene conversion is associated with metal species leaching. Higher metal species leaching leads to higher alkene conversion because the conversion is partly due to homogeneous catalysis by dissolved molybdenum species (some molybdeum species maybe redeposit on the solid support after the completion of the reaction that can not be detected by ICP-AES). This will be explained later more detailedly (hot filtration test in Chapter 2.3.3.8.4). It is noted that there is higher metal species leaching in the first run compared to the following runs. This can be explained that some weakly bound metal species dissociated from the support primarily. Therefore, molybdenum species leaching decreases in the consecutive reaction runs and then leads to a decrease in alkene conversions.

In the epoxidation of cyclohexene, the byproducts are mainly cyclohexenol and cyclohexenone due to allylic oxidation as well as cyclohexane diol arising from epoxide ring-opening. However, the oxirane selectivity remains above 96%. In the epoxidation of 1,2-dihydronaphthalene, the oxirane selectivity (75-84%) is low due to the formation of diol. In the epoxidation of (R)-(+)-limonene, the double bond in the ring is mainly epoxidized to yield the monooxirane with a selectivity of around 90%. Byproducts are the dioxirane and products arising from isomerization and allylic oxidation. The amount of molybdenum in the reaction solutions is extremely low (below 18 μg except for the first run). In the epoxidation of styrene, 1,2-dihydronaphthalene and (R)-(+)-limonene, very small amounts of molybdenum in the reaction solutions (below 2 μg) were detected by ICP-AES after extraction of the reaction residues with concentrated HNO_3. Maybe the extraction from the reaction residues was not complete.

In most cases, after a comparatively rapid increase in the product yield in the earlier stages, the reaction slows down considerably during the course of the catalytic run. Several factors can be responsible for this behavior. Together with the normal decrease of activity as a result of the consumption of both substrate and oxidizing agent, molybdenum species leaching or hindrance of the reaction by one of the reaction products can play an important role[44,49]. The oxidizing agent TBHP is transformed to *tert*-butyl alcohol (TBA) during the course of the reaction. This byproduct slows down the reaction rate since it can also coordinate to the molybdenum centre. The influence of the byproduct *tert*-butyl alcohol was examined[36]. It is found that when 10% of the alcohol was added in the beginning of the reaction, a noticeable decrease in yield in comparison to the reaction without alcohol addition is observed. When the alcohol is added after 1 h, there is still a pronounced effect. Evidently, the alcohol competes for coordination to the molybdenum centre and therefore slows down the reaction rate. A conclusion was drawn that *tert*-butyl alcohol acts as a competitive inhibitor for the TBHP attack, and leads to a significant reduction in the catalytic activity with the increase of reaction time[36].

In the epoxidation of liquid alkenes, a problem is the non-productive decomposition of alkyl hydroperoxides. The rate of decomposition of TBHP (14 wt.% in xylene at 110 ^{o}C) in the presence of 0.02 wt.% of molybdenum naphthenate has been shown to be fast, with around 75% decomposition in 2 h[61]. Using TGMDA-Mo(OEt)$_5{}^{1.50\%Mo}$, the non-productive decomposition of TBHP was not observed under the normal reaction conditions used (< 1%).

In the epoxidation of liquid alkenes using polymer-supported metal catalysts, the work of Sherrington et al. is outstanding[55]. PBI-Mo (Mo(VI) compounds supported on polybenzimidazole) was claimed to be the best catalyst by Sherrington. Although PBI-Mo is highly active and has been recycled nine times with no detectable loss of molybdenum species from the support into the reaction solutions, this catalyst needs an activation by pretreatment with TBHP for periods up to 48 h and 5.2% of molybdenum initially loaded on the support was lost during the activation process[65]. The solvent effect was also investigated in their work. Cyclohexene oxide yield decreases with the sequence using different solvents for the PBI-Mo catalyzed epoxidations: 1,2-dichloroethane > toluene > *tert*-butanol > methanol. Coordinating solvents like alcohols generally compete with substrate at the active metallic centre and this occurs here using methanol[65]. In addition, the detection limit of the AAS instrument used in their work is ~0.5 ppm, which corresponds to ~0.2% Mo. The detection limit of molybdenum (~0.2 ppm) for the reactions described in this work is more accurate and PTFE filters used in our work really do not adsorb the dissolved molybdenum species unlike some alumina filters.

In summary, TGMDA-Mo(OEt)$_5^{1.50\%Mo}$ exhibits desired results for the epoxidation of liquid alkenes with respect to stability and activity. This shows that it is possible to prepare efficient catalysts through the curing of epoxy resins by homopolymerization with *d*-block metal complexes as initiators.

Table 7: Epoxidation of liquid alkenes using TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$ and TBHP[a].

Run no.[b]	Cyclohexene				1-Octene			
	Conv.[c] (%)	Sel.[d] (%)	Mo[e] leached (μg)	Mo[f] content (%)	Conv. (%)	Sel. (%)	Mo leached (μg)	Mo content (%)
1	97	97	41.56	99.45	45	>99	22.99	99.69
2	91	97	14.31	99.26	48	>99	5.35	99.62
3	93	97	11.17	99.11	15	>99	1.48	99.60
4	80	96	4.08	99.06	22	>99	0.78	99.59
5	77	96	2.93	99.02	32	>99	0.95	99.58
6	100	97	17.42	98.79	80	>99	15.71	99.37
7	100	97	12.84	98.62	80	>99	16.50	99.15
8	100	97	11.64	98.46	75	>99	13.90	98.96
9	100	97	11.55	98.31	76	>99	15.15	98.76
10	95	96	5.81	98.23	81	>99	16.40	98.54

Run no.	*trans*-2-Octene				Styrene		Limonene		DHNT[g]	
	Conv. (%)	Sel. (%)	Mo leached (μg)	Mo content (%)	Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)
1	76	>99	11.05	99.85	43	>99	62	89	43	84
2	69	>99	5.08	99.78	43	>99	71	89	40	82
3	66	>99	5.26	99.71	49	>99	66	88	41	78
4	55	>99	4.11	99.66	45	>99	61	88	41	77
5	55	>99	4.25	99.60	41	>99	68	89	43	77
6	92	>99	7.04	99.51	85	>99	86	90	70	76
7	96	>99	8.23	99.40	90	>99	78	90	70	75
8	97	>99	9.07	99.28	88	>99	80	91	67	77
9	95	>99	7.81	99.18	75	>99	81	90	57	76
10	89	>99	5.04	99.11	72	>99	77	90	62	75

[a] Reaction conditions: 0.50 g catalyst, 10 mmol substrate, 12 mmol TBHP (36 wt.% TBHP in toluene), 90 °C. [b] Runs 1-5 with a reaction time of 7 h, runs 6-10 with a reaction time of 24 h. [c] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [d] Byproducts are cyclohexenol, cyclohexenone and diol. [e] Determined by ICP-AES by dissolving the reaction residues in 2 g of concentrated 65% HNO_3. [f] Percentage of Mo initially loaded on the catalyst. [g] DHNT: 1,2-dihydronaphthalene.

2.3.3.3 Epoxidation of liquid alkenes using TGMDA-MoO$_2$(TMHD)$_2$$^{0.50\%Mo}$ and TBHP

TGMDA-MoO$_2$(TMHD)$_2$$^{0.50\%Mo}$ was investigated in the epoxidation of liquid alkenes and the results are given in Table 8. In Table 8, it is seen that the conversions of liquid alkenes using TGMDA-MoO$_2$(TMHD)$_2$$^{0.50\%Mo}$ are lower than in the case of TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$ in the reactions with a reaction time of 24 h. In the epoxidation of cyclohexene, the conversions of cyclohexene vary between 64 and 76% and the selectivities to its oxirane are beyond 93%. Byproducts in the epoxidation of cyclohexene arise from allylic oxidation of cyclohexene and epoxide ring-opening. In the epoxidation of 1-octene, the conversions of 1-octene vary between 13 and 43%. However, the selectivities to its oxirane are beyond 99% and no other products were detected by GC-MS and GC-FID. In the epoxidation of styrene, the conversions of styrene vary between 67 and 76% similar to the epoxidation of cyclohexene, and the selectivities to its oxirane are beyond 99%. In five consecutive reactions, no molybdenum species leaching was detected by ICP-AES. This shows that TGMDA-$MoO_2(TMHD)_2^{0.50\%Mo}$ is not very active but extremely stable in the epoxidation of liquid alkenes. This conclusion is in agreement with the fact that $MoO_2(TMHD)_2$ has a lower activity than $MoO_2(acac)_2$ in the epoxidation of cyclohexene and $MoO_2(TMHD)_2$ has an excellent solubility in TGMDA. High solubility of $MoO_2(TMHD)_2$ in TGMDA leads to a homogeneous dispersion of molybdenum species in polymer network. Low conversion of liquid alkenes used results from the nature of molybdneum precursor and the low concentration of dissolved molybdenum species leached from the support. Another possible explanation for the lower conversions of liquid alkenes is lower molybdenum loading in this catalyst (0.50%).

Table 8: Epoxidation of liquid alkenes using TGMDA-$MoO_2(TMHD)_2^{0.50\%Mo}$ and TBHP[a].

Run no.	Cyclohexene			1-Octene			Styrene		
	Conv.[b] (%)	Sel.[c] (%)	Mo[d] leached (μg)	Conv. (%)	Sel. (%)	Mo leached (μg)	Conv. (%)	Sel. (%)	Mo leached (μg)
1	76	95	<1.00	13	>99	<1.00	68	>99	<1.00
2	69	97	<1.00	26	>99	<1.00	67	>99	<1.00
3	64	96	<1.00	21	>99	<1.00	68	>99	<1.00
4	75	93	<1.00	19	>99	<1.00	76	>99	<1.00
5	72	95	<1.00	43	>99	<1.00	67	>99	<1.00

[a] Reaction conditions: 0.50 g catalyst, 10 mmol substrate, 12 mmol TBHP (36 wt.% TBHP in toluene), 90 °C, 24 h. [b] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [c] Byproducts are cyclohexenol, cyclohexenone and diol. [d] Determined by ICP-AES by dissolving the reaction residues in 2 g of concentrated 65% HNO_3.

2.3.3.4 Epoxidation of liquid alkenes using TGMDA-$H_3Mo_{12}O_{40}P•xH_2O^{3.00\%Mo}$ and TBHP

TGMDA-$H_3Mo_{12}O_{40}P•xH_2O^{3.00\%Mo}$ was used as catalyst for the epoxidation of liquid alkenes and the results are shown in Table 9. In Table 9, it can be seen that the conversion of liquid alkenes is low. In the epoxidation of cyclohexene, the conversions of cyclohexene vary between 47 and 63% and the selectivities to its oxirane are beyond 93% (the formation of byproducts is suggested due to the allylic oxidation of cyclohexene and the epoxide ring-opening). In the epoxidation of 1-octene, the conversions of 1-octene vary between 25 and 40% and the selectivities to its oxirane are beyond 99%. No byproducts were detected by GC-MS and GC-FID. In the epoxidation of styrene, the conversions of styrene are 62-76% and the selectivities to its oxirane are beyond 99%. The epoxidation of 1-octene is more difficult than the epoxidation of cyclohexene and styrene using TGMDA-$H_3Mo_{12}O_{40}P•xH_2O^{3.00\%Mo}$ as catalyst. In five consecutive runs, no molybdenum species leaching was detected by ICP-AES. These results show that TGMDA-$H_3Mo_{12}O_{40}P•xH_2O^{3.00\%Mo}$ is moderately active but very stable in the epoxidation of liquid alkenes. As already mentioned, $H_3Mo_{12}O_{40}P•xH_2O$ can not be dissolved in TGMDA very well, but a high solubility can be obtained with the addition of methanol. Therefore, the low molybdenum species leaching is due to the high solubility of $H_3Mo_{12}O_{40}P•xH_2O$ in TGMDA and methanol leading to a homogeneous molybdenum species distribution in polymer network. Low conversions in the epoxidation of liquid alkenes probably arise from the low molybdenum species leaching during the reactions.

Table 9: Epoxidation of liquid alkenes using TGMDA-$H_3Mo_{12}O_{40}P{\bullet}xH_2O^{3.00\%Mo}$ and TBHP[a].

Run no.	Cyclohexene			1-Octene			Styrene		
	Conv.[b] (%)	Sel.[c] (%)	Mo[d] leached (µg)	Conv. (%)	Sel. (%)	Mo leached (µg)	Conv. (%)	Sel. (%)	Mo leached (µg)
1	63	95	<1.00	40	>99	<1.00	76	>99	<1.00
2	56	93	<1.00	33	>99	<1.00	65	>99	<1.00
3	47	95	<1.00	25	>99	<1.00	62	>99	<1.00
4	48	96	<1.00	38	>99	<1.00	66	>99	<1.00
5	50	94	<1.00	34	>99	<1.00	68	>99	<1.00

[a] Reaction conditions: 0.50 g catalyst, 10 mmol substrate, 12 mmol TBHP (36 wt.% TBHP in toluene), 90 °C, 24 h. [b] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [c] Byproducts are cyclohexenol, cyclohexenone and diol. [d] Determined by ICP-AES by dissolving the reaction residues in 2 g of concentrated 65% HNO_3.

2.3.3.5 Epoxidation of styrene using TGMDA-$W(OEt)_5^{1.50\%W}$ and TBHP

In order to compare with supported molybdenum catalysts, the tungsten catalyst TGMDA-$W(OEt)_5^{1.50\%W}$ was prepared and evaluated in the epoxidation of styrene with TBHP. The results are summarized in Table 10. Ten consecutive runs were carried out (runs 1-5 with a reaction time of 7 h and runs 6-10 with a reaction time of 24 h). The conversions of styrene in runs 1-5 vary between 41 and 44% and the conversions of styrene in runs 6-10 vary between 71 and 78%. The selectivities to its oxirane are beyond 99% and no byproducts were detected by GC-MS and GC-FID. In ten consecutive runs, the amount of tungsten species leached from the support can not be detected by ICP-AES. These results show that TGMDA-$W(OEt)_5^{1.50\%W}$ has a lower catalytic activity than TGMDA-$Mo(OEt)_5^{1.50\%Mo}$ and a high stability in the epoxidation of styrene with TBHP. Low tungsten species leaching is probably due to the high solubility of $W(OEt)_5$ in TGMDA and low conversions of styrene are maybe due to the low tungsten species leaching during the epoxidation reactions.

Table 10: Epoxidation of styrene using TGMDA-W(OEt)$_5^{1.50\%W}$ and TBHP[a].

Run no.[b]	Conversion[c] (%)	Selectivity[d] (%)	W[e] leached (μg)
1	44	>99	<3.00
2	38	>99	<3.00
3	42	>99	<3.00
4	41	>99	<3.00
5	41	>99	<3.00
6	74	>99	<3.00
7	71	>99	<3.00
8	78	>99	<3.00
9	75	>99	<3.00
10	77	>99	<3.00

[a] Reaction conditions: 0.50 g catalyst, 10 mmol styrene, 12 mmol TBHP (36 wt.% TBHP in toluene), 90 °C. [b] Runs 1-5 with a reaction time of 7 h, runs 6-10 with a reaction time of 24 h. [c] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [d] Determined by GC-MS and GC-FID. [e] Determined by ICP-AES by dissolving the reaction residues in 2 g of concentrated 65% HNO_3.

2.3.3.6 Epoxidation of liquid alkenes using TGMDA-Mo(OEt)$_5^{0.50\%Mo}$-W(OEt)$_5^{0.50\%W}$ and TBHP

In order to compare with epoxy resins containing only one metal type, the molybdenum/tungsten catalyst TGMDA-Mo(OEt)$_5^{0.50\%Mo}$-W(OEt)$_5^{0.50\%W}$ was investigated in the epoxidation of liquid alkenes with TBHP. The results are summarized in Table 11. It is seen that TGMDA-Mo(OEt)$_5^{0.50\%Mo}$-W(OEt)$_5^{0.50\%W}$ has a high catalytic activity in the epoxidation of liquid alkenes. In the epoxidation of cyclohexene, the conversions are beyond 95% and the selectivities to its oxirane are beyond 94% (the formation of byproducts is due to allylic oxidation of cyclohexene and epoxide ring-opening). In the epoxidation of 1-octene, the conversions of 1-octene vary between 70 and 78% and no byproducts were detected by GC-MS and GC-FID. In the epoxidation of styrene, the conversions vary between 85 and 97% and the selectivities to its oxirane are beyond 99%. Lower conversions are obtained in the epoxidation of 1-octene using this mixed metal catalyst compared to TGMDA-Mo(OEt)$_5^{1.50\%Mo}$. These results show that

TGMDA-Mo(OEt)$^{0.50\%Mo}$-W(OEt)$_5^{0.50\%W}$ exhibits a high long-term stability and catalytic activity in the epoxidation of liquid alkenes with TBHP.

Table 11: Epoxidation of liquid alkenes using TGMDA-Mo(OEt)$^{0.50\%Mo}$-W(OEt)$_5^{0.50\%W}$ and TBHP[a].

Run no.	Cyclohexene		1-Octene		Styrene	
	Conv.[b] (%)	Sel.[c] (%)	Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)
1	98	97	72	>99	97	>99
2	96	94	77	>99	92	>99
3	97	98	78	>99	90	>99
4	96	96	76	>99	92	>99
5	95	95	70	>99	91	>99

[a] Reaction conditions: 0.50 g catalyst, 10 mmol substrate, 12 mmol TBHP (36 wt.% TBHP in toluene), 90 °C, 24 h. [b] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [c] Byproducts are cyclohexenol, cyclohexenone and diol.

2.3.3.7 Epoxidation of cyclohexene using TGMDA-Ti(EH)$_4^{3.00\%Ti}$ and TBHP

Heterogeneous titanium catalysts such as Ti(IV)/SiO$_2$ and the titanium silicalite 1 (TS-1) are well known in the epoxidation reactions[31]. Therefore, TGMDA-Ti(EH)$_4^{3.00\%Ti}$ was evaluated in the epoxidation of cyclohexene using TBHP as oxidant. The results are summarized in Table 12. In Table 12, it is seen that the conversions of cyclohexene are low, only around 14% and the selectivities to its oxirane are beyond 92% (the formation of byproducts is due to allylic oxidation of cyclohexene and epoxide ring-opening). No titanium species leaching was detected by ICP-AES. These results show that TGMDA-Ti(EH)$_4^{3.00\%Ti}$ is slightly catalytically active but highly stable in the epoxidation of liquid alkenes using TBHP as oxidant.

Table 12: Epoxidation of cyclohexene using TGMDA-Ti(EH)$_4^{3.00\%Ti}$ and TBHP[a].

Run no.	Conversion[b] (%)	Selectivity[c] (%)	Ti[d] leached (µg)
1	14	92	<3.00
2	12	94	<3.00
3	12	93	<3.00
4	11	93	<3.00
5	15	94	<3.00

[a] Reaction conditions: 0.50 g catalyst, 10 mmol substrate, 12 mmol TBHP (36 wt.% TBHP in toluene), 90 °C, 24 h. [b] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [c] Byproducts are cyclohexenol, cyclohexenone and diol. [d] Determined by ICP-AES by dissolving the reaction residues in 2 g of concentrated 65% HNO_3.

2.3.3.8 Epoxidation of liquid alkenes using TGAP-Mo(EH)$_n^{1.50\%Mo}$ and TBHP

2.3.3.8.1 Comparison of different reaction systems

In order to compare TGAP-Mo(EH)$_n^{1.50\%Mo}$ with homogeneous Mo(EH)$_n$, the epoxidation of cyclohexene was investigated using TBHP as oxidant under different reaction conditions (Figure 14 and Table 13). TGAP-Mo(EH)$_n^{1.50\%Mo}$ provides a similar conversion of cyclohexene and higher selectivity to the corresponding oxirane compared to the homogeneous Mo(EH)$_n$ catalyst. Furthermore, the resin-based catalyst can be easily separated from the reaction mixture.

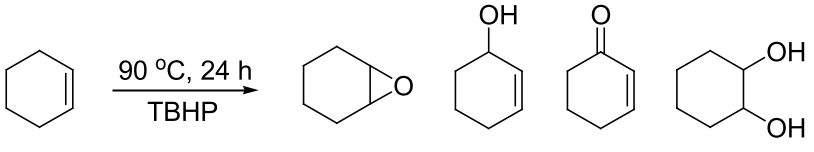


Figure 14: Epoxidation of cyclohexene with TBHP (possible byproducts include cyclohexenol, cyclohexenone and diol).

Table 13: Epoxidation of cyclohexene with TBHP under different reaction systems[a].

Entry	Catalyst	Conv.[b] (%)	Sel.[c] (%)
1	-	13	20
2	$Mo(EH)_n$ (0.05 g)	99	78
3	TGAP-$Mo(EH)_n^{1.50\%Mo}$ (0.50 g)	93	96

[a] Reaction conditions: 10 mmol substrate, 12 mmol TBHP (36 wt.% TBHP in toluene), 90 ^{o}C, 24 h. [b] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [c] Byproducts are cyclohexenol, cyclohexenone and diol determined by GC-MS and GC-FID.

2.3.3.8.2 Epoxidation of liquid alkenes using TGAP-$Mo(EH)_n^{1.50\%Mo}$ and TBHP

TGAP-$Mo(EH)_n^{1.50\%Mo}$ was investigated in the epoxidation of liquid alkenes with TBHP and the results are summarized in Table 14. Ten consecutive reactions were run (runs 1-5 with a reaction time of 7 h and runs 6-10 with a reaction time of 24 h).

In the epoxidation of cyclohexene, the conversions of cyclohexene vary between 53 and 82% in runs 1-5, and between 87 and 93% in runs 6-10, the selectivities to its oxirane are beyond 93% except the first and second runs. The amount of molybdenum in the reaction solutions is below 2.71 µg corresponding to 1 ppm. The lower conversion in the first run is probably due to an induction period where the molybdenum catalyst is activated[64]. Monometallic species are responsible for the epoxidation of alkenes as proposed by Sharpless[72,73] and Mimoun[74] using TBHP as oxidant. However, polyoxometallic species could be present in the polymer network[29,30]. Therefore, it is proposed that cleavage of Mo-O-Mo bridges in polymetallic species occurs and mononuclear Mo(VI) centres analogous to the structures proposed by Sharpless and Mimoun form during the reactions. In situ activation during the epoxidation reactions appears to occur and molybdenum species leach to the reaction solutions. Another possibility is that epoxy resins containing molybdenum species have an oxo-bridged polymetallic structure with both a Mo(V) and a Mo(VI) centre[64]. Therefore, the existence of Mo(V) species oxidized to active Mo(VI) species and the cleavage of the Mo-O-Mo bridges in polymetallic species to monometallic species by the mono-oxygen donor TBHP could lead to an induction period[64].

Cyclohexenol and cyclohexenone are produced due to allylic oxidation of cyclohexene. The formation of diol is probably due to epoxy ring opening. The amounts of molybdenum species leached from the catalyst to the reaction solutions are significant. In most cases, the catalytic activity of TGAP-Mo(EH)$_n^{1.50\%Mo}$ correlates with molybdenum species leaching. The higher the molybdenum species leaching, the higher the conversion of cyclohexene. This can be seen in runs 1-5 and runs 6-10. After the completion of ten consecutive runs, 99.77% of molybdenum initially loaded on the catalyst are still present for a long-term application.

In the epoxidation of 1-octene, the conversions of 1-octene in runs 1-5 are low and vary between 14 and 23%, and in runs 6-10 they increase to values between 57 and 66%. No byproducts were detected in the epoxidation of 1-octene with TBHP by GC-MS and GC-FID. The amount of molybdenum in the reaction solutions after the reactions is below 1.35 µg which corresponds to 0.35 ppm per run. It is suggested that the higher conversions of 1-octene in runs 6-10 result from the higher molybdenum species leaching and longer reaction time. After ten consecutive runs, 99.91% of molybdenum originally loaded on the support are retained. The allylic oxidation of 1-octene was not observed under the reaction conditions used. Compared to the epoxidation of cyclohexene, metal species leaching is lower and it can be seen that the leaching depends on the type of alkene.

In the epoxidation of styrene, the conversions of styrene in runs 1-5 vary between 63 and 77%, and in runs 6-10 vary between 90 and 95%. No byproducts were detected by GC-MS and GC-FID. No molybdenum species leaching was detected by ICP-AES. Maybe the extraction of molybdenum from the reaction residues is not complete.

In summary, TGAP-Mo(EH)$_n^{1.50\%Mo}$ exhibits excellent activity and stability in the epoxidation of liquid alkenes using TBHP as oxidant. After the completion of ten consecutive recycling runs, beyond 99.70% of molybdenum initially loaded on the support can be retained. The amount of molybdenum in the reaction solutions is below 3 µg corresponding to 0.75 ppm per run. TGAP-Mo(EH)$_n^{1.50\%Mo}$ can be isolated and recovered by simple filtration, then reused with fresh reactants without any treatments. According to the obtained results, a long-term application over weeks or months should be possible.

Table 14: Epoxidation of liquid alkenes using TGAP-Mo(EH)$_n^{1.50\%Mo}$ and TBHP[a].

	Cyclohexene				1-Octene				Styrene	
Run no.[b]	Conv.[c] (%)	Sel.[d] (%)	Mo[e] leached (µg)	Mo[f] content (%)	Conv. (%)	Sel. (%)	Mo leached (µg)	Mo content (%)	Conv. (%)	Sel. (%)
1	53	88	0.86	99.99	23	>99	0.34	99.99	77	>99
2	82	89	0.85	99.98	15	>99	0.21	99.99	71	>99
3	70	94	0.99	99.96	15	>99	0.22	99.99	63	>99
4	74	93	0.91	99.95	14	>99	0.21	99.99	74	>99
5	70	93	1.08	99.94	18	>99	0.52	99.98	68	>99
6	92	95	2.39	99.91	57	>99	1.25	99.97	93	>99
7	87	97	2.38	99.87	61	>99	1.04	99.95	94	>99
8	93	95	2.69	99.84	62	>99	1.35	99.94	90	>99
9	93	96	2.71	99.80	66	>99	1.08	99.92	94	>99
10	92	95	2.69	99.77	64	>99	0.89	99.91	95	>99

[a] Reaction conditions: 500 mg catalyst (particle size: 300-500 µm), 12 mmol TBHP (36 wt.% TBHP solution in toluene), 10 mmol substrate, 90 °C. [b] Runs 1-5 with a reaction time of 7 h, runs 6-10 with a reaction time of 24 h. [c] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [d] Byproducts are cyclohexenol, cyclohexenone and diol determined by GC-MS. [e] Determined by ICP-AES by dissolving the reaction residues in concentrated HNO_3. [f] Percentage of molybdenum initially loaded on the catalyst.

2.3.3.8.3 Long-term investigation on the epoxidation of cyclohexene using TGAP-Mo(EH)$_n^{1.50\%Mo}$ and TBHP

In order to obtain information about the activity and stability of the catalyst, a long-term observation of the catalytic performance is necessary to be carried out. The long-term activity and stability of TGAP-Mo(EH)$_n^{1.50\%Mo}$ in the epoxidation of cyclohexene using TBHP as oxidant at 90 °C were investigated and the results are summarized in Table 15. It is noted that runs 1-5 were conducted with a reaction time of 7 h, the following reactions were carried out with a reaction time of 24. The low conversion of cyclohexene in the first run shows that the catalyst used needs an induction period to become active. The low activity in the 11th run is due to an interruption of some months between run 10 and run 11.

In most cases, the conversion of cyclohexene is around 90% and the selectivity to its oxirane is higher than 93%. The byproducts are cyclohexenol, cyclohexenone (allylic oxidation of cyclohexene) and diol (epoxide ring-opening). The selectivity to diol is between 2 and 4%. It can be seen that molybdenum species leaching increases with the runs. Runs 6-10, the amount of molybdenum in the reaction solutions is between 2 and 3 µg, in runs 11-30, the amount of molybdenum in the reaction solutions lies in the range of 4 to 8 µg per run, in runs 31-40, the amount of molybdenum in the reaction solutions is beyond 10 µg per run. This shows that the catalyst gets instable and molybdenum species (probably soluble molybdenum oxo compounds) are easily released to the reaction solutions with the increase of reaction time. However, molybdneum loading on the catalyst after 40 reactions is still 96.19% of the original value, as determined by ICP-AES.

With respect to the relation of metal species leaching and catalytic activity, no conclusions can be drawn. In some cases, higher molybdenum species leaching leads to higher conversions of cyclohexene, but in other cases, higher conversion of cyclohexene can be obtained even with lower metal species leaching. Therefore, any conclusions drawn from correlations of activity with metal species leaching and recycling have to be tentative.

According to the obtained results, TGAP-Mo(EH)$_n^{1.50\%Mo}$ shows a high catalytic activity and long-term stability in the epoxidation of cyclohexene with TBHP and can be used in at least 40 runs with a total reaction time of 875 h without loss of activity.

Table 15: Long-term investigation on the epoxidation of cyclohexene using TGAP-Mo(EH)$_n^{1.50\%Mo}$ and TBHP[a].

Run no.[b]	Conv.[c] (%)	Sel.[d] (%)	Mo[e] leached (µg)	Mo[f] content (%)	Run no.	Conv. (%)	Sel. (%)	Mo leached (µg)	Mo content (%)
1	53	88	0.86	99.99	21	89	93	7.36	98.88
2	82	89	0.85	99.98	22	86	95	5.31	98.81
3	70	94	0.99	99.96	23	90	96	6.26	98.73
4	74	93	0.91	99.95	24	82	93	6.24	98.65
5	70	93	1.08	99.94	25	90	94	8.27	98.54
6	92	95	2.39	99.91	26	93	95	5.51	98.47
7	87	97	2.38	99.87	27	89	93	5.94	98.39
8	93	95	2.69	99.84	28	87	95	4.60	98.33
9	93	96	2.71	99.80	29	89	95	7.46	98.23
10	92	95	2.69	99.77	30	86	94	5.81	98.15
11	73	94	8.38	99.66	31	93	97	11.13	98.00
12	84	95	4.69	99.60	32	94	97	11.28	97.85
13	92	96	5.24	99.53	33	96	95	16.90	97.63
14	93	95	8.24	99.42	34	94	97	14.75	97.44
15	89	96	5.70	99.35	35	91	97	12.71	97.27
16	93	96	5.13	99.28	36	93	97	12.88	97.10
17	93	97	6.38	99.20	37	95	95	17.19	96.87
18	92	97	5.43	99.13	38	93	96	12.51	96.71
19	91	97	6.16	99.05	39	95	97	13.38	96.53
20	96	96	5.77	98.98	40	97	94	25.84	96.19

[a] Reaction conditions: 500 mg catalyst (particle size: 300-500 µm), 10 mmol cyclohexene, 12 mmol TBHP (36 wt.% TBHP/toluene), 90 °C. [b] The catalyst was used in the first 5 runs with a reaction time of 7 h, the following 35 runs were conducted with a reaction time of 24 h. [c] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [d] Byproducts are cyclohexenol, cyclohexenone and diol determined by GC-MS. [e] Determined by ICP-AES by dissolving the reaction residues in concentrated 65% HNO_3. [f] Percentage of molybdneum initially loaded on the catalyst.

2.3.3.8.4 Hot filtration test in the epoxidation of cyclohexene using TGAP-Mo(EH)$_n^{1.50\%Mo}$ and TBHP

Hot filtration test was carried out to distinguish homogeneous or heterogeneous catalysis. The filtrates from runs 21-30 were used as samples and equivalent amounts of fresh reactants were added after separating from the solid catalyst particles. The component content in the reaction solutions was analyzed by GC-FID using a standard calibration curve prior to the start of the filtration reactions. After the completion of filtration test, the component content was analyzed again. The contribution of homogeneous catalysis can be calculated by this method. The results are given in Table 16.

In Table 16, it can be seen that the conversion of cyclohexene is mainly due to homogeneous catalysis resulting from the leached, dissolved metal species. Only a little conversion is due to true surface catalysis. However, as shown in Table 15, the amount of molybdenum in the reaction solutions is between 4 and 9 µg which corresponds to 2 ppm. Maybe the amount is higher and redeposition occurs.

With respect to the discussion of reaction mechanism, Sherrington[65] claimed that the major catalytic component is molybdenum species heterogenized on the polymer and molybdneum species leaching is not responsible for the observed decay in activity on recycling the PBI-Mo catalyst system. They proposed a blockage of active sites by accumulation of byproducts. Therefore, they gave the conclusion that the imidazole ligand on the polymer appeared to bind the Mo centres very effectively. However, the detection limit of ICP-AES measurements was very high and no metal enrichment techniques were employed.

In summary, the conversion of cyclohexene attributes to homogeneous and heterogeneous catalysis and homogeneous catalysis plays a more important role in the epoxidation of cyclohexene using TGAP-Mo(EH)$_n^{1.50\%Mo}$ and TBHP. In most cases, the conversion of cyclohexene correlates to the amount of molybdenum species leached from the support into the reaction solutions.

Table 16: Hot filtration test in the epoxidation of cyclohexene using TGAP-Mo(EH)$_n^{1.50\%Mo}$ and TBHP[a].

Run no.[b]	Conversion (%) from dissolved active species[c]
21	98
22	86
23	96
24	74
25	96
26	96
27	98
28	94
29	92
30	98

[a] Reaction conditions: 500 mg catalyst (particle size: 300-500 μm), 10 mmol cyclohexene, 12 mmol TBHP (36 wt.% TBHP/toluene), 90 °C, 24 h. [b] The filtrates from runs 21-30 in the long-term test of cyclohexene epoxidation were used (see Table 15). [c] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard.

2.3.3.9 Epoxidation of liquid alkenes using Novolac-Mo(EH)$_n^{1.50\%Mo}$ and TBHP

In order to compare with TGAP-Mo(EH)$_n^{1.50\%Mo}$ and investigate the influence of the resin type, Novolac-Mo(EH)$_n^{1.50\%Mo}$ was evaluated in the epoxidation of liquid alkenes using TBHP. The results are summarized in Table 17.

In the epoxidation of cyclohexene, runs 1-5 were carried out at 90 °C with a reaction time of 7 h and runs 6-10 were carried out at 90 °C with a reaction time of 24 h. In runs 1-5, the conversions of cyclohexene vary between 71 and 90% and the selectivities to its oxirane are beyond 91% (byproducts are due to allylic oxidation of cyclohexene and epoxide ring-opening). It can be seen that higher molybdenum species leaching leads to higher cyclohexene conversion. The amount of molybdenum in the reaction solutions is below 3.8 μg and corresponds to 1 ppm per run. In runs 6-10, the conversions of cyclohexene increase with the reaction time and are beyond 90%, the selectivities to its oxirane also increase. The amount of molybdenum in the reaction solutions is below 4 μg corresponding to 1 ppm per run. After ten consecutive reaction runs, 99.66% of molybdenum initially loaded on the support are retained and make a long-term application possible.

In the epoxidation of 1-octene, runs 1-5 were carried out at 90 °C with a reaction time of 7 h and runs 6-10 were carried out at 90 °C with a reaction time of 24 h. In runs 1-5, the conversions of 1-octene are lower than in the case of cyclohexene under identical reaction conditions and are between 25 and 42%. No byproducts were detected by GC-MS and GC-FID. The amount of molybdenum in the reaction solutions is below 2.3 µg corresponding to 0.5 ppm per run. In runs 6-10, the conversions of 1-octene increase so much and can reach 80%. The amount of molybdenum in the reaction solutions also increases significantly. This is different from other epoxy resins containing molybdenum species in the epoxidation of 1-octene. In the epoxidation of liquid alkenes using other molybdenum catalysts based on epoxy resins, molybdneum species leaching in the epoxidation of cyclohexene is higher than in the case of 1-octene. Maybe there is an influence from $Mo(EH)_n$ and Novolac matrix. Although there is molybdenum species leaching from the support, after ten consecutive reaction runs, 98.98% of molybdenum initially loaded on the support can be retained.

In the epoxidation of styrene, runs 1-5 were carried out at 90 °C with a reaction time of 7 h and runs 6-10 were carried out at 90 °C with a reaction time of 24 h. In runs 1-5, the conversions of styrene are around 80%. The conversions increase up to 99% in runs 6-10. Styrene is almost quantitatively converted to the corresponding oxirane. The selectivities to its oxirane are still high and no byproducts were observed. The metal species leaching could not be determined, maybe the extraction of molybdenum from the reaction residues was not complete.

In summary, Novolac-$Mo(EH)_n^{1.50\%Mo}$ shows a higher catalytic activity than TGAP-$Mo(EH)_n^{1.50\%Mo}$ together with a higher molybdenum species leaching. A long-term application is over weeks or months should be possible.

Table 17: Epoxidation of liquid alkenes using Novolac-Mo(EH)$_n^{1.50\%Mo}$ and TBHP[a].

Run no.[b]	Cyclohexene				1-Octene				Styrene	
	Conv.[c] (%)	Sel.[d] (%)	Mo[e] leached (μg)	Mo[f] content (%)	Conv. (%)]	Sel. (%)	Mo leached (μg)	Mo content (%)	Conv. (%)	Sel. (%)
1	90	94	3.74	99.95	42	>99	2.23	99.97	88	>99
2	84	94	2.10	99.92	30	>99	2.27	99.94	86	>99
3	77	94	1.44	99.90	28	>99	2.25	99.91	83	>99
4	71	91	0.90	99.89	28	>99	2.26	99.88	84	>99
5	72	93	1.19	99.86	25	>99	1.93	99.85	85	>99
6	92	96	2.93	99.84	74	>99	10.26	99.72	>99	>99
7	93	95	3.48	99.79	81	>99	12.48	99.55	>99	>99
8	91	96	3.56	99.74	80	>99	11.65	99.40	>99	>99
9	93	95	2.97	99.70	82	>99	14.36	99.20	>99	>99
10	94	95	3.59	99.66	85	>99	16.89	98.98	>99	>99

[a] Reaction conditions: 500 mg catalyst (particle size: 300-500 μm), 12 mmol TBHP (36 wt.% TBHP solution in toluene), 10 mmol substrate, 90 °C. [b] Runs 1-5 with a reaction time of 7 h, runs 6-10 with a reaction time of 24 h. [c] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [d] Byproducts are cyclohexenol, cyclohexenone and diol determined by GC-MS. [e] Determined by ICP-AES by dissolving the reaction residues in concentrated HNO_3. [f] Percentage of molybdenum initially loaded on the catalyst.

2.3.3.10 Epoxidation of 3-butene-2-ol using TGMDA-VO(OPr)$_3^{1.50\%V}$ and TBHP

Vanadyl catalysts are very effective in the epoxidation of allylic alcohols[69,70] with TBHP. Therefore, TGMDA-VO(OPr)$_3^{1.50\%V}$ was investigated in the epoxidation of 3-butene-2-ol using TBHP as oxidant at 90 °C with a reaction time of 7 h. The results are given in Table 18. The conversions of 3-butene-2-ol vary between 62 and 74%. No byproducts were detected by GC-MS and GC-FID. Unfortunately, high vanadium species leaching was observed. It can be seen that there is a relation between vanadium species leaching and the conversion of 3-butene-2-ol. The conversion of 3-butene-2-ol increases with the increase of vanadium species leaching. High vanadium species leaching is probably due to the low solubility of $VO(OPr)_3$ in TGMDA that leads to inhomogeneous distribution of vanadium species and poor bonding of vanadium species to the polymer network. Leadbeater et al. reported that microencapsulated $VO(acac)_2$ (MC-$VO(acac)_2$) was used as a catalyst for the epoxidation of allylic alcohols using TBHP as oxidant[70]. They claimed that MC-$VO(acac)_2$ is reusable without significant loss of activity. However, the amount of vanadium in the reaction solutions in four consecutive runs with a reaction time of 2.5 h is always beyond 118 ppm[70] per run and higher than in the case of epoxy resins containing vanadium species (the amount of vanadium in the reaction solutions is below 65 ppm per run).

Table 18: Epoxidation of 3-butene-2-ol using TGMDA-VO(OPr)$_3$$^{1.50\%V}$ and TBHP[a].

Run no.	Conv. [b] (%)	Sel.[c] (%)	V[d] leached (µg)	V[e] content (%)
1	62	>99	193	97.43
2	66	>99	192	94.87
3	74	>99	258	91.43
4	70	>99	181	89.00
5	65	>99	173	86.71

[a] Reaction conditions: 500 mg catalyst (particle size: 300-500 µm), 10 mmol 3-butene-2-ol, 12 mmol TBHP (36 wt.% TBHP/toluene), 90 °C, 7 h. [b] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [c] Determined by GC-MS. [d] Determined by ICP-AES by dissolving the reaction residues in concentrated 65% HNO_3. [e] Percentage of vanadium initially loaded on the catalyst.

2.3.3.11 Epoxidation of allyl alcohol using TGAP-V(NAPH)$_n$$^{1.00\%V}$ and CHP

In order to decrease the metal species leaching, TGAP-V(NAPH)$_n$$^{1.00\%V}$ was prepared via homopolymerization of TGAP using vanadium naphthenate (vanadium naphthenate in naphthenic acid containing 2.8% V) as initiator and evaluated in the epoxidation of allyl alcohol. In order to compare with TGMDA-VO(OPr)$_3$$^{1.50\%V}$, TBHP should be used as oxidant to be consistent with the reaction conditions in the epoxidation of 3-butene-2-ol using TGMDA-VO(OPr)$_3$$^{1.50\%V}$. However, the retention time of TBHP in GC-FID is very close to the retention time of allyl alcohol and it is not clear to distinguish the difference. Therefore another organic hydroperoxide - cumyl hydroperoxde (CHP) was chosen as oxidant for the epoxidation of allyl alcohol. The results are given in Table 19.

In five consecutive runs, the conversions of allyl alcohol are between 70 and 81%, the selectivities to its oxirane are beyond 99% and no byproducts were detected by GC-MS and GC-FID, vanadium species leaching using TGAP-V(NAPH)$_n^{1.00\%V}$ is much lower than in the case of TGMDA-VO(OPr)$_3^{1.50\%V}$ and the amount of vanadium in the reaction solutions varies between 15 and 129 µg per run. The amount of vanadium in the reaction solutions decreases with the reaction runs (11.73 ppm, 11.10 ppm, 3.82 ppm, 3.82 ppm, 1.36 ppm, respectively) and it is lower than using the catalyst reported by Leadbeater[70]. After five consecutive runs with a reaction time of 7 h at 90 °C, 95.32% of vanadium originally loaded on the support are retained.

Table 19: Epoxidation of allyl alcohol using TGAP-V(NAPH)$_n^{1.00\%V}$ and CHP[a].

Run no.	Conv. [b] (%)	Sel.[c] (%)	V[d] leached (µg)	V[e] content (%)
1	74	>99	129	97.42
2	70	>99	122	94.98
3	73	>99	43	94.12
4	81	>99	42	93.28
5	77	>99	15	92.98

[a] Reaction conditions: 500 mg catalyst (particle size: 300-500 µm), 10 mmol allyl alcohol, 12 mmol cumyl hydroperoxide (17.6 wt.% in toluene and cumene), 90 °C, 7 h. [b] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [c] Determined by GC-MS. [d] Determined by ICP-AES by dissolving the reaction residues in concentrated 65% HNO_3. [e] Percentage of vanadium initially loaded on the catalyst.

2.3.3.12 Epoxidation of cyclohexene using ERL4221/HMPA-Mo(EH)$_n^{1.50\%Mo}$ and TBHP

In order to compare with epoxy resins containing transition metal species prepared via homopolymerization of the epoxy resins, ERL4221/HMPA-Mo(EH)$_n^{1.50\%Mo}$ was prepared via polyaddition using HMPA and Mo(EH)$_n$ as hardener and accelerator and evaluated in the epoxidation of cyclohexene using TBHP as oxidant. The results are summarized in Table 20.

In the epoxidation of cyclohexene using ERL4221/HMPA-Mo(EH)$_n^{1.50\%Mo}$ and TBHP, the reactions were carried out at 90 °C with a reaction time of 24 h. The conversions of cyclohexene are beyond 98%, the selectivities to its oxirane are beyond 92%, other products are cyclohexenol, cyclohexenone arising from allylic oxidation of cyclohexene and diol arising from the epoxide ring-opening. The amount of molybdenum in the reaction solutions is comparatively high and beyond 10 ppm per run. The amount of molybdenum in the reaction solutions using epoxy resins containing molybdenum species prepared via homopolymerization of the epoxy resins is below 3 ppm per run. Higher molybdenum species leaching reflects that HMPA has an important influence on the chemical and thermal stability of obtained materials. In addition, higher conversion of cyclohexene is proposed to result from more dissolved active molybdenum species in the reaction solutions. The curing of epoxy resins via homopolymerization seems to be the superior method for the immobilization of active transition metal species.

Table 20: Epoxidation of cyclohexene using ERL4221/HMPA-Mo(EH)$_n^{1.50\%MO}$ and TBHP[a].

Run no.	Conv.[b] (%)	Sel.[c] (%)	Mo[d] leached (µg)	Mo[e] content (%)
1	98	93	48.72	99.35
2	98	95	46.34	98.73
3	99	95	42.55	98.16
4	99	96	41.91	97.60
5	99	92	40.08	97.07

[a] Reaction conditions: 500 mg catalyst (particle size: 300-500 µm), 12 mmol TBHP (36 wt.% TBHP solution in toluene), 10 mmol cyclohexene, 90 °C, 24 h. [b] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [c] Byproducts are cyclohexenol, cyclohexenone and diol determined by GC-MS. [c] Determined by ICP-AES by dissolving the reaction residues in concentrated HNO_3. [e] Percentage of molybdenum initially loaded on the catalyst.

2.3.4 Summary

In the epoxidation of liquid alkenes, epoxy resins containing transition metal species were investigated using organic hydroperoxides as oxidants. Epoxy resins containing molybdenum species prepared via homopolymerization of epoxy resins show a better long-term stability than those prepared via polyaddition of epoxy resins and anhydrides. The supported molybdenum catalysts TGMDA-Mo(OEt)$_5^{1.50\%Mo}$, TGAP-Mo(EH)$_n^{1.50\%Mo}$ and Novolac-Mo(EH)$_n^{1.50\%Mo}$ exhibit good catalytic activity and long-term stability. Epoxy resins containing titanium and tungsten species do not display as high activities as molybdenum species-containing systems. In the epoxidation of allylic alcohols, TGMDA-VO(OPr)$_3$$^{1.50\%V}$ and TGAP-V(NAPH)$_n$$^{1.00\%V}$ show good catalytic activity but higher vanadium species leaching using TBHP or CHP. The metal species leaching depends on the nature of investigated liquid alkenes using TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$ as catalyst. Among the investigated liquid alkenes, 1-octene is more difficult to be epoxidized by TBHP than other alkenes. The byproducts result from allylic oxidation of cyclohexene and epoxide ring-opening in the epoxidation of cyclohexene using TBHP. In the epoxidation of (R)-(+)-limonene, the double bond in the ring is mainly epoxidized and byproducts are the dioxirane and products arising from isomerization and allylic oxidation. Using other liquid alkenes such as 1-octene, *trans*-2-octene and styrene, the selectivities to their corresponding oxiranes are all beyond 99%. ICP-AES analysis of transition metals in the recycled reaction solutions shows that the amount of metals in the reaction solutions is extremely low using epoxy resins containing *d*-block metal species as catalysts. A long-term test in the epoxidation of cyclohexene exhibits that TGAP-Mo(EH)$_n$$^{1.50\%Mo}$ is highly stable and can be used over a period of at least 875 h. Hot filtration test shows that the catalytic activity is due to homogeneous catalysis in combination with surface catalysis. In most cases, the conversions of liquid alkenes correspond to the metal species leaching. The higher the metal species leaching, the higher the alkene conversion.

Epoxy resins containing Mo, W, Ti or V species can be used as catalysts directly and do not need any activation and other further treatments. The catalysts can be easily separated by simple filtration and reused without any treatments. The contamination of reaction products by transition metal species can be minimized. This shows that the immobilization of active metal species on epoxy resins via homopolymerization is a reliable and feasible method and obtained materials are highly active and long-term stable in the epoxidation of liquid alkenes using organic hydroperoxides as oxidants.

2.4 Epoxy resins containing molybdenum species for the epoxidation of propene

2.4.1 Developments of propene epoxidation catalysts

Propene oxide, which is also known as propylene oxide, methyloxirane, or epoxypropane, is one of the most important starting materials in the chemical industry. In 1999, the total production for propene oxide amounted to ~5.8 million tons per year[77]. This market is annually growing by ~4-5%[77]. The major application of propene oxide is in the production of polyether polyols or polyglycol ethers for polyurethane foams. The second and third largest applications are in the production of propene glycols (30%) and propene glycol ethers (4%), respectively[78]. Propene glycols are mainly used in the production of polyesters, whereas propene glycol ethers are primarily used as solvents.

The simplest oxirane, ethylene oxide, is manufactured by vapor-phase oxidation of ethylene with air or oxygen over a heterogeneously supported silver catalyst. Unfortunately, this method is not applicable to propene, which gives only low yields of propene oxide owing to competing oxidation of allylic C-H bonds. Propene oxide is currently produced using two different types of commercial processes: the chlorohydrin process (Figure 15) and the hydroperoxide process (Figure 16).

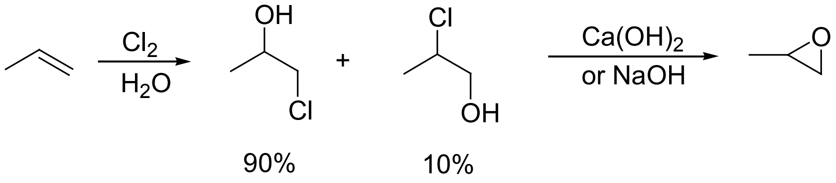


Figure 15: Propene epoxidation using the chlorohydrin process.

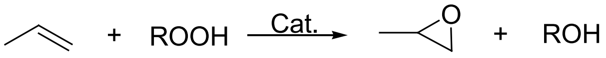


Figure 16: Propene epoxidation using the hydroperoxide process.

In 1999, the production capacity was distributed evenly between these two processes. However, because of the environmental impacts of the chlorohydrin process, the most recently built plants are all using hydroperoxide process technologies. Currently, two variants of the hydroperoxide process are applied commercially[79,80]. The first is the propene oxide-styrene monomer (SMPO or Shell) process[81]. In this process, a heterogeneous Ti(IV)/SiO_2 catalyst is used with ethylbenzene hydroperoxide (EBHP) in a continuous, fixed-bed operation. Ethylbenzene is oxidized to EBHP, which reacts with propene to produce propene oxide and α-phenyl ethanol. The α-phenyl ethanol is then dehydrated to produce styrene (Figure 17).

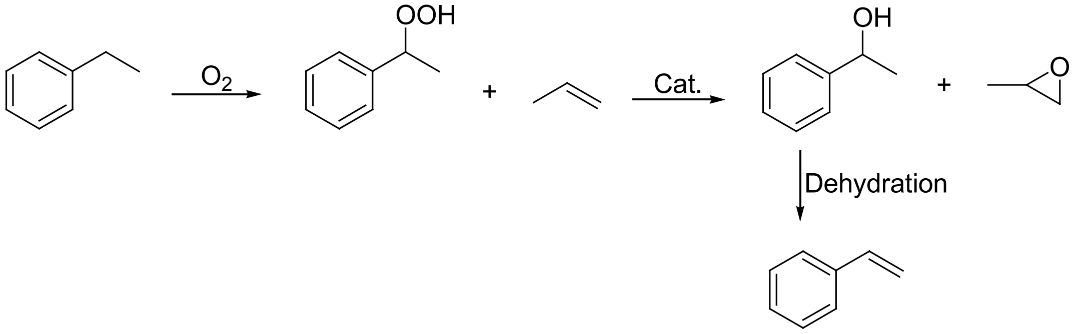


Figure 17: Propene epoxidation in SMPO (Shell) process.

The second process in use is the propene oxide-*tert*-butyl alcohol (PO-TBA, ARCO) process[82]. In this process, molybdenum compounds are used in combination with *tert*-butyl hydroperoxide (TBHP). Isobutane is oxidized to TBHP, which reacts with propene to produce propene oxide and *tert*-butyl alcohol. This can be dehydrated to isobutene or converted directly with methanol to methyl-*tert*-butyl ether (MTBE), a high-octane component for gasoline (Figure 18).

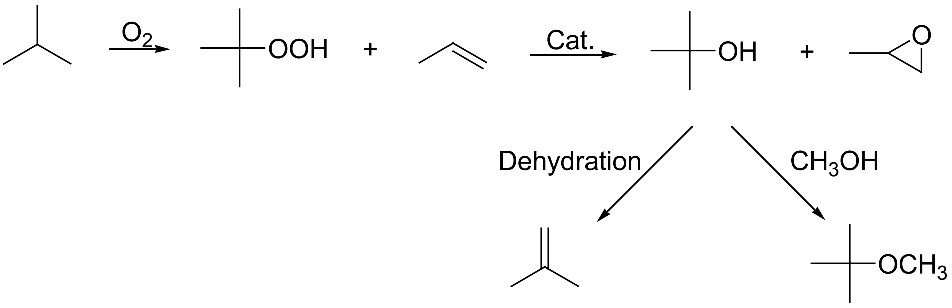


Figure 18: Propene epoxidation in ARCO process.

Although other combination processes with O_2 or air are possible, no others have been applied so far. Other possibilities include, for example, acetaldehyde to acetic acid, 2-propanol to acetone, isopentane (via *tert*-pentyl alcohol) to isoprene, cumene (via dimethylphenyl methanol) to α-methylstyrene, and cyclohexene (via cyclohexanol) to cyclohexanone.

A recent development in the production of propene oxide is the use of hydrogen peroxide (HPPO process; titanium silicalite TS-1 as catalyst) produced in an integrated process from molecular oxygen[79]. Haruta et al. have reported vapor-phase epoxidation of propene using H_2 and O_2 over Au/Ti-MCM-48[83]. Different tungsten-containing catalysts have been prepared using H_2O_2 directly[84] or produced in one step for the epoxidation of propene[85]. Beckman reported that H_2O_2 can be produced in CO_2 for the direct synthesis of propene oxide using Pd-TS-1[86]. Propene can also be epoxidized to propene oxide over Pd-modified-MCM-22[87], Ti-modified silicalite catalysts[88] or a catalyst system containing palladium and a peroxyheteropoly compound[89] in methanol. In addition, a conceptual process for the epoxidation of propene using molten alkali-nitrate salts has also been developed[90]. Sherrington et al. reported a series of polymer-supported molybdenum catalysts such as polybenzimidazole-supported molybdenum(VI) (PBI-Mo)[91,92], poly(glycidylmethacrylate)-2-aminomethyl pyridine-supported molybdenum(VI) (PGMA-AMP-Mo)[92], chloromethylated polystyrene-2-pyridyl-2-imidazole-supported-molybdenum(VI) (Ps-PyIm-Mo)[92], poly(glycidylmethacrylate)-2-pyridyl-2-imidazole-supported molybdenum(VI) (PGMA-PyIm-Mo)[92], chloromethylated polystyrene-5-

benzimidazolecarboxylate-supported molybdenum(VI) (Ps-5BzCO2-Mo)[92] and chloromethylated polystyrene-N-(2-hydroxypropyl)-aminomethyl-2-pyridine-supported moylybdenum(VI) (Ps-HPP-Mo)[92] for the epoxidation of propene using TBHP as the oxygen source. All supported molybdenum complexes were prepared using a ligand exchange procedure by refluxing $MoO_2(acac)_2$ with the respective polymer in toluene.

2.4.2 Epoxy resins containing molybdenum species for the epoxidation of propene using TBHP

A series of epoxy resins containing molybdenum species prepared via homopolymerization using molybdenum complexes as polymerization initiators were evaluated in the epoxidation of propene using TBHP as oxidant. These epoxy resins containing molybdenum species include TGMDA-$Mo(OEt)_5^{1.50\%Mo}$, TGAP-$Mo(OEt)_5^{1.42\%Mo}$-$Pd(PPh_3)_4^{0.50\%Pd}$, Novolac-$Mo(EH)_n^{1.50\%Mo}$, TGAP-$Mo(EH)_n^{1.50\%Mo}$ and TGAP/PT30-$Mo(OEt)_5^{0.75\%Mo}$ (A resin blend of TGAP and PT30 was cured using $Mo(OEt)_5$ as polymerization initiator with a molybdenum loading of 0.75%. After the curing of the resin blend, the obtained solid plate was crushed and then the obtained solid particle material was annealed and sieved and named as TGAP/PT30-$Mo(OEt)_5^{0.75\%Mo}$). The structure of PT30 and the curing process of cyanate ester monomers are shown in later. The catalytic epoxidation reactions were carried out in an autoclave, employing conditions similar to the epoxidation of liquid alkenes. The selectivity to propene oxide was determined by GC-FID and the yield of propene oxide was obtained based on the consumption of TBHP determined by iodometric titration[76]. Reaction solutions were assayed for molybdenum using ICP-AES.

2.4.2.1 Epoxidation of propene using TGMDA-$Mo(OEt)_5^{1.50\%Mo}$

TGMDA-$Mo(OEt)_5^{1.50\%Mo}$ was investigated in the epoxidation of propene with TBHP at 90 ^{o}C with a reaction time of 24 h and the results are summarized in Table 21. TGMDA-$Mo(OEt)_5^{1.50\%Mo}$ was pre-used in five consecutive runs to reach a stable performance. Propene oxide was the only oxidation product detected by GC-FID. In five consecutive runs, the yields of propene oxide vary between 67 and 78%. The amount of molybdenum in the reaction solutions is below 34 µg which corresponds to below 2.65 ppm per run and decreases to 5 µg in run 5. In the first run, there was much more molybdenum species present in the reaction solution compared to the following reactions. Probably some weakly bound species were removed preferentially. In the fifth run, the amount of molybdenum in the reaction solution is only 0.36 ppm. After the completion of five recycling reactions, 99.07% of original molybdenum loaded on the catalyst are retained on the catalyst. The catalyst can be isolated by simple filtration and reused without any treatments. The epoxidation of propene has been investigated using PBI-Mo by Sherrington[91,92]. In the first run, 2.9% of molybdenum species originally present on the catalyst leached into the reaction solution. In the following nine runs, they claimed that no molybdenum species leaching was detected (the detection limit was 0.5 ppm). The extremely low levels of molybdenum species leaching observed during recycling were explained by the strong binding of molybdenum species to the imidazole functionalities present in the PBI resin. They observed an increase in activity and they proposed that this was due to the increase of the number of active Mo^{VI} sites available arising from longer exposure of PBI-Mo to TBHP.

Table 21: Epoxidation of propene using TGMDA-$Mo(OEt)_5^{1.50\%Mo}$ and TBHP[a].

Run no.	Yield[b] (%)	Sel.[c] (%)	Mo[d] leached (µg)	Mo[e] content (%)
1	75	>99	33.59	99.41
2	72	>99	12.54	99.33
3	78	>99	21.26	99.19
4	70	>99	13.88	99.10
5	67	>99	4.71	99.07

[a] Reaction conditions: 80 ml steel autoclave, 8 bar starting pressure of propene, 50 mmol TBHP (34.5 wt.% solution of TBHP in a mixture of toluene and dodecane), 1.00 g catalyst (particle size: 150-300 µm) (pre-used in 5 runs), 20-25 bar operating pressure, 90 °C, 24 h. [b] Yields are based on TBHP consumption determined by iodometric titration. [c] Determined by GC-FID and GC-MS. [d] Determined by ICP-AES analysis by dissolving the reaction residues in concentrated HNO_3. [e] Percentage of molybdenum originally loaded on the catalyst.

2.4.2.2 Epoxidation of propene using TGAP-$Mo(OEt)_5^{1.42\%Mo}$-$Pd(PPh_3)_4^{0.50\%Pd}$

In order to compare with epoxy resins containing only molybdenum species, TGAP-$Mo(OEt)_5^{1.42\%Mo}$-$Pd(PPh_3)_4^{0.50\%Pd}$ was used as catalyst for the epoxidation of propene in the presence of TBHP at 90 °C with a reaction time of 24 h. The results are given in Table 22. In five continuous runs, propene oxide is the only product detected by GC-FID. The yields of propene oxide vary between 48 and 73% and the amounts of molybdenum in the reaction solutions decrease with reaction runs and vary between 3 and 20 µg corresponding to 0.23 and 1.56 ppm molybdenum in the reaction solutions. Molybdenum species leaching is lower than in the case of TGMDA-$Mo(OEt)_5^{1.50\%Mo}$, it is probable that the addition of Pd species has an effect on the obtained material. After five consecutive runs, 99.69% of molybdenum originally present on the support can be retained on the catalyst and a long-term application should be possible.

Table 22: Epoxidation of propene using TGAP-$Mo(OEt)_5^{1.42\%Mo}$-$Pd(PPh_3)_4^{0.50\%Pd}$ and TBHP[a].

Run no.	Yield[b] (%)	Sel.[c] (%)	Mo[d] leached (µg)	Mo[e] content (%)
1	73	>99	19.79	99.87
2	62	>99	14.38	99.78
3	69	>99	7.58	99.73
4	55	>99	3.08	99.71
5	48	>99	3.02	99.69

[a] Reaction conditions: 80 ml steel autoclave, 8 bar starting pressure of propene, 50 mmol TBHP (34.5 wt.% solution of TBHP in a mixture of toluene and dodecane), 1.00 g catalyst (particle size: 150-300 µm), 20-25 bar operating pressure, 90 °C, 24 h. [b] Yields are based on TBHP consumption determined by iodometric titration. [c] Determined by GC-FID and GC-MS. [d] Determined by ICP-AES analysis by dissolving the reaction residues in concentrated HNO_3. [e] Percentage of molybdenum originally loaded on the catalyst.

2.4.2.3 Epoxidation of propene using Novolac-$Mo(EH)_n^{1.50\%Mo}$

In the epoxidation of liquid alkenes using TBHP, Novolac-$Mo(EH)_n^{1.50\%Mo}$ exhibits a high catalytic activity. Therefore, Novolac-$Mo(EH)_n^{1.50\%Mo}$ was also evaluated in the epoxidation of propene. Recycling reactions were carried out at 90 °C with a reaction time of 24 h. The results are summarized in Table 23. In five consecutive runs, the yields of propene oxide vary between 55 and 88%. No byproducts were detected by GC-FID. The amount of molybdenum present in the reaction solutions is between 16 and 117 µg corresponding to 1.25 and 9.12 ppm. Leaching is much higher than in the case of TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$ and TGAP-Mo(OEt)$_5$$^{1.42\%Mo}$-Pd(PPh$_3$)$_4$$^{0.50\%Pd}$, especially in the first run. Molybdenum 2-ethylhexanoate contains much 2-ethylhexanoic acid and this probably interferes with the resin crosslinking. Despite higher molybdenum species leaching, 98.60% of molybdenum originally present on the support can be retained after 5 reactions.

Table 23: Epoxidation of propene using Novolac-Mo(EH)$_n$$^{1.50\%Mo}$ and TBHP[a].

Run no.	Yield[b] (%)	Sel.[c] (%)	Mo[d] leached (µg)	Mo[e] content (%)
1	88	>99	117.00	99.22
2	63	>99	29.16	99.03
3	72	>99	23.18	98.87
4	55	>99	16.27	98.76
5	64	>99	23.98	98.60

[a] Reaction conditions: 80 ml steel autoclave, 8 bar starting pressure of propene, 50 mmol TBHP (34.5 wt.% solution of TBHP in a mixture of toluene and dodecane), 1.00 g catalyst (particle size: 300-500 µm), 20-25 bar operating pressure, 90 °C, 24 h. [b] Yields are based on TBHP consumption determined by iodometric titration. [c] Determined by GC-FID and GC-MS. [d] Determined by ICP-AES analysis by dissolving the reaction residues in concentrated HNO$_3$. [e] Percentage of molybdenum originally loaded on the catalyst.

2.4.2.4 Epoxidation of propene using TGAP-Mo(EH)$_n$$^{1.50\%Mo}$

TGAP-Mo(EH)$_n$$^{1.50\%Mo}$ is more stable than Novolac-Mo(EH)$_n$$^{1.50\%Mo}$ in the epoxidation of liquid alkenes using TBHP as oxidant. For the purpose of comparison, TGAP-Mo(EH)$_n$$^{1.50\%Mo}$ was investigated in the epoxidation of propene under identical reaction conditions using TBHP. Recycling reactions were carried out at 60 and 75 °C with a reaction time of 24 h, and at 90 °C with a reaction time of 8 and 24 h. The results are summarized in Table 24. In all of the reactions, propene oxide is the only product detected by GC-FID. In the reactions at 90 °C with a reaction time of 24 h, the yields of propene oxide vary between 61 and 74%. However, when the reaction time was decreased to 8 h, only 18-26% of TBHP was converted to propene oxide. The yields of propene oxide vary between 35 and 44% at 75 °C and 14 and 21% at 60 °C with a reaction time of 24 h. In the reactions at 90 °C with a reaction time of 24 h, the amounts of molybdenum present in the reaction solutions are between 2.62 and 16.23 μg corresponding to 0.20 and 1.26 ppm per run. It is much lower than in the case of Novolac-Mo(EH)$_n^{1.50\%Mo}$. When the reactions were carried out at 90 °C with a reaction time of 8 h, the amounts of molybdenum present in the reaction solutions are between 0.49 and 2.08 μg corresponding to 0.04 and 0.16 ppm per run. The amounts of molybdenum in the reactions are between 1.67 and 5.10 μg (0.13 and 0.40 ppm) at 75 °C and between 1.19 and 1.80 μg (0.09 and 0.14 ppm) at 60 °C with a reaction time of 24 h per run. There is a clear trend that the yield of propene oxide and the amount of molybdenum in the reaction solutions decrease with the decrease of reaction time and reaction temperature. After the completion of five consecutive runs, beyond 99.70% of molybdenum initially loaded on the support are retained. According to these results, TGAP-Mo(EH)$_n^{1.50\%Mo}$ provides better stability than Novolac-Mo(EH)$_n^{1.50\%Mo}$.

Table 24: Epoxidation of propene using TGAP-Mo(EH)$_n^{1.50\%Mo}$ and TBHP[a]

Run no.	90 °C, 24 h Yield[b] (%)	Sel.[c] (%)	Mo[d] leached (µg)	Mo[e] content (%)	90 °C, 8 h Yield (%)	Sel. (%)	Mo leached (µg)	Mo content (%)
1	74	>99	16.23	99.89	26	>99	0.66	99.99
2	71	>99	7.39	99.84	22	>99	0.49	99.99
3	67	>99	12.79	99.76	23	>99	0.50	99.99
4	62	>99	6.33	99.72	18	>99	2.08	99.98
5	61	>99	2.62	99.70	21	>99	1.99	99.97

Run no.	75 °C, 24 h Yield (%)	Sel. (%)	Mo leached (µg)	Mo content (%)	60 °C, 24 h Yield (%)	Sel. (%)	Mo leached (µg)	Mo content (%)
1	44	>99	5.10	99.97	16	>99	1.48	99.99
2	37	>99	2.22	99.96	14	>99	1.80	99.97
3	38	>99	2.42	99.95	21	>99	1.19	99.96
4	35	>99	1.67	99.94	20	>99	1.65	99.94
5	42	>99	3.99	99.92	14	>99	1.25	99.93

[a] Reaction conditions: 80 ml steel autoclave, 8 bar starting pressure of propene, 50 mmol TBHP (34.5 wt.% solution of TBHP in a mixture of toluene and dodecane), 1.00 g catalyst (particle size: 150-300 µm), 20-25 bar operating pressure. [b] Yields are based on TBHP consumption determined by iodometric titration. [c] Determined by GC-FID and GC-MS. [d] Determined by ICP-AES or AAS analysis by dissolving the reaction residues in concentrated HNO_3. [e] Percentage of molybdenum originally loaded on the catalyst.

2.4.2.5 Epoxidation of propene using TGAP/PT30-Mo(OEt)$_5^{0.75\%Mo}$

In order to compare with conventional epoxy resins containing molybdenum species, the resin blend (TGAP mixed with the cyanate ester PT30) was cured using Mo(OEt)$_5$ as initiator via homopolymerization and the obtained material was investigated in the epoxidation of propene using TBHP as oxidant. The structure of cyanate ester PT30 is depicted in Figure 19 and the curing process of the cyanate ester monomers is shown in Figure 20.

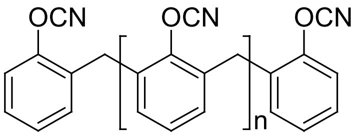


Figure 19: The structure of cyanate ester monomer (PT30).

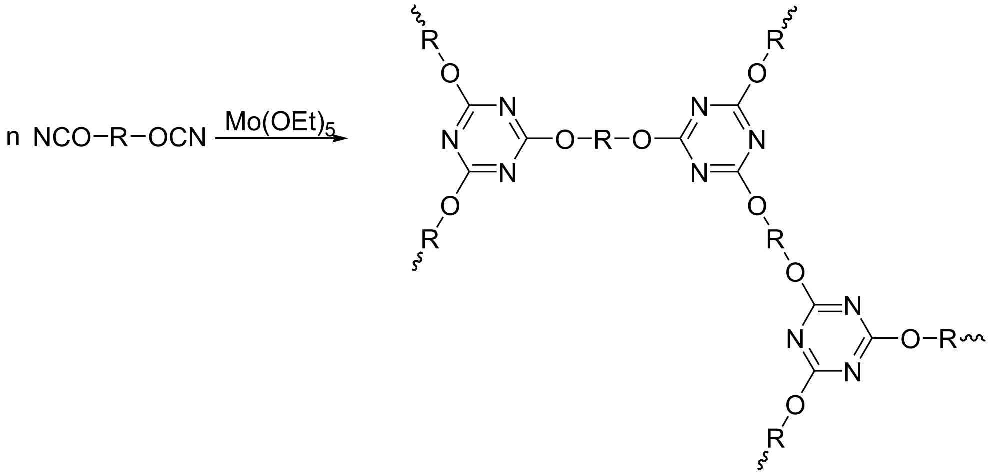


Figure 20: The curing process of the cyanate ester monomers.

The reactions were carried out 90 °C with a reaction time of 24 h. The results are summarized in Table 25. In ten consecutive runs, the yields of propene oxide vary between 63 and 88%. Only propene oxide was produced during the reactions. The amount of molybdenum present in the reaction solutions is between 14 and 145 µg corresponding to 1.09 and 11.31 ppm per run. After the completion of ten consecutive runs, 91.85% of molybdenum initially present on the catalyst are retained. The relation between the yield of propene oxide and the amount of molybdenum in the reaction solutions is not clear and do not coincide with the normal rules. The yields of propene oxide also decrease with the reaction runs slowly.

Table 25: Epoxidation of propene using TGAP/PT30-Mo(OEt)$_5$$^{0.75\%Mo}$ and TBHP[a].

Run no.	Yield[b] (%)	Sel.[c] (%)	Mo[d] leached (μg)	Mo[e] content (%)
1	83	>99	78	98.96
2	85	>99	145	97.03
3	87	>99	119	95.44
4	88	>99	96	94.16
5	69	>99	52	93.47
6	72	>99	24	93.15
7	75	>99	21	92.87
8	75	>99	29	92.48
9	66	>99	14	92.29
10	63	>99	33	91.85

[a] Reaction conditions: 80 ml steel autoclave, 8 bar starting pressure of propene, 50 mmol TBHP (34.5 wt.% solution of TBHP in a mixture of toluene and dodecane), 1.00 g catalyst (particle size: 150-300 μm), 20-25 bar operating pressure, 90 ^{o}C, 24 h. [b] Yields are based on TBHP consumption determined by iodometric titration. [c] Determined by GC-FID and GC-MS. [d] Determined by ICP-AES analysis by dissolving the reaction residues in concentrated HNO_3. [e] Percentage of molybdenum originally loaded on the catalyst.

2.4.3 Summary

Propene epoxidation with TBHP has been investigated using molybdenum catalysts based on epoxy resins such as single metal species catalyst (TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$, Novolac- Mo(EH)$_n$$^{1.50\%Mo}$ and TGAP-Mo(EH)$_n$$^{1.50\%Mo}$), double metal species catalyst (TGAP- Mo(OEt)$_5$$^{1.42\%Mo}$-Pd(PPh$_3$)$_4$$^{0.50\%Pd}$) and the resin blend containing molybdenum species catalyst (TGAP/PT30-Mo(OEt)$_5$$^{0.75\%Mo}$) for the first time. The yield of propene oxide and molybdenum species leaching can be controlled by reaction conditions and decrease with the decrease of reaction temperature and reaction time. There is an irregular relation between the yield of propene oxide and metal species leaching in the epoxidation of propene. In some cases, the yield of propene oxide is high when molybdenum species leaching is comparatively low. Among the investigated catalysts, Novolac-Mo(EH)$_n$$^{1.50\%Mo}$ exhibits comparatively low stability. In most cases, the yields of propene oxide decrease with reaction runs. The catalysts can be isolated from the reaction solutions by simple filtration and reused without any treatments. In recycling reactions, these epoxy resins containing molybdenum species all show a remarkable long-term activity and stability. Compared to other reported polymer-supported Mo^{VI} epoxidation catalysts[91,92], the performance of epoxy resins containing molybdenum species is outstanding. This, coupled with the potential for use under more severe reaction conditions, means that the molybdenum catalysts based on epoxy resins could be used for technological applications. In addition, the use of epoxy resins containing transition metal species is not restricted to propene epoxidation and they can be used in a series of other catalytic reactions.

2.5 TGAP containing palladium species for Suzuki coupling of haloarene with arylboronic acid

2.5.1 Developments of Suzuki coupling catalysts

Amongst the growing number of palladium-catalyzed C-C coupling reactions the Suzuki-Miyaura-reaction plays a leading role. In this reaction an aryl-halogenide is coupled with an aryl- or vinyl-boronic acid or boronic-ester to unsymmetric biaryls[93-96]. Major advantages of Suzuki-reaction are: (1) the stability of the boron-reagents (boronic acids and esters are crystalline, easy to handle, thermally stable, non-toxic and relatively inert to water and oxygen); (2) the easy access to a broad variety boronic-acids through different synthetic pathways[97-99]; (3) the tolerance for different functional group; (4) the simple experimental conditions.

The Suzuki-Miyaura-reaction was also extended to B-alkyl compounds[100]. The effects of the catalysts, ligands, solvents and substrates have been investigated[101]. The catalyst $Pd(PPh_3)_4$ is the most common, but also other homogeneous catalysts as well as immobilized or heterogeneous palladium catalysts have been used. Recently, a wide range of transition metals including platinum[102], copper[103-105] and ruthenium[105] have been investigated since all of these metals have been shown to act as catalysts for the Suzuki reaction either individually or together, attention particularly being focussed on nickel and palladium. Some nickel complexes such as $NiCl_2(PCy_3)_2$[106],

$NiCl_2(dppf)_2$[107-109], $NiCl_2(NEt_3)_2$[110], $NiCl_2(bipy)$[110], $Ni(P(OMe)_3)_2Cl_2$[109] and $NiCl_2$[111], and charcoal supported nickel[112,113] have been used as catalysts in Suzuki coupling. Palladium complexes[114-126] such as 1,6-diene palladium(0) monophosphine[114], palladium-imidazole-2-ylidene[115,116], palladium-phosphine oxide[117], oxime-carbapalladacycle[118], $[Pd_2(dba)_3]$[119,120] and $Pd(OAc)_2$[120,121] and other catalysts have been extensively investigated in Suzuki coupling. Supported nanoparticulate palladium catalysts such as dendrimer-Pd[127-129], poly(N-vinyl-2-pyrrolidone)-Pd[127,130-132], covalently modified silicas-Pd[133], macrocellular polymeric supports-Pd[134], core/shell superparamagnetic Pd[135,136] and layer double hydroxide and Merrifield resin-Pd[137] nanoparticles have also been highlighted recently. Of the many supported palladium catalysts, polymer-supported palladium catalysts such as oxime carbapalladacycle covalently anchored on a soluble polyethyleneglycol scaffold[138], polymer-supported dialkylphosphinobiphenyl $Pd_2(dba)_3$[139], Merrifield polymer-supported palladium[140], polystyrene-bound palladium[141], polyurea-encapsulated $Pd(OAc)_2$[142], amphiphilic polymer supported palladium[143], chitosan-based palladium[144] and polyaniline-supported Pd(0)[145] have been developed for Suzuki coupling. Other supported palladium catalysts such as Pd-containing perovskites[146,147], Pd/C[148-154], $[Pd(NH_3)_4]^{2+}$-exchanged sepiolite clay[155], oxime-carbapalladacycle anchored to silica[156], palladium-doped alumina[157,158], alkali-exchanged sepiolites supported Pd[159], Pd(OH)/C[160], nanocrystalline MgO-stabilized Pd(0)[161], Pd/SiO_2[162,163], SBA-Si-PEG-$Pd(PPh_3)_n$[164], Pd(0)-Y zeolite[165] are very interesting in practical applications, especially Pd/C[148-154]. Virtually all forms of palladium can be used as precatalysts for the simpler reactions (e.g., activation of aryl iodides), yet specifically designed catalysts are required for activation of bulky or electronically unactivated substrates.

Two critical questions have dominated modern research on Suzuki couplings[166]. The first is how can a catalyst be designed to activate aryl chlorides, as they are the cheapest and most abundant class of aryl halides available for use as substrates? The second question is how can catalyst costs and metal contamination of the product be minimized? Researchers have addressed themselves to this topic in several ways, including the development of high turnover number catalysts and the design and utilization of heterogeneous Suzuki precatalysts. In view of practical applications, the use of heterogeneous catalysts is important for product separation and catalyst recycling, but in the pursuit of the best heterogeneous catalysts, more and more people suggested that only leached, soluble palladium species were true catalytic species in Suzuki couplings[146,147,152], even in some cases, extremely small amounts of palladium (ppm or ppb levels)[167-169] are sufficient to give very high turnover frequencies. Hot filtration test and elemental analysis showed that the metal species leaching was extremely low and catalytic activity was not associated with the liquid phase[148,161,163,165,170]. Later studies indicated that redeposition of leached, soluble palladium species can occur and there was a leaching/redeposition equilibrium during the coupling reactions[146,147,152] that mask leaching if filtration test was used as the only or the primary mode of evaluating leaching. In order to evaluate our palladium catalysts based on epoxy resins prepared via homopolymerization, Suzuki coupling reactions of different haloarenes with arylboronic acids were investigated. In addition, solvent effects, base effects and ratio effects of solvent mixtures were studied for the optimization of reaction conditions, and some experimental methods such as hot filtration test, poisoning test, redeposition test and competition reaction were used to distinguish the true active species and the reaction rates of different substrates in the Suzuki coupling reactions. Suzuki coupling of haloarene with arylboronic acid is depicted in Figure 21.

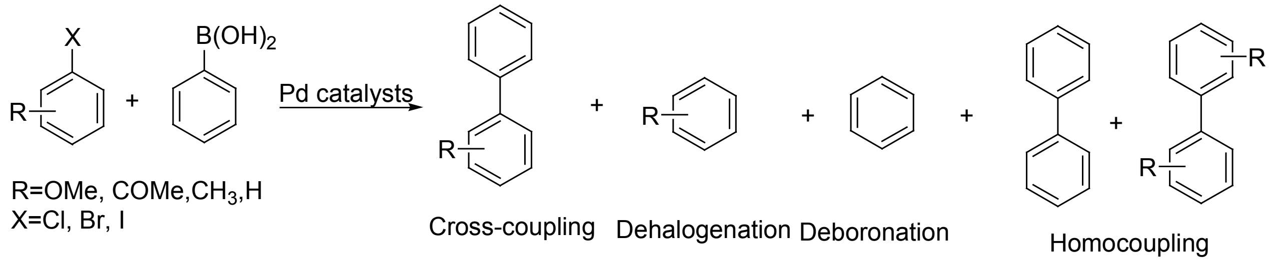


Figure 21: Suzuki coupling of haloarene with arylboronic acid catalyzed by palladium catalysts (another byproduct is $XB(OH)_2$).

2.5.2 Homogeneous or heterogeneous catalytic mechanism in Suzuki coupling

The standard catalytic cycle in Suzuki coupling[96] in most organic chemistry textbooks involves a postulated molecular, homogeneous palladium catalyst that cycles between the Pd(0) and Pd(II) oxidation states during the course of the catalytic reaction. Usually, a precatalyst in the Pd(II) oxidation state is used, and this precatalyst is presumed to be reduced to Pd(0) in situ, allowing it to then oxidatively add the aryl halide forming a Pd(II) intermediate. After the Pd(II) complex undergoes a transmetalation step with the nucleophile being derived from an arylboronic acid, reductive elimination gives the product species. The mechanism in homogeneously catalyzed reactions is depicted in Figure 22 ($R^2B(R^4)_2$: boron complex; OR^3: hydroxide ions).

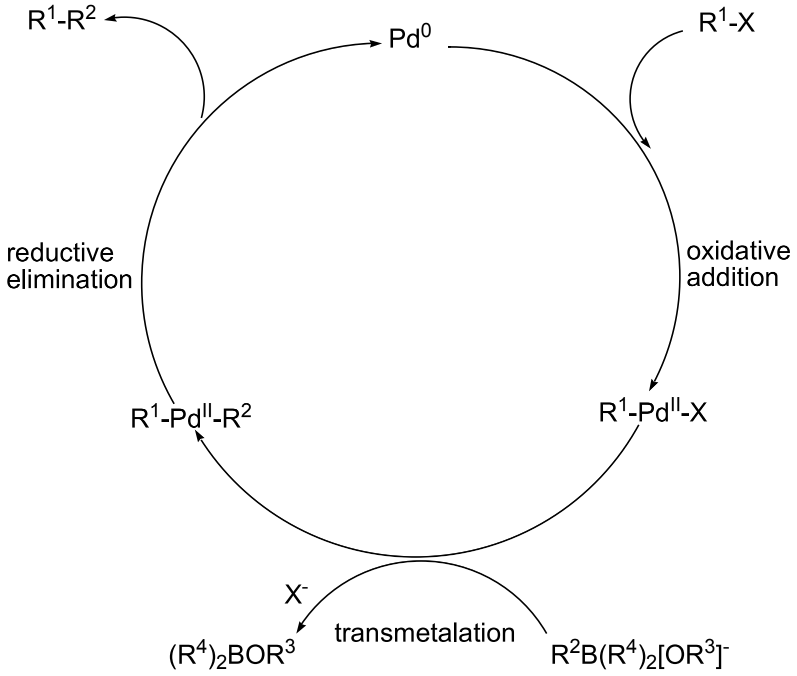


Figure 22: Homogeneous catalytic cycle for the Suzuki coupling reaction.

Nowadays, there are two debates about the catalytic mechanism in the Suzuki coupling reaction using supported metal catalysts. A focus is whether Suzuki coupling occurs by surface catalysis[148,161,163,165,170] or the reaction is due to the species leached from the support into the solution being then reprecipitated on the support after the consumption of aryl halides[146,147,152]. In the liquid-phase reactions, the dissolving and reprecipitation of active metal species are normally unavoidable and the degree of dissolving/redeposition closely depends on the nature of supports used. Recently, Leadbeater reported that even in some cases, extremely small amounts of palladium (ppm or ppb levels)[167-169] are sufficient to give very high turnover frequencies. These reports have challenged a strictly heterogeneous reaction mechanism. If leached palladium species are enough to catalyze Suzuki coupling, and the redeposition of dissolved palladium species is complete as soon as possible, hot filtration test and elemental analyses do not work in the investigation of the reaction mechanism. The proposed catalytic cycle for the Pd/C-catalyzed Suzuki coupling[161] is depicted in Figure 23. The palladium species leaching from Pd/C is due to the oxidative addition of ArBr and then ArPdBr is formed.

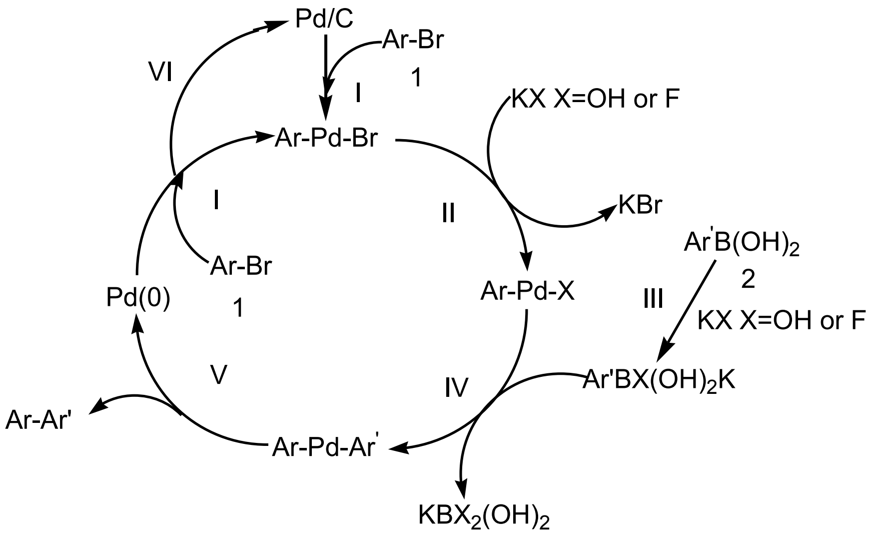


Figure 23: Proposed catalytic cycle for the Pd/C-catalyzed Suzuki-Miyaura cross-coupling. I: Oxidative addition; II: Halide metathesis; III: Formation of tetrahedral intermediate; IV: Transmetalation; V: Reductive elimination; VI: Pd precipitation.

2.5.3 Investigation on the reaction parameters in 4-iodoanisole Suzuki coupling with phenylboronic acid using TGAP-Pd(PPh$_3$)$_4^{1.00\%\mathrm{Pd}}$

Optimization of reaction conditions has been studied recently. This has included the use of additives and changing the solvents and bases. Major focus is on the use of environmentally benign media. Suzuki reactions in supercritical CO$_2$[170], in ionic liquids[171] and solventless Suzuki couplings[158] have already been developed. In addition to a range of organic solvents, there has been considerable recent interest in the use of water as a reaction medium. The use of water as a solvent for chemical reactions clearly has both economical and environmental advantages because it is inexpensive, abundant, nontoxic, nonflammable, and readily separable from organic compounds[173-175]. Suzuki coupling reactions of water-soluble aryl iodides have been performed in water with simple palladium salts[149,176-178] or amphiphilic polymer supported palladium catalysts[179]. Badone and co-workers have investigated the effects of solvent, including water, on the rate of the ligand-free palladium acetate catalyzed Suzuki reaction of a range of aryl bromides, iodides, and triflates[180]. An additional advantage of performing the Suzuki reaction in water is the readily tuning of the pH of the media, which has a critical influence on the reaction rate. It has also been shown that Suzuki reactions in water are frequently more efficient in the absence of a phosphane ligand[181] and are less sensitive to air[182,183]. Mechanistic studies have shown that the formation of borate intermediates (for example, by the addition of base or a fluoride salt) can facilitate the reactions[184]. Potassium carbonate in this system produces hydroxide, which in turn generates the tetrahedral boronate anion necessary for the transmetalation step. Badone et al. reported a great acceleration of a Suzuki coupling catalyzed by ligand-free palladium acetate by the addition of one equivalent of tetrabutylammonium bromide (TBAB) in water[180]. Some parameters such as solvent effect and base effect were investigated in Suzuki coupling of 4-iodoanisole with phenylboronic acid using TGAP-$Pd(PPh_3)_4^{1.00\%Pd}$.

2.5.3.1 Solvent effect

Sowa et al. studied Pd/C catalysts for Suzuki couplings[148] and reported that proper choice of solvent was critical in preventing the homocoupling reaction. Choudary et al. prepared Pd nanoparticles on basic layered hydroxide supports via reduction of the $[PdCl_4]^{2-}$-exchanged solids[137] and claimed that there was a large solvent effect in Suzuki coupling. Shieh and co-workers studied the Suzuki coupling of 2-bromoanisole and phenylboronic acid using a commercial triarylphosphine-poly(styrene)resin[185]. It was discovered that leaching occurred to a lower extent by using nonpoplar solvents. The polymer-incarcerated Pd was also successfully used in Suzuki[186] couplings of aryl bromides and aryl iodides. Leaching of Pd species from the polymer was largely dependent on the solvent used, with undetectable amounts of leaching in water/toluene and water/ethanol systems. In order to find the best reaction conditions, a series of reactions catalyzed by TGAP-Pd(PPh_3)$_4^{1.00\%Pd}$ was carried out at 60 °C with a reaction time of 4 h to investigate the solvent effect in 4-iodoanisole Suzuki coupling with phenylboronic acid. The results are summarized in Table 26.

In Table 26, it can be seen that water is very important for a good conversion and an appropriately chosen solvent system strongly favors the cross-coupling pathway. Only organic solvents were used (Entry 3 and 5), the conversion of 4-iodoanisole is too low under identical reaction conditions. Of the many mixed water and organic solvent systems, dioxane/water and 2-propanol/water show better activity rather than other systems. However, 4-iodoanisole can not dissolved in 2-propanol completely using 2-propanol/water. Therefore, in the following reactions, the dioxane/water solvent system was mostly chosen. After the completion of 4-iodoanisole Suzuki coupling with phenylboronic acid using dioxane/water, the solid catalyst particles mainly located in the interphase between organic and water phase. Therefore, it is supposed that the catalytic reactions mainly occur in this interphase. This could explain the low conversions of 4-iodoanisole only using organic solvents.

Table 26: Solvent effect on 4-iodoanisole Suzuki coupling with phenylboronic acid catalyzed by TGAP-Pd$(PPh_3)_4{}^{1.00\%Pd[a]}$.

Entry	Solvent (vol. ratio:10 ml /10 ml)	Base	Conv.[c] (%)
1	Dioxane/water	K_2CO_3	80
2	Ethanol/water	K_2CO_3	75
3	NMP[b]	KOAc	3
4	DMF/water	K_2CO_3	72
5	*p*-Xylene[b]	K_2CO_3	1
6	Acetonitrile/water	K_2CO_3	72
7	2-Propanol/water	K_2CO_3	82

[a] Reaction conditions: 0.50 g catalyst (particle size: 300–500 μm), 5 mmol 4-iodoanisole, 6 mmol phenylboronic acid, 20 mmol base, 10 ml organic solvent, 10 ml distilled water, 60 °C, 4 h. [b] 10 ml NMP or *p*-xylene was used as solvent. [c] Determined by GC-FID using calibration curves obtained with standard solutions and dodecane as external standard.

2.5.3.2 Base effect

According to the reaction mechanism, base produces hydroxide, which in turn generates the tetrahedral boronate anion necessary for the transmetalation step in Suzuki coupling. Artok and Bulut found that the reaction rates depended strongly on the base used, a common observation in many coupling reactions with Pd(0)-loaded NaY zeolite in water/DMF[165]. El-Sayed also observed that Pd black precipitation varied with the base used, pH and other factors[132]. In order to investigate the base effect, different bases and mixed bases were used in Suzuki coupling of 4-iodoanisle with phenylboronic acid at 60 °C with a reaction time of 4 h. The results are given in Table 27.

In Table 27, KOAc is the worst base in 4-iodoanisole Suzuki coupling with phenylboronic acid under identical reaction conditions. Cs_2CO_3 did not display the desired effect and the conversions of 4-iodoanisole decrease with the sequence: $KO^tBu > K_2CO_3 > Cs_2CO_3 > Na_2CO_3 >$ KOAc. Due to the strong basic property of KO^tBu leading to much more homocoupling products, KO^tBu was excluded. Therefore, K_2CO_3 was preferred in the later experiments. In addition, mixed bases were also investigated. The conversions of 4-iodoanisole increase using two systems with mixed bases.

Table 27: Base effect on 4-iodoanisole Suzuki coupling with phenylboronic acid catalyzed by TGAP-$Pd(PPh_3)_4^{1.00\%Pd}$[a].

Entry	Dioxane/water (g/g)	Base (mmol/mmol)	Conv.[b] (%)
1	10/10	K_2CO_3 (20)	80
2	10/10	Na_2CO_3 (20)	59
3	10/10	Cs_2CO_3 (20)	68
4	10/10	KOAc (20)	10
5	10/10	KO^tBu (20)	85
6	10/10	K_2CO_3/KOAc (10/10)	85
7	10/10	$K_2CO_3/N(Et)_3$ (10/10)	87

[a] Reaction conditions: 0.50 g catalyst (particle size: 300–500 μm), 5 mmol 4-iodoanisole, 6 mmol phenylboronic acid, 10 g dioxane, 10 g distilled water, 60 °C, 4 h. [b] Determined by GC-FID using calibration curves obtained with standard solutions and dodecane as external standard.

2.5.3.3 Ratio effect of dioxane and distilled water

The ratio between organic solvent and water is important to obtain desired conversions of haloarene. Therefore, some reactions with different dioxane/water ratios were carried out in Suzuki coupling of 4-iodoanisole with phenylboronic acid using TGAP-$Pd(PPh_3)_4^{1.00\%Pd}$ as catalyst at 60 °C with a reaction time of 4 h. The results are listed in Table 28. From Table 28, it is seen that sufficient water is very important for the desired conversion of 4-iodoanisole. When no water or less water was used, the conversion of 4-iodoanisole is very low. When the ratio between dioxane and water is 1/1, the conversion of 4-iodoanisole can reach 80%. Therefore, dioxane/water in a weight ratio of 1:1 is an appropriate solvent system for 4-iodoanisole Suzuki coupling and it was often used in the later described reactions.

Table 28: Ratio effect of dioxane and water on 4-iodoanisole Suzuki coupling with phenylboronic acid catalyzed by TGAP-Pd(PPh_3)$_4$$^{1.00\%Pd[a]}$.

Entry	Dioxane/water (g/g)	Base	Conv.[b] (%)
1	20/1	K_2CO_3	0
2	15/3	K_2CO_3	2
3	15/5	K_2CO_3	7
4	10/10	K_2CO_3	80
5	5/15	K_2CO_3	79

[a] Reaction conditions: 0.50 g catalyst (particle size: 300–500 μm), 5 mmol 4-iodoanisole, 6 mmol phenylboronic acid, 20 mmol K_2CO_3, 60 °C, 4 h. [b] Determined by GC-FID using calibration curves obtained with standard solutions and dodecane as external standard.

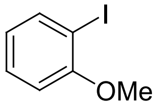
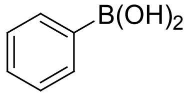
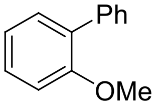
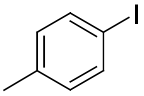
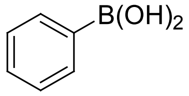
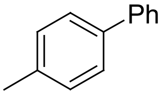
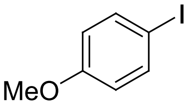
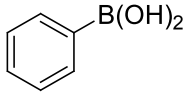
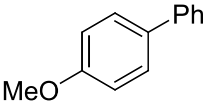
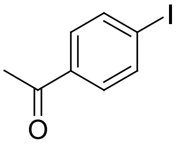
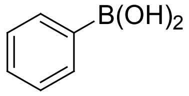
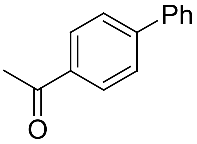
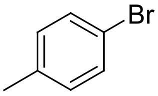
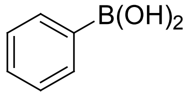
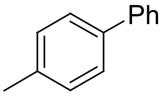
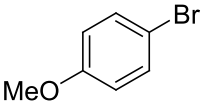
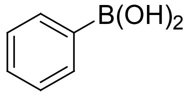
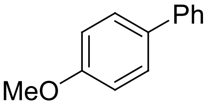
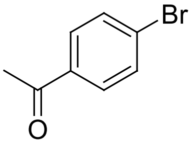
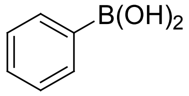
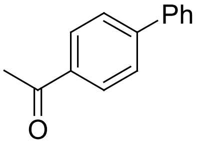
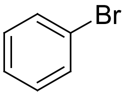
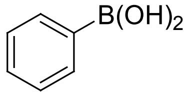
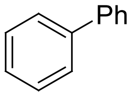
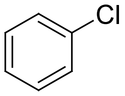
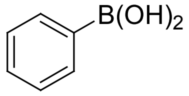
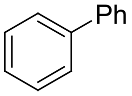
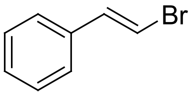
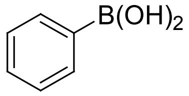
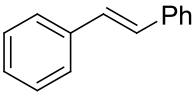
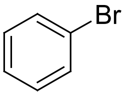
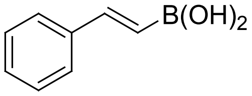
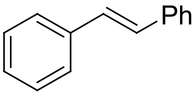
2.5.4 Suzuki coupling of haloarene with arylboronic acid using TGAP-Pd(PPh_3)$_4$$^{0.50\%Pd}$

In order to evaluate the catalytic performance of TGAP-Pd(PPh_3)$_4$$^{0.50\%Pd}$ in Suzuki coupling, a wide range of haloarenes was investigated. In addition, a competition reaction was carried out to compare the reaction rates of haloarenes with different functional groups and a long-term test in Suzuki coupling of chlorobenzene with phenylboronic acid was carried out to investigate the stability of TGAP-Pd(PPh_3)$_4$$^{0.50\%Pd}$.

2.5.4.1 Suzuki coupling of haloarene with arylboronic acid

TGAP-Pd(PPh_3)$_4$$^{0.50\%Pd}$ was used as catalyst in Suzuki coupling of haloarene with arylboronic acid at 90 °C with a reaction time of 24 h. The results are summarized in Table 29. In Table 29, it can be clearly seen that the conversions of haloarene normally decrease with the sequence: aryl iodide > aryl bromide > aryl chloride without considering the influence from different functional groups in benzene ring. In the Suzuki coupling of different aryl bromides, the conversions decrease with the sequence: 4-bromoacetophenone > 4-bromotoluene > 4-bromoanisole. The selectivities to Suzuki coupling products are all beyond 99% as determined by GC-MS and GC-FID. In most cases, below 1% of homocoupling and dehalogenation products were produced and this shows Suzuki coupling possessing high selectivity for cross-coupling. Aryl iodides can be quantitatively converted to their corresponding Suzuki coupling products under the chosen reaction conditions. In Suzuki coupling of aryl bromides with phenylboronic acid, the conversions of aryl bromides decrease very much compared to aryl iodides and the best conversion is 55% obtained in 4-bromoacetophenone Suzuki coupling with phenylboronic acid. The conversion of 4-bromoanisole is only 7% showing that 4-bromoanisole is the most inactive substrate among the aryl bromides to cross-couple with phenylboronic acid. This can be explained by the decrease of reactivity from electron-withdrawing to neutral or electron-rich arylbromides as 4-bromoacetophenone (electron-withdrawing), bromobenzene (neutral), 4-bromotoluene (electron-donating) and 4-bromoanisole (electron-donating). This observation is in agreement with some reports from other groups[148]. It is interesting that 22% of chlorobenzene can be converted to biphenyl under identical reaction conditions. In the beginning, it was excluded that biphenyl is obtained from homocoupling of chlorobenzene and phenylboronic acid by the addition of only phenylboronic acid or chlorobenzene to the reaction media and there is no doubt that biphenyl is really produced via cross-coupling of chlorobenzene with phenylboronic acid. It is noted that the success of the reaction is dependent on the purity of the boronic acid. In an attempt to develop the methodology further, the coupling of alkenylboronic acid with arylhalide and alkenylhalide with arylboronic acid were investigated, the products in both cases being the same substituted alkenes. In both cases, the desired disubstituted alkene product is formed and the conversion in the latter reaction (9%) is better than in the case of the former (2%). Only *trans*-stilbene was produced. According to the obtained results, TGAP-Pd$(PPh_3)_4^{0.50\%Pd}$ can be applied in Suzuki coupling of a wide range of haloarenes with arylboronic acids and shows promising catalytic activity that could be optimized.

Table 29: Suzuki coupling of haloarenes with arylboronic acids catalyzed by TGAP-Pd(PPh_3)$_4$$^{0.50\%Pd[a]}$.

Entry	Haloarene	Arylboronic acid	Product	Conv.[b] (%)
1				100
2				100
3				100
4				100
5				19
6				7
7				55
8				32
9				22
10				2
11				9

[a] Reaction conditions: 0.50 g catalyst (particle size: 150-300 μm), 5 mmol haloarene, 6 mmol arylboronic acid, 20 mmol K_2CO_3, 10 g dioxane, 10 g distilled water, 90 °C, 24 h. [b] Determined by GC-FID using calibration curves obtained with standard solutions and dodecane as external standard.

2.5.4.2 Competition reaction of different substituted arylbromides in Suzuki coupling with phenylboronic acid

In order to investigate the substituent effect of different functional groups in Suzuki coupling of a haloarene with arylboronic acid, a competition experiment using different arylbromides including bromobenzene, 5-bromo-*m*-xylene, 4-bromoacetophenone, 4-bromotoluene and 4-bromoanisole with phenylboronic acid catalyzed by TGAP-Pd$(PPh_3)_4^{0.50\%Pd}$ was performed. In this case, different functional arylbromides compete to cross-couple with phenylboronic acid. Oxidative addition to Pd and the following catalytic cycles proceed with different reaction rates and are catalyzed by the same metal species. This can reflect the reaction rates of different arylbromides in Suzuki coupling accurately. The same reaction conditions as described in Chapter 2.5.4.1 were employed. The results are summarized in Table 30.

In Table 30, the conversions of different arylbromides decrease in the order: 4-bromoacetophenone (55%) > bromobenzene (32%) > 4-bromotoluene (19%) > 5-bromo-*m*-xylene (10%) > 4-bromoanisole (7%). 4-Bromoacetophenone is easier to couple with phenylboronic acid rather than other arylbromides under the same reaction conditions. This confirms the results described in Chapter 2.5.4.1 and the same conversions were observed. The selectivity for cross-coupling is high and no homocoupling was observed.

Table 30: Competition reaction of different substituted arylbromides in Suzuki coupling with phenylboronic acid catalyzed by TGAP-Pd(PPh$_3$)$_4$$^{0.50\%Pd[a]}$.

Arylbromide	Conversion[b] (%)	Selectivity[c] (%)
4-Bromoacetophenone	55	>99
Bromobenzene	32	>99
4-Bromotoluene	19	>99
5-Bromo-*m*-xylene	10	>99
4-Bromoanisole	7	>99

[a] Reaction conditions: 0.50 g catalyst (particle size: 150-300 μm), 6 mmol phenylboronic acid, 20 mmol K_2CO_3, 10 g dioxane, 10 g distilled water, 1 mmol bromobenzene, 1 mmol 4-bromoanisole, 1 mmol 5-bromo-*m*-xylene, 1 mmol 4-bromoacetophenone, 1 mmol 4-bromotoluene, 90 ^{o}C, 24 h. [b] Determined by GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [c] Determined by GC-MS and GC-FID.

2.5.4.3 Long-term test in Suzuki coupling of chlorobenzene with phenylboronic acid

In order to investigate the long-term activity and stability of TGAP-Pd(PP$_3$)$_4$$^{0.50\%Pd}$ in chlorobenzene Suzuki coupling with phenylboronic acid, recycling experiments were conducted at 90 ^{o}C with a reaction time of 24 h. TGAP-Pd(PPh$_3$)$_4$$^{0.50\%Pd}$ was isolated by filtration and reused without any treatments. The results are summarized in Table 31. In five consecutive runs, around 20% conversion of chlorobenzene was obtained in each run. Homocoupling experiments using only chlorobenzene or phenylboronic acid provide below 1% biphenyl yields under identical reaction conditions and confirm that biphenyl is produced by Suzuki coupling of chlorobenzene with phenylboronic acid. No byproducts were formed. It is noted that the purity of phenylboronic acid is very important for the success of Suzuki coupling. The palladium species leaching was also measured. In five consecutive runs, the amounts of palladium in the reaction solutions are between 3.24 and 5.06 μg corresponding to 0.15 and 0.24 ppm per run. The palladium species leaching is extremely low and it seems that the conversion of chlorobenzene is not associated with the leached palladium species. After the completion of five consecutive runs, 99.18% of palladium initially loaded on the catalyst are retained. In addition, Pd(PPh$_3$)$_4$ was also used as homogeneous catalyst in Suzuki coupling of chlorobenzene with phenylboronic acid under the same reaction conditions and surprisingly, no Suzuki coupling product was produced.

Table 31: Long-term test in Suzuki coupling of chlorobenzene with phenylboronic acid using TGAP-Pd(PPh_3)$_4$$^{0.50\%Pd[a]}$.

Run no.	Conv.[b] (%)	Sel.[c] (%)	Pd[d] leached (µg)	Pd[e] content (%)
1	21	>99	5.06	99.80
2	22	>99	3.94	99.64
3	19	>99	3.24	99.51
4	23	>99	3.44	99.37
5	20	>99	4.89	99.18

[a] Reaction conditions: 0.50 g catalyst (particle size: 150-300 µm), 5 mmol chlorobenzene, 6 mmol phenylboronic acid, 20 mmol K_2CO_3, 10 g dioxane, 10 g distilled water, 90 °C, 24 h. [b] Determined by GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [c] Determined by GC-MS and GC-FID. [d] Determined by ICP-AES. [e] Percentage of palladium initially loaded on the catalyst.

2.5.5 Investigation on the nature of active species in 2-iodoanisole Suzuki coupling with phenylboronic acid

Nowadays, understanding the nature of the true active species using solid catalysts in liquid media remains relatively less studied. Indeed, in many cases, solids act as truly heterogeneous catalysts, with the reaction occurring on the particle surface, whereas in others, it is increasingly found that leached, soluble species are the true catalytic entities. Leadbeater and co-workers[167,169] carried out an interesting study and found that Suzuki coupling reactions can be catalyzed by trace amounts of Pd (50 ppb) in the reaction solutions. Similar results were reported by Dupont and co-workers[187], who showed that ppt amounts of residual Pd in previously used glassware are sometimes sufficient to catalyze the reactions. Biffis et al.[188] also note that only a very small amount of leaching was necessary to give excellent catalytic rates in Pd-catalyzed reactions. Thus, assessing what is the active catalyst and where is the active catalyst (support vs. solution) can be extraordinarily difficult. Indeed, if ppt levels of palladium are capable of easily catalyzing Suzuki coupling, probing the nature of the true catalyst by most spectroscopic or other techniques may be currently impossible.

Up to now, a variety of experiments has been used to judge the heterogeneity/ homogeneity of the catalytic species in Suzuki coupling. However, it must be emphasized that there is no single definitive experiment for making this distinction. A commonly cited work on the issue of homogeneous vs. heterogeneous catalysis is the nice paper by Finke and coworkers[189]. This review considers the various experiments that have been used to distinguish homogeneous and heterogeneous catalysis. Of the many experiments, hot filtration test is commonly used to elucidate the nature of the true active species[190]. People applied the hot filtration technique or split test to effectively probe whether leached transition metal species were responsible for the observed catalysis and suggested that such a test can provide rigorous proof for catalysis by leached vs. truly heterogeneous species. Indeed, this technique works extremely well and can provide valuable information about the nature of the true catalyst[137,147,170,191]. Unfortunately, this test, when applied alone, can not be rigorously used to assess catalysis by leached species during Suzuki coupling due to the speed at which leached palladium species can redeposit back onto the support[192]. Lipshutz has suggested that the leached metal species can deposit so quickly it may not be detected by a hot filtration test[193]. Furthermore, as noted above, the amount of leached palladium species that needs to be present in solution for catalysis can be so small, that it might not be detected by many techniques such as elemental analysis.

Three-phase test has been developed as a clear test for the discrimination of homogeneous catalysis in the determination of heterogeneity in Pd-catalyzed coupling reactions[170,191]. Davies et al. conclusively show that a Suzuki coupling reaction proceeded by a solution phase mechanism using polymer beads immobilized with one of the two reagents in the case of aryl iodide Suzuki coupling[194]. Using this test, one reagent is immobilized on a solid support and the catalyst is immobilized on a second, different solid support. The remaining reagents are then added to the solution. Ideally, if there is no background reaction in the absence of catalyst, the immobilized reagent should only be converted if there is catalyst or substrate leaching. This is a very useful test to assess homogeneous catalysis and it is an excellent complimentary technique for use in conjunction with filtration test. However, there are subtleties involved. For example, it must be insured that the species needed to induce leaching are present in the solution phase. Thus, if leaching proceeds via oxidative addition of aryl halide to immobilized Pd species, the aryl halide or another free aryl halide must be present in the reaction solution. Another issue concerns the relative rates of conversion of the tethered vs. the soluble reactants. For example, if an easy to convert aryl halide is used in solution (e.g., an aryl iodide) but a slow reacting aryl halide is tethered (e.g., a deactivated aryl bromide), the halide in the solution might be converted completely before any hypothetical leached palladium species have time to diffuse and convert the surface-bound reagent. Thus, if the surface-bound reagent is slow reacting, the soluble palladium species may deactivate before it can convert much or any of the bound substrate. Nonetheless, three-phase test can be a powerful tool in the arsenal of the catalysis scientist in elucidating the nature of the true catalytic species if these subtleties are considered.

Poisoning test is a fascinating methodology to distinguish the differences between homogeneous and heterogeneous catalysis[189]. One of the most popular is Hg poisoning test by amalgamating metal and thus blocking its catalytic activity[150]. However, Hg(0) is not expected to have a poisoning effect on the dissolved metals. But some people also suggested that a mercury test may be problematic and confirmed a homogeneneous catalytic system but not a heterogeneous one[195]. Mercury poisoning test has been widely used in Suzuki coupling and provides a proof for a heterogeneous catalytic mechanism[150]. A method is that a solution of precatalyst was stirred with Hg(0), the solution was then filtered, and a catalytic run was started. Hg(0) was also kept in the reaction solution during the overall reaction process or added after the catalytic reaction had already begun. Recently, a new poisoning test occurred. Poly(vinylpyridine) (PVPy) poisons at least some homogeneous catalysts by binding strongly to them during the reactions[196,197]. Poisoning with PVPy is in principle a nice complement of mercury poisoning experiment decribed earlier. If PVPy completely inhibits catalysis, but a properly performed Hg(0) experiment has little effect on catalysis, then there is a strong evidence for homogeneous catalysis.

Thathagar[198] reported a new general technique permitting the testing of individual reactions using a simple approach based on physical exclusion by a membrane technique for distinguishing the homogeneous or heterogenous mechanism. It is very attractive to judge the nature of true active species in coupling reactions catalyzed by palladium catalysts by using a physical method instead of chemical experiments.

In order to investigate the nature of the true active species in Suzuki coupling of 2-iodoanisole with phenylboronic acid catalyzed by TGAP containing palladium species, hot filtration, poisoning and redeposition tests were conducted.

2.5.5.1 Hot filtration test in 2-iodoanisole Suzuki coupling with phenylboronic acid

In order to investigate the nature of the true active species in Suzuki coupling, it is necessary to carry out hot filtration test. The filtrate was separated from the catalyst particles after the reaction at 60 °C, then used in a new reaction along with the addition of equivalent fresh reactants including 2-iodoanisole, phenylboronic acid, K_2CO_3, dioxane and water. Before the reaction began, the reaction solution was analyzed by GC-FID. After the completion of the reaction, the reaction solution was measured again by GC-FID. The conversion of 2-iodoanisole from leached, dissolved palladium species was then obtained. Thus, five consecutive runs were carried out using this filtration test. Reactions with the filtrates were performed under the same reaction conditions as in the presence of the solid catalyst and the results are summarized in Table 32.

When TGAP-Pd$(PPh_3)_4^{1.00\%Pd}$ was used as catalyst, the conversion of 2-iodoanisole is 100%. However, the conversion of 2-iodoanisole is between 29 and 39% in the filtration test. This suggests that around 30% conversion of 2-iodoanisole is from dissolved palladium species during the reactions using TGAP-Pd$(PPh_3)_4^{1.00\%Pd}$ as catalyst. According to these results, we can not exclude heterogeneous catalysis and draw a conculsion that the reactions are due to homogeneous (around 30%) and heterogenous catalysis (around 70%).

Table 32: Hot filtration test in 2-iodoanisole Suzuki coupling with phenylboronic acid[a].

Run no.	Conversion in the presence of TGAP-Pd(PPh_3)$_4$$^{1.00\%Pd}$[b] (%)	Conversion from dissolved active species in the reaction filtrate[b] (%)
1	100	38
2	100	36
3	100	29
4	100	34
5	100	39

[a] 5 mmol 2-iodoanisole, 6 mmol phenylboronic acid, 20 mmol K_2CO_3, 10 g dioxane and 10 g distilled water were added to the filtrate (isolated from the former reaction in the presence of the solid catalyst) and then the reaction was carried out at 90°C with a reaction time of 24 h. [b] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard.

2.5.5.2 Poisoning test in 2-iodoanisole Suzuki coupling with phenylboronic acid using TGAP-Pd(PPh_3)$_4$$^{1.00\%Pd}$

In order to find more information about the true active species, poisoning test was carried out using TGAP-Pd(PPh_3)$_4$$^{1.00\%Pd}$ at 90 °C with a reaction time of 24 h. In the poisoning test, Hg(0) and PVPy were used to poison the catalytic species on the support and in solution, respectively and the results are summarized in Table 33.

In the common reactions, 2-iodoanisole can be converted completely using TGAP-Pd(PPh_3)$_4$$^{1.00\%Pd}$ at 90 °C with a reaction time of 24 h. Using Hg(0) poisoning, there is no change in the conversion of 2-iodoanisole. 2-iodoanisole was quantitatively converted to the corresponding Suzuki coupling product. According to this mechanism of Hg(0) poisoning test, the leached, dissolved palladium species should be responsible for all of the activity. There is no contribution from the surface catalysis. However, Dupont et al.[195] also suggested that a mercury test may be problematic and confirmes a homogeneneous catalytic system but not a heterogeneous one. Therefore, we can not ensure that all the activity is due to homogeneous catalysis because there is no previously reported successful example using Hg(0) poisoning test in Suzuki coupling. Therefore, PVPy poisoning test was also performed. Insoluble cross-linked PVPy has been shown to be an excellent scavenger for dissolved palladium species[196,197]. This is a complement for Hg(0) poisoning test and a combination of hot filtration, Hg(0) and PVPy poisoning tests should allow to distinguish heterogenous or homogeneous catalysis. In the presence of excess PVPy, less than 1% of 2-iodoanisole was converted to the corresponding Suzuki coupling product using TGAP-Pd$(PPh_3)_4{}^{1.00\%Pd}$ at 90 °C with a reaction time of 24 h. This suggests that the catalytic activity is solely from leached, dissolved palladium species. Due to the strong binding ability of PVPy, the dissolved palladium species are adsorbed on the surface of PVPy and can not remove to the solution and then catalyze Suzuki coupling of 2-iodoanisole with phenylboronic acid. According to the combination PVPy poisoning test with Hg(0) poisoning test, there is a definite proof that activity is due to homogeneous catalysis and TGAP-Pd$(PPh_3)_4{}^{1.00\%Pd}$ acts as a reservoir of catalytically active palladium species in 2-iodoanisole Suzuki coupling.

Table 33: Poisoning test in 2-iodoanisole Suzuki coupling with phenylboronic acid using TGAP-Pd$(PPh_3)_4{}^{1.00\%Pd[a]}$.

Entry	Hg(0) poisoning of heterogeneous catalyst	PVPy poisoning of homogeneous catalyst
1	>99 % conversion[b]	<1 % conversion[b]
2	>99 % conversion	<1 % conversion
3	>99 % conversion	<1 % conversion

[a] Reaction conditions: 0.50 g catalyst (particle size: 300-500 μm), 5 mmol 2-iodoanisole, 6 mmol phenylboronic acid, 20 mmol K_2CO_3, 10 g dioxane, 10 g distilled water, 90 °C, 24 h. In the Hg(0) poisoning test, Hg(0) (3 mmol, 6.00 g) was used. In the PVPy poisoning test, PVPy (1.18 g) was used.
[b] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard.

2.5.5.3 Dissolving/redeposition test in 2-iodoanisole Suzuki coupling with phenylboronic acid using $Pd(PPh_3)_4$ and TGAP-Mo$(EH)_n{}^{1.50\%Mo}$

According to hot filtration and poisoning test, a self-contradictory conclusion was obtained, as the dissolved palladium species are responsible for all the activity, but only around 30% conversion of 2-iodoanisole was obtained in hot filtration test. In order to explain this phenomenon, a dissolving/redeposition test was carried out. In this test, $Pd(PPh_3)_4$ was used as homogeneous catalyst and TGAP-Mo$(EH)_n{}^{1.50\%Mo}$ (it was confirmed that this resin shows no catalytic activity in the 2-iodoanisole Suzuki coupling) was used as the support. After the reaction with a reaction time of 2 h was finished, the dissolved palladium species were separated from the reaction mixture by filtration and solid polymer particles were washed and extracted at room temperature by stirring for two days using distilled water and dioxane. After drying, this resin was tested as catalyst in additional five consecutive runs using a new flask. Using this approach, information about the adsorption ability of TGAP-Mo$(EH)_n^{1.50\%Mo}$ for the dissolved palladium species can be obtained and the results are summarized in Table 34.

In the initial run, using $Pd(PPh_3)_4$ as catalyst 2-iodoanisole can be quantitatively converted. During the initial run, dissolved palladium species were adsorbed on the surface of TGAP-Mo$(EH)_n^{1.50\%Mo}$. Despite treatment to remove the active palladium species, TGAP-Mo$(EH)_n^{1.50\%Mo}$ still catalyzed 2-iodoanisole Suzuki coupling with phenylboronic acid in runs 1-5. In five consecutive runs, the conversions of 2-iodoanisole vary between 80 and 100%, and decrease with the reaction runs. No byproducts were observed. This indicates that TGAP-Mo$(EH)_n^{1.50\%Mo}$ was active in the 2-iodoanisole Suzuki coupling due to the presence of palladium species adsorbed on the surface of the resin. The decrease of catalytic activity is probably due to the loss of palladium species adsorbed on the surface of TGAP-Mo$(EH)_n^{1.50\%Mo}$ as measured by ICP-AES. Amounts of dissolved palladium in the reaction solutions are between 2.47 and 21.97 µg corresponding to 0.10 and 0.92 ppm in runs 1-5. The amount of leached palladium species is extremely low. Therefore, it is suggested that ICP-AES data only provide the amount of soluble palladium species and do not show the more palladium species redeposited onto the support after the completion of the reaction as it occurs in the initial run. Extremely low palladium species leaching is able to catalyze Suzuki coupling of 2-iodoanisole with phenylboronic acid as described by Leadbeater[167,169]. Therefore, low conversions of 2-iodoanisole in hot filtration test is due to homogeneous catalysis by the soluble palladium species after the reaction but not all the dissolved palladium species during the reactions because some dissolved palladium species during the reactions reprecipitated on the support after the completion of the reaction. This indicates that epoxy resins as supports can adsorb active palladium species as charcoal.

The occurrence of dissolving/redeposition process could be present in most reactions to some extent and the readsorption degree depends on the nature of the support. If the heterogeneous catalysts lose the active species very slowly and there is complete redeposition of active metal species, the catalysts are very interesting for technological applications.

Table 34: Dissolving/redeposition test in 2-iodoanisole Suzuki coupling with phenylboronic acid using $Pd(PPh_3)_4$ and TGAP-$Mo(EH)_n^{1.50\%Mo}$[a].

Run no.	Conv.[b] (%)	Sel.[c] (%)	Pd[d] leached (μg)
Initial run	100	>99	-
1	100	>99	21.97
2	100	>99	6.24
3	96	>99	4.12
4	88	>99	4.15
5	80	>99	2.47

[a] Initial run: 0.4458 g TGAP-$Mo(EH)_n^{1.50\%Mo}$ (particle size: 150-300 μm), 0.0809 g $Pd(PPh_3)_4$, 2.3808 g (10 mmol) 2-iodoanisole, 1.4695 g (12 mmol) phenylboronic acid, 2.7935 g (20 mmol) K_2CO_3, 10.3419 g (10 ml) dioxane, 10.4406 g (10 ml) distilled water, 90 °C, 2 h. Runs 1-5: 0.4034 g TGAP-$Mo(EH)_n^{1.50\%Mo}$ from the initial run, 10 mmol 2-iodoanisole, 12 mmol phenylboronic acid, 20 mmol K_2CO_3, 10 ml dioxane, 10 ml distilled water, 90 °C, 24 h. [b] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [c] Determined by GC-MS and GC-FID. [d] Determined by ICP-AES.

2.5.6 Summary

In this part, TGAP containing palladium species was investigated as catalyst in Suzuki coupling of haloarenes with arylboronic acids. The investigation on the solvent effect shows that the activity of catalysts is closely related to the solvent used and dioxane/water mixtures were chosen for the reactions. There is also important impact from the used bases on the catalytic activity and promising results were obtained using K_2CO_3. Water is very important for the desired conversion of haloarene. It is suggested that polar water leads to more palladium species leaching from the support promoting the reaction rate and Suzuki coupling probably occurs in the interphase between organic and water phase. Sufficient water is necessary for Suzuki coupling and the optimum ratio between dioxane and water is 1:1. TGAP containing palladium species can be applied in a wide range of haloarenes. The catalysts can be easily recycled by simple filtration and reused without any treatments. A competition reaction shows that substituents at aryl bromides have an important influence on the reaction rate and the reaction rate decreases in the order: electron-withdrawing > neutral > electron-donating arylbromides. The reaction rate of haloarene decreases with the sequence: aryl iodides > aryl bromides > aryl chlorides. A hot filtration test shows that only around 30% conversion of 2-iodoanisole is due to homogeneous catalysis by dissolved palladium species but Hg(0) and PVPy poisoning tests show that only dissolved palladium species are responsible for the catalytic activity. Redeposition tests show that there is a considerable amount of dissolved but redeposited palladium species on the support after the completion of the reaction, and there is an equilibrium in the dissolving/redeposition process. It is suggested that 2-iodoanisole leads to the leaching of palladium species from the support due to the oxidative addition. In summary, TGAP containing palladium species acts as a reservoir of catalytically active species and Suzuki coupling occurs in the homogeneous phase. Although a homogeneous catalysis mechanism was confirmed, TGAP containing palladium species is a very promising catalyst system due to the slow release of active palladium species and the existence of a dissolving/redeposition process so that the catalysts could be used for a long period without loss of activity.

2.6 TGAP containing palladium species as catalyst for Heck coupling

2.6.1 Developments of Heck coupling catalysts

Heck-reaction[199] was discovered in the end of the 1960s and has since then achieved the status of a standard-reaction in organic synthesis[200]. In the Heck-reaction an alkene is coupled with an aryl- or alkenyl- halogenide to vinylarenes or dienes (Figure 24).

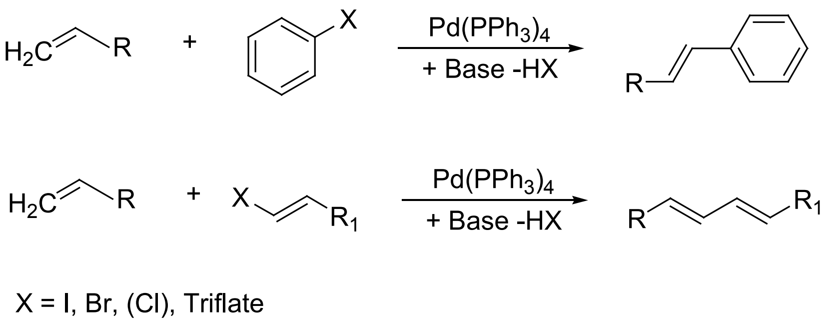


Figure 24: Heck coupling catalyzed by $Pd(PPh_3)_4$.

The reaction is catalyzed by palladium(0) complexes with tertiary phosphine-ligands. The catalyst is either added directly, i.e. as tetrakistriphenylphosphine palladium(0) or, more common, the catalyst is produced in situ by reduction of palladium-salts in the presence of a suitable phosphine-ligand. Because of the oxidative addition of R-X to the $Pd(PPh_3)_2$ fragment (Figure 25) the rate determining step is the reactivity of halogenides (ArI > ArBr > ArCl)[201].

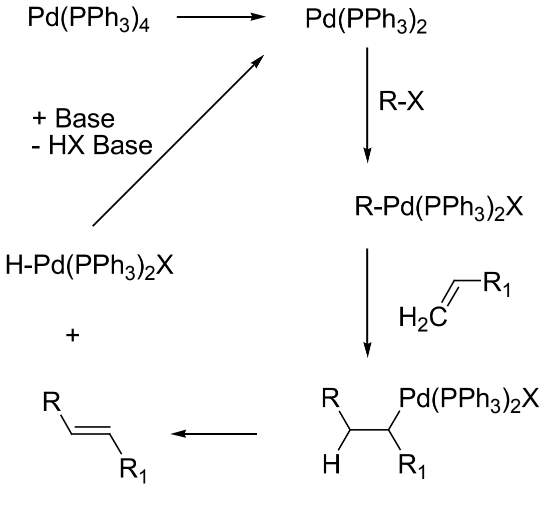


Figure 25: Heck coupling mechanism catalyzed by $Pd(PPh_3)_4$.

Terminal alkenes are appropriate substrates for the Heck-reaction and react at the non-substituted carbon. Non-terminal, 1,2-disubstituted alkenes give usually product mixtures, with a preference for the less sterically hindered carbon[202]. Nowadays, numerous homogeneous palladium catalysts such as $PdCl_2(SEt_2)_2$[187] and palladacycles[195,203,204] have been studied in Heck coupling[188]. Supported palladium catalysts are more attractive due to the ease of product separation and catalyst recycling. Many heterogeneous Heck coupling catalysts have been prepared by different preparation methods. Oxide–supported palladium catalysts[205] such as Pd/SiO_2[206,207], Pd/TiO_2[208], Pd/Al_2O_3[207,208] and Pd/MgO[207], and Pd/C[206,207,209] have been prepared by impregnation or sol-gel processes. Silica immobilized palladium catalysts have been prepared via either amide or urea linkages[197,210,211] or sol-gel processes[209,212,213]. Pd-zeolites have been prepared by ion-exchange[207,208,214,215] or grafting techniques[216,217]. Polymer-supported palladium catalysts have also been developed by polymer cross-linking[197,210,211,218]. These polymers include Merrifield resin[197,210,211] and soluble poly(norbornene)[197,210,211]. Irrespective of the catalyst precursor, none of these catalysts are stable at higher temperatures. They all have a tendency to form soluble palladium(0) colloids or nanoparticles, certainly with less reactive substrates such as aryl bromides or chlorides[219]. In almost all of these studies some degree of leaching of palladium species was observed during the reaction, although palladium species were redeposited on the carrier at the end of the reaction. Arai and co-workers were the first to propose that it is indeed the leached palladium species are responsible for the reaction if supported palladium catalysts are used in the Heck reaction of iodobenzene with methyl acrylate[206,220,221]. Recently, Sommer et al. reported that SCS-pincer Pd(II) complexes merely act as precatalysts decomposing into soluble palladium species that perform the catalytic reaction[197,210,211]. Djakovitch et al. investigated many homogeneous and supported palladium catalysts and the results indicated that dissolved molecular Pd species were responsible for the Heck coupling using heterogeneous catalysts[207]. By using a three phase test with an aryl iodide attached to a solid support, Davies et al. were able to show that the Pd/C becomes active in the Heck reaction with butyl acrylate only after the addition of a soluble monomeric aryl iodide or bromide[194]. Interestingly, he also found that the rate increased with increasing amounts of NaOAc. This suggests that the heterogeneous catalyst is solubilized by oxidative addition of the aryl halide and enters the catalytic cycle in the form of a soluble anionic species such as $[ArPd(OAc)Br]^-$ or $[ArPd(OAc)_n]^-$. Köhler and co-workers performed extensive studies on a range of Pd/C catalysts[208] and found a good correlation between palladium in solution and the conversion of aryl bromide, and palladium species leaching correlates significantly with the Pd species dispersion and palladium oxidation state and the reaction parameters. During the reaction about one third of the palladium species goes into solution, but after the reaction is finished, less than 1 ppm of palladium is found in solution. This indicates that there is a redeposition process after the completion of the reaction. A possible catalytic cycle for the Heck reaction with supported palladium catalysts is depicted in Figure 26. Palladium species leaching is due to the oxidative addition of haloarene.

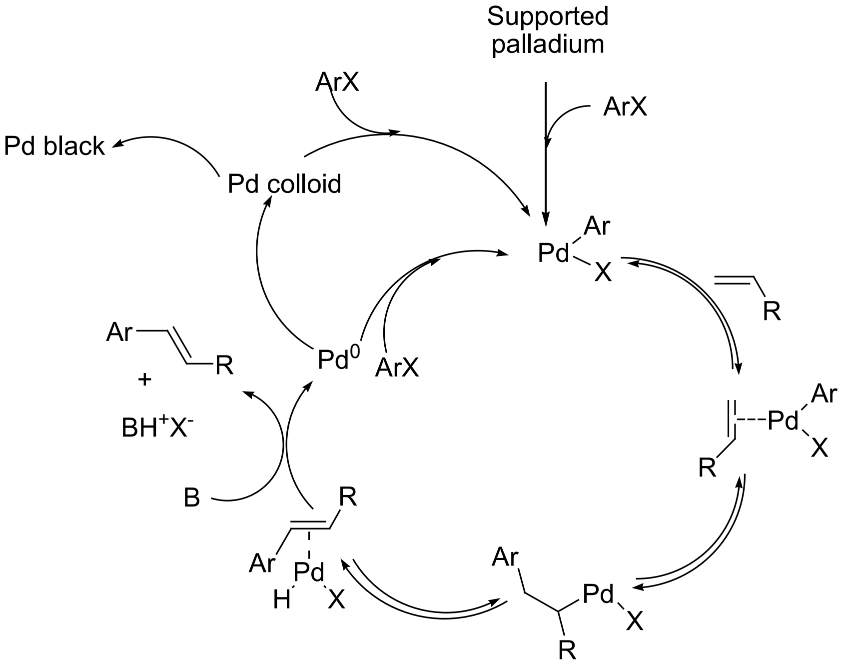


Figure 26: A possible catalytic cycle for the Heck reaction with supported palladium catalysts.

According to above investigations, palladium species dissolving and reprecipitation are crucial and inherent parts of the Heck catalytic cycle and only dissolved palladium species are responsible for Heck coupling. The optimization of supported palladium catalysts and reaction parameters can decrease the palladium species leaching and promote the rate of redeposition process so that a long-term application is possible.

2.6.2 Heck coupling using TGAP-Pd(PPh_3)$_4^{1.00\%Pd}$

In order to investigate the catalytic performance of epoxy resins containing palladium species, TGAP-Pd(PPh_3)$_4^{1.00\%Pd}$ was used as catalyst in the Heck coupling of iodobenzene, 2-iodoanisole and 4-iodoanisole with styrene or butyl acrylate. The reactions were carried out under different reaction conditions using K_2CO_3 or triethylamine (TEA) as base. Heck couplings of iodobenzene with styrene and butyl acrylate are depicted in Figure 27 and 28, respectively. The results are summarized in Table 35.

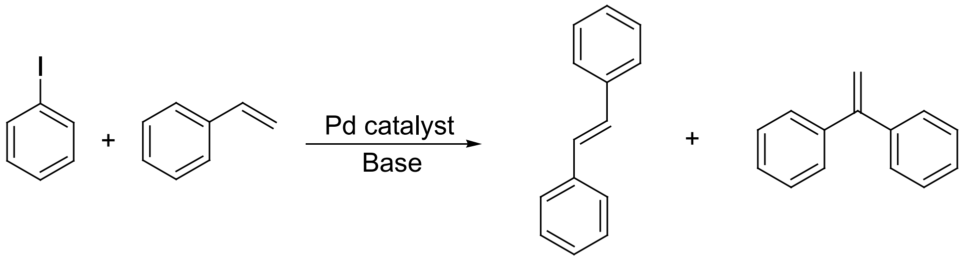


Figure 27: Heck coupling of iodobenzene with styrene catalyzed by Pd catalysts.

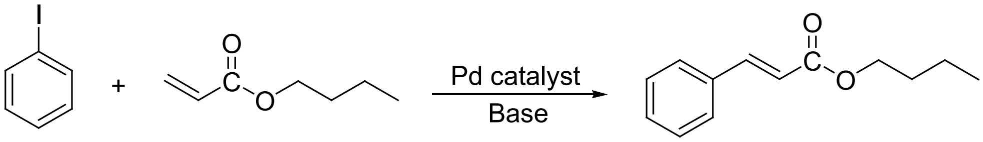


Figure 28: Heck coupling of iodobenzene with butyl acrylate catalyzed by Pd catalysts.

Heck coupling reactions of iodobenzene, 2-iodoanisole and 4-iodoanisole with butyl acrylate were carried out in dioxane/water using K_2CO_3 as base at 90 °C with a reaction time of 24 h. Beyond 99% of aryl iodides were converted and no byproducts were detected in this reaction. It is suggested that water promotes the reaction rate of Heck coupling. Heck coupling of iodobenzene with butyl acrylate was also carried out at 150 °C with a reaction time of 12 h using *N*-methyl-2-pyrrolidinone (NMP) as solvent and K_2CO_3 as base. The results show that iodobenzene is almost quantitatively converted and the selectivity of Heck coupling product is beyond 99%. However, the reaction temperature is too high and the phase-transfer reagent tetrabutylammonium bromide (TBAB) has to be added to the reaction solution. Triethylamine was used as both solvent and base in Heck coupling of styrene with iodobenzene at 80 °C with a reaction time of 24 h. In this case, the conversion of iodobenzene is 52%. (Z)+(E) stilbene and 1,1-diphenylethylene were obtained and the selectivity is 88 and 12%, respectively. The TEA system is an alternative in which TEA acts as solvent and base. However, higher conversion of iodobenzene can not be obtained and the reaction has to be conducted around 80 °C due to the low boiling point of TEA.

Table 35: Heck reaction using TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$[a].

Entry	Reactant 1	Reactant 2	Solvent	Base	T (℃)	Conv.[b] (%)	Sel.[c] (%)
1	Iodobenzene	Butyl acrylate	Dioxane/water	K_2CO_3	90	>99	>99
2	2-Iodoanisole	Butyl acrylate	Dioxane/water	K_2CO_3	90	>99	>99
3	4-Iodoanisole	Butyl acrylate	Dioxane/water	K_2CO_3	90	>99	>99
4	Iodobenzene	Butyl acrylate	NMP	K_2CO_3	150	>99	>99
5	Iodobenzene	Styrene	TEA	TEA	80	52	>99

[a] Entries 1-3: 0.50 g catalyst (particle size: 150-300 μm), 6 mmol butyl acrylate, 5 mmol aryl halide, 10 mmol K_2CO_3, 10 g dioxane, 10 g distilled water, 90 °C, 24 h. Entry 4: 0.50 g catalyst (particle size: 150-300 μm), 12 mmol butyl acrylate, 10 mmol iodobenzene, 10 g *N*-methyl-2-pyrrolidinone, 12 mmol K_2CO_3, 6 mmol tetrabutylammonium bromide, 150 °C, 12 h. Entry 5: 0.50 g catalyst (particle size: 150-300 μm), 12 mmol styrene, 10 mmol iodobenzene, 30 mmol triethylamine (used as both base and solvent), 80 °C, 24 h. [b] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [c] Determined by GC-MS and GC-FID.

2.6.3 Summary

TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$ was tested as catalyst in the Heck coupling of iodobenzene, 2-iodoanisole and 4-iodoanisole with butyl acrylate or styrene. Three reaction systems were used and dioxane/water as solvent gave the most promising results. Using NMP as solvent, a high reaction temperature and the addition of TBAB are necessary for the desired aryl iodide conversion. TEA can be used as both solvent and base. However a lower conversion of iodobenzene was obtained in the reaction with styrene. TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$ can be recovered by simple filtration and aryl iodides can be quantitatively converted under mild reaction conditions. Leached, dissolved palladium species are probably responsible for the catalytic activity as shown for Suzuki coupling reactions.

2.7 TGAP containing metal species for the hydrogenation of unsaturated esters and aldehydes

2.7.1 Developments and applications of hydrogenation catalysts

Catalyst-mediated hydrogenation reactions represent a high percentage of industrially important processes. Numerous transition metal complexes[222-224] have been used in hydrogenation reactions and recent research focus is still on heterogeneous catalysts. Besides the hydrogenation reactions of sorbic acid[222], 2-ethylanthraquinone[225], dimethyl oxalate[223], *trans*-3-buten-4-phenyl-2-one[226], 9-decen-1-ol[227], 2-propen-1-ol[228], acetone[224], allyl alcohol[229] and olefins[230], the hydrogenations of crotonaldehyde[231-237], cinnamaldehyde[226,233], substituted nitrobenzenes[238-241] and acrolein[233,242] have been attracting much interest in the area of heterogeneous catalysis. In the hydrogenation reactions, noble metal based catalysts such as Au[226,231,237,242,243], Pt[232,234,236,244,245,247,248] or Pd[227-230,238-240,244,246,248] based systems are the most commonly used.

2.7.2 TGAP containing metal species for the hydrogenation of unsaturated esters and aldehydes

Pd catalysts are well known to be very selective with respect to the hydrogenation of the C=C bond[249]. Therefore, palladium catalysts based on epoxy resins prepared via homopolymerization were investigated in the hydrogenation of *trans*-ethylcrotonate, *trans*-ethylcinnamate, crotonaldehyde and *trans*-cinnamaldehyde (Figure 29).

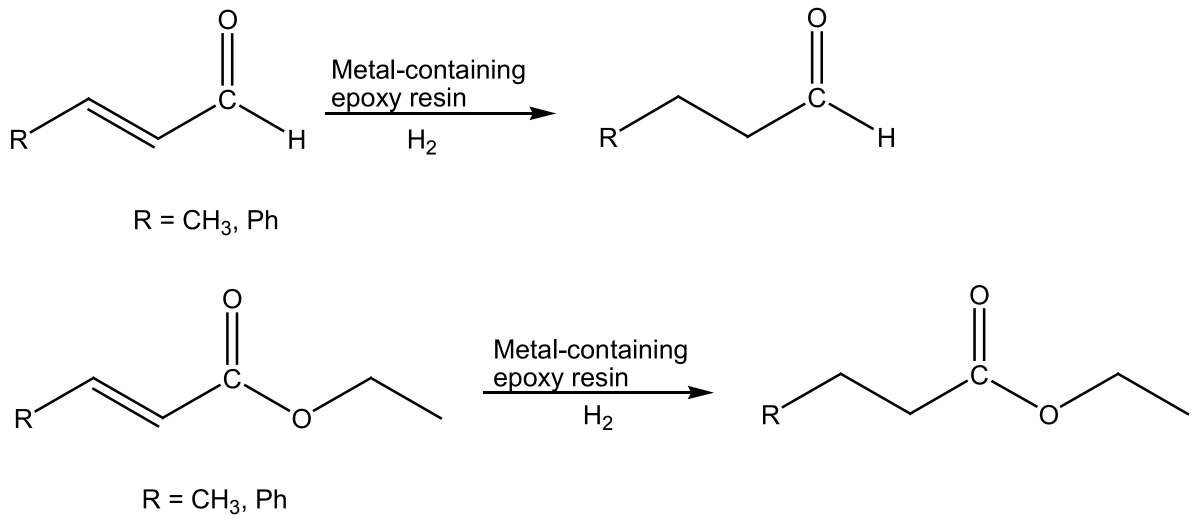


Figure 29: Hydrogenation of different unsaturated substrates catalyzed by palladium catalysts based on epoxy resins.

2.7.2.1 Hydrogenation of unsaturated esters using TGAP-$Mo(OEt)_5^{1.42\%Mo}$-$Pd(PPh_3)_4^{0.50\%Pd}$

TGAP-$Mo(OEt)_5^{1.42\%Mo}$-$Pd(PPh_3)_4^{0.50\%Pd}$, a catalyst system that was already used in the epoxidation of propene (Chapter 2.4.2.2), was evaluated in the hydrogenation of *trans*-ethylcrotonate and *trans*-ethylcinnamate. The catalytic performance and metal leaching of several test reactions are given in Table 36.

In Table 36, it can be seen that the TGAP-$Mo(OEt)_5^{1.42\%Mo}$-$Pd(PPh_3)_4^{0.50\%Pd}$ catalyst is very active in the hydrogenation of *trans*-ethylcrotonate and *trans*-ethylcinnamate. Even at room temperature, the hydrogenation of *trans*-ethylcinnamate can be catalyzed by TGAP-$Mo(OEt)_5^{1.42\%Mo}$-$Pd(PPh_3)_4^{0.50\%Pd}$. The conversion of *trans*-ethylcinnamate can be maintained between 33 and 48% in five consecutive reactions and only ethyl 3-phenylpropionate is formed. The hydrogenation of *trans*-ethylcinnamate was also investigated at 60 °C. The conversions of *trans*-ethylcinnamate are beyond 94% and increase up to 100% in run 5. Besides ethyl 3-phenylpropionate no other products were detected by GC-FID. The metal species leaching is extremely low. The amount of palladium in the reaction solutions is below 200 ng corresponding to 0.01 ppm per run in five recycling runs, and beyond 99.96% of the initial Pd loaded on TGAP is still present after five reactions.

In the hydrogenation of *trans*-ethylcrotonate, the conversions of *trans*-ethylcrotonate in five recycling runs are all beyond 96% after a reaction time of 4 h and only n-butyric acid ethyl ester was formed. The metal leaching determined by AAS is extremely low and the average amount of palladium in the reaction solutions is below 200 ng per run.

The lifetime or reusability is very important for industrial applications. In the hydrogenation of *trans*-ethylcrotonate and *trans*-ethylcinnamate, TGAP-Mo(OEt)$_5$$^{1.42\%Mo}$-Pd(PPh$_3$)$_4$$^{0.50\%Pd}$ can be efficiently recycled five times and there is no change in activity, even the conversions of the two substrates increase along with the reaction runs. This suggests that TGAP-Mo(OEt)$_5$$^{1.42\%Mo}$-Pd(PPh$_3$)$_4$$^{0.50\%Pd}$ is a highly active and long-term stable catalyst in the hydrogenation of *trans*-ethylcrotonate and *trans*-ethylcinnamate.

Table 36: Catalytic performance of TGAP-Mo(OEt)$_5^{1.42\%Mo}$-Pd(PPh$_3$)$_4^{0.50\%Pd}$ in the hydrogenation of *trans*-ethylcrotonate and *trans*-ethylcinnamate[a].

Run no.	*trans*-Ethylcinnamate (RT, 4 h)				*trans*-Ethylcinnamate (60 °C, 4 h)			
	Conv.[b] (%)	Sel.[c] (%)	Pd[d] leached (ng)	Pd[e] content (%)	Conv. (%)	Sel. (%)	Pd leached (ng)	Pd content (%)
1	33	>99	<300	>99.99	99	>99	<200	>99.99
2	37	>99	<300	>99.98	94	>99	<200	>99.98
3	48	>99	<300	>99.96	98	>99	<200	>99.98
4	39	>99	<300	>99.95	99	>99	<200	>99.97
5	41	>99	<300	>99.94	100	>99	<200	>99.96

Run no.	*trans*-Ethylcrotonate (60 °C, 4 h)				*trans*-Ethylcrotonate (60 °C, 24 h)			
	Conv. (%)	Sel. (%)	Pd leached (ng)	Pd content (%)	Conv. (%)	Sel. (%)	Pd leached (ng)	Pd content (%)
1	97	>99	<180	>99.99	100	>99	<310	>99.99
2	96	>99	<170	>99.99	100	>99	<300	>99.98
3	98	>99	<180	>99.98	100	>99	<290	>99.96
4	100	>99	<190	>99.97	100	>99	<320	>99.95
5	100	>99	<200	>99.96	100	>99	<310	>99.94

[a] Reaction conditions: 0.50 g catalyst (particle size: 150-300 μm), 20 ml methanol, 10 mmol substrate, 2.5 bar H_2. [b] Determined by GC-FID (external standard: dodecane). [c] Determined by GC-MS and GC-FID. [d] Determined by AAS by dissolving the reaction residues in concentrated HNO_3. [e] Percentage of palladium initially loaded on the catalyst.

2.7.2.2 Hydrogenation of unsaturated esters and aldehydes using TGAP-Pd(PPh$_3$)$_4^{1.00\%Pd}$

TGAP-Pd(PPh$_3$)$_4^{1.00\%Pd}$ was evaluated in the hydrogenation of *trans*-ethylcinnamate and *trans*-ethylcrotonate. In order to compare the reaction rate in the hydrogenation of C=O double bond with the reaction rate in the hydrogenation of C=C double bond, *trans*-cinnamaldehyde and crotonaldehyde were also used as substrates. The results are summarized in Table 37.

In the hydrogenation of *trans*-ethylcinnamate, TGAP-Pd(PPh$_3$)$_4^{1.00\%Pd}$ shows high catalytic activity and long-term stability using methanol as solvent. Beyond 95% conversions of *trans*-ethylcinnamate can be obtained in the reactions with a reaction time of 4 h. The selectivity to the hydrogenation product ethyl 3-phenylpropionate is beyond 99% and no other byproducts can be detected by GC-FID. In five consecutive reactions, TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$ can be recycled by simple filtration and used in the next run without any treatments. When TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$ was used in the fourth and fifth runs, *trans*-ethylcinnamate was quantitatively converted to the corresponding hydrogenation product ethyl 3-phenylpropionate. ICP-AES analyses can not measure the concentration of palladium in the reaction solutions. Therefore, AAS was used to measure the amount of palladium in the reaction solutions. The obtained results show that the amounts of palladium in the solutions are below 210 ng in every run and beyond 99.98% of initially loaded palladium are retained in the epoxy matrix after five reactions. This suggests that TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$ possesses a high long-term activity and stability and could be suitable for technological applications.

In the hydrogenation of *trans*-ethylcrotonate, TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$ shows a similar activity and long-term stability as in the hydrogenation of *trans*-ethylcinnamate using methanol as solvent. TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$ can be recycled by simple filtration and used in five consecutive runs without any treatments. The conversions of *trans*-ethylcrotonate after a reaction time of 4 h are all beyond 96% and increase with the reaction runs. In the fourth run, *trans*-ethylcrotonate can be completely converted to the corresponding hydrogenation product n-butyric acid ethyl ester. No other byproducts can be detected by GC-FID and GC-MS. Obtained AAS data show that the amount of palladium in the reaction solutions is extremely low. In all of the reactions, the amounts of palladium in the reaction solutions are below 210 ng per run and beyond 99.98% of initially loaded Pd are saved in the epoxy matrix after five reactions. This suggests that TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$ is highly catalytically active and long-term stable in the hydrogenation of *trans*-ethylcrotonate.

Considering the hydrogenation of crotonaldehyde using TGAP-Pd(PPh$_3$)$_4$$^{1.00\%Pd}$ as catalyst and toluene as solvent, some results are also summarized in Table 37. The hydrogenation of crotonaldehyde has been investigated extensively using different metal catalysts including impregnated Cu/SiO_2[235] and $Cu\text{-}ZnO/SiO_2$[235], coprecipitated $Cu\text{-}Al_2O_3$[235] and $Cu_x\text{-}Zn_yO_{2y}\text{-}ZnAl_2O_4$[235], Pt/SiO_2[232], Pt/Al_2O_3[232], Pt/TiO_2[232], $Pt/ZnCl_2/SiO_2$[234], Sn/Pt(111) alloy model catalysts[236], Au/ZnO[237], Au/ZrO_2[231], $Rh\text{-}Sn/SiO_2$[233] and Ag/SiO_2[233]. Three possible products in the hydrogenation of C=C and of C=O double bonds of crotonaldehyde are butyraldehyde, crotyl alcohol and butanol. The ratio of three products can be changed using different supports, modified species and reaction conditions[233]. For example, butyraldehyde is the main product in the hydrogenation of crotonaldehyde using Pt/SiO_2[232], Pt/Al_2O_3[232], Cu/SiO_2[235], Cu/Al_2O_3[235], Pt(111)[236] and Au/SiO_2[231] as catalysts. However, when using Ag/SiO_2[233], S-Au/ZnO[231,237], $Pt/ZnCl_2/SiO_2$[234], Pt/TiO_2[232] and $Cu\text{-}ZnO/SiO_2$[235] as catalysts, the selectivity to crotyl alcohol increases so much and can reach 80% in some cases. It is well known that in the hydrogenation of crotonaldehyde[234,235] the competitive hydrogenation of C=C bond is usually faster than C=O bond hydrogenation on noble metals. Although crotyl alcohol is more useful as valuable intermediate for the production of perfumes, flavoring and pharmaceuticals, the formation of butyraldehyde in the hydrogenation of crotonaldehyde under mild reaction conditions is also desired. In the hydrogenation of crotonaldehyde using $TGAP\text{-}Pd(PPh_3)_4^{1.00\%Pd}$ as catalyst and toluene as solvent, only butyraldehyde was formed. The reaction condition is milder than in the cases of other supported metal catalysts[231,233,234,237]. $TGAP\text{-}Pd(PPh_3)_4^{1.00\%Pd}$ can be recycled by simple filtration and used in the next run without any treatments. In five consecutive runs with a reaction time of 24 h, crotonaldehyde was converted to butyraldehyde completely and $TGAP\text{-}Pd(PPh_3)_4^{1.00\%Pd}$ shows no loss in activity. The amount of palladium in the reaction solution is below 320 ng per run as measured by sensitive AAS analyses. After the fifth run, beyond 99.97% of initially loaded Pd on the catalyst are still kept in the epoxy matrix. This shows that $TGAP\text{-}Pd(PPh_3)_4^{1.00\%Pd}$ is a highly effective, long-term active and stable catalyst for the hydrogenation of crotonaldehyde.

$TGAP\text{-}Pd(PPh_3)_4^{1.00\%Pd}$ was also used as catalyst in the hydrogenation of *trans*-cinnamaldehyde. The reactions were also carried out with a reaction time of 24 h at

60 °C using toluene as solvent and the results are given in Table 37. Au/Fe_2O_3[226] was used as catalyst for the hydrogenation of *trans*-cinnamaldehyde and the conversion of *trans*-cinnamaldehyde can reach 100%. The selectivity to cinnamyl alcohol is higher than 85% claimed by the authors. Our results show that only hydrogenation of the C=C double bond occurs. Five consecutive reactions were carried out and TGAP-$Pd(PPh_3)_4^{1.00\%Pd}$ showed no loss of activity. The conversions of *trans*-cinnamaldehyde are around 80%. TGAP-$Pd(PPh_3)_4^{1.00\%Pd}$ can be recycled by simple filtration and used in the next run without any treatments. The obtained AAS data show that the amount of palladium in the reaction solutions is below 330 ng per run and beyond 99.97% of initial Pd loaded on the support were saved after five runs. These results show that TGAP-$Pd(PPh_3)_4^{1.00\%Pd}$ is a highly active and long-term stable catalyst for the hydrogenation of *trans*-cinnamaldehyde under mild reaction conditions.

In summary, TGAP-$Pd(PPh_3)_4^{1.00\%Pd}$ shows high activity and long-term stability for the hydrogenation of C=C double bonds and C=O double bonds are not converted. TGAP-$Pd(PPh_3)_4^{1.00\%Pd}$ can easily be recycled from the reaction solutions and reused.

Table 37: Catalytic performance of TGAP-Pd$(PPh_3)_4$$^{1.00\%Pd}$ in the hydrogenation of different substrates[a].

Run no.	*trans*-Ethylcinnamate (60 °C, 4 h) Conv.[b] (%)	Sel.[c] (%)	Pd[d] leached (ng)	Pd[e] content (%)	*trans*-Ethylcrotonate (60 °C, 4 h) Conv. (%)	Sel. (%)	Pd leached (ng)	Pd content (%)
1	95	>99	<210	>99.99	96	>99	<200	>99.99
2	99	>99	<210	>99.99	98	>99	<200	>99.99
3	97	>99	<200	>99.99	98	>99	<210	>99.99
4	100	>99	<200	>99.98	100	>99	<170	>99.98
5	100	>99	<210	>99.98	100	>99	<180	>99.98

Run no.	Crotonaldehyde (60 °C, 24 h) Conv. (%)	Sel. (%)	Pd leached (ng)	Pd content (%)	*trans*-Cinnamaldehyde (60 °C, 24 h) Conv. (%)	Sel. (%)	Pd leached (ng)	Pd content (%)
1	100	>99	<320	>99.99	88	>99	<300	>99.99
2	100	>99	<310	>99.99	81	>99	<320	>99.99
3	100	>99	<300	>99.98	85	>99	<220	>99.98
4	100	>99	<310	>99.98	79	>99	<300	>99.98
5	100	>99	<320	>99.97	81	>99	<330	>99.97

[a] Reaction conditions: 0.50 g catalyst (particle size: 300-500 µm), 10 mmol substrate, 20 ml toluene in the hydrogenation of crotonaldehyde and *trans*-cinnamaldehyde or 20 ml methanol in the hydrogenation of *trans*-ethylcrotonate and *trans*-ethylcinnamate, 2.5 bar H_2. [b] Determined by GC-FID (external standard: dodecane). [c] Determined by GC-MS and GC-FID. [d] Determined by AAS by dissolving the reaction residues in concentrated HNO_3. [e] Percentage of palladium originally loaded on the catalyst.

2.7.2.3 Hydrogenation of *trans*-ethylcrotonate using TGAP-Nb$(OEt)_5$$^{1.00\%Nb}$

In order to compare with supported palladium catalysts based on epoxy resins, TGAP-Nb$(OEt)_5$$^{1.00\%Nb}$ was prepared via homopolymerization of TGAP using Nb$(OEt)_5$ as initiator (supported niobium catalysts are well known in the hydrogenation of alkenes[250]) and evaluated in the hydrogenation of *trans*-ethylcrotonate under identical reaction conditions as in the Pd-catalyzed reactions. The results are summarized in Table 38. In five consecutive runs, the conversion of *trans*-ethylcrotonate is low and varies beteen 16 and 23%. The conversion of *trans*-ethylcrotonate increases with the reaction runs gradually. This suggests that there is an induction period for the catalyst to become more active. The selectivity to n-butyric acid ethyl ester is beyond 99% and no byproducts were detected by GC-MS and GC-FID. This shows that TGAP-Nb$(OEt)_5$$^{1.00\%Nb}$ is not as catalytically active as TGAP-Pd(PPh_3)$_4$$^{1.00\%Pd}$. The catalyst can be recycled by simple filtration and reused without any treatments.

Table 38: Hydrogenation of *trans*-ethylcrotonate using TGAP-Nb(OEt)$_5$$^{1.00\%Nb}$[a].

Run no.	Conversion[b] (%)	Selectivity[c] (%)
1	16	>99
2	18	>99
3	19	>99
4	20	>99
5	23	>99

[a] Reaction conditions: 0.50 g catalyst (particle size: 300-500 µm), 10 mmol substrate, 20 ml methanol, 2.5 bar H_2, 60 ^{o}C, 4 h. [b] Determined by GC-FID (external standard: dodecane). [c] Determined by GC-MS and GC-FID.

2.7.3 Summary

In the hydrogenation of unsaturated esters and aldehydes such as *trans*-ethylcrotonate, *trans*-ethylcinnamate, crotonaldehyde and *trans*-cinnamaldehyde, three TGAP supported catalysts TGAP-Mo(OEt)$_5$$^{1.42\%Mo}$-Pd($PPh_3$)$_4$$^{0.50\%Pd}$, TGAP-Pd($PPh_3$)$_4$$^{1.00\%Pd}$ and TGAP-Nb(OEt)$_5$$^{1.00\%Nb}$ were investigated. TGAP-Nb(OEt)$_5$$^{1.00\%Nb}$ exhibits low catalytic activity. However, TGAP-Mo(OEt)$_5$$^{1.42\%Mo}$-Pd($PPh_3$)$_4$$^{0.50\%Pd}$ and TGAP-Pd(PPh_3)$_4$$^{1.00\%Pd}$ show high activities and selectivities. *trans*-Ethylcrotonate, *trans*-ethylcinnamate and crotonaldehyde can be quantitatively converted to the corresponding hydrogenation products. In the case of unsaturated aldehydes, hydrogenation occurs only at the C=C double bond. The catalysts can be separated and recovered by simple filtration and reused without any treatments. The amount of palladium in the reaction solutions is extremely low and below 330 ng corresponding to 0.02 ppm per run. After five consecutive runs, beyond 99.97% of palladium initially loaded on the catalyst are retained and make a long-term application possible.

2.8 Magnetic catalysts based on epoxy resins

2.8.1 Developments and applications of magnetic catalysts

Magnetic catalysts are attractive due to the ease of product separation and catalyst recycling by magnetic decantation[251]. Nowadays, numerous magnetic catalysts have been developed. Recycling of homogeneous Pd catalysts using superaramagnetic nanoparticles as novel supports for Suzuki, Heck, and Sonogashira cross-coupling reactions have been reported by Stevens et al.[252-254]. Phan et al.[255] reported that diaminosilane-functionalized cobalt spinel ferrite ($CoFe_2O_4$) magnetic nanoparticles were synthesized and used as efficient heterogeneous base catalysts for Knoevenagel condensations of aromatic and heteroaromatic aldehydes with malononitrile. Quantitative conversion of the reactants was achieved under mild conditions and the supported catalyst was reused five times without significant decrease in catalytic activity. Tsang et al. reported magnetically separable, carbon-supported nanocatalysts for the manufacture of fine chemicals[256]. Hu et al. reported magnetically recoverable chiral catalysts immobilized on magnetite nanoparticles for asymmetric hydrogenation of aromatic ketones[257]. Yoon et al.[258] reported that magnetic nanoparticle-supported Rh catalysts showed very effective catalytic activity in the hydroformylation of olefins and could be easily recovered from the reaction mixture by magnetic decantation to be used in subsequent reactions. Abu-Rezig et al.[259] reported that supported Rh catalysts based on dendronized magnetic nanoparticles were highly selective hydroformylation catalysts. In addition, magnetic nanocomposite catalysts have been applied in the selective hydrogenation reactions[260-262].

2.8.2 Investigations on the catalytic activities and stabilities of magnetic catalysts

Some magnetic catalysts have been prepared via epoxy resin homopolymerization after the addition of Fe particles (particle size: < 10 μm). Their catalytic activity and long-term stability were evaluated in the epoxidation of cyclohexene, Suzuki coupling of

4-iodoanisole with phenylboronic acid and hydrogenation of unsaturated esters and aldehydes. These magnetic catalysts include Novolac$^{64\%}$/Fe$^{29\%}$-Mo(EH)$_n^{1.00\%Mo}$ and TGAP$^{44\%}$/Fe$^{50\%}$-Pd(PPh$_3$)$_4^{0.50\%Pd}$.

2.8.2.1 Epoxidation of cyclohexene using Novolac$^{64\%}$/Fe$^{29\%}$-Mo(EH)$_n^{1.00\%Mo}$ and TBHP

Novolac$^{64\%}$/Fe$^{29\%}$-Mo(EH)$_n^{1.00\%Mo}$ was used as catalyst in the epoxidation of cyclohexene with TBHP as oxidant. The reactions were carried out 90 ^{o}C with a reaction time of 7 h in runs 1-5, and with a reaction time of 24 h in runs 6-10. The results are summarized in Table 39.

In Table 39, it can be seen that the catalyst has low activity and beyond 92% selectivity to cyclohexene epoxide. In runs 1-5 with a reaction time of 7 h, the conversion of cyclohexene varies between 60 and 68% and in runs 6-10 with a reaction time of 24 h, it varies between 61 and 82%. This is lower than using Novolac-Mo(EH)$_n^{1.50\%Mo}$ under the same reaction conditions. Byroducts are cyclohexenol and cyclohexenone arising from allylic oxidation of cyclohexene as well as diol arising from epoxide ring-opening. Molybdenum species leaching is significant and the amount of molybdenum in the reaction solutions varies between 2.03 and 12.32 µg corresponding to 0.5-3.0 ppm. Molybdenum species leaching is higher than in the case of Novolac-Mo(EH)$_n^{1.50\%Mo}$. After ten consecutive runs, 98.55% of molybdenum originally loaded on the catalyst are retained. Lower activity and higher molybdenum species leaching could be due to the presence of iron particles. Maybe the presence of iron promotes the decomposition of TBHP. Another possibility could be that active metal sites are blocked by iron particles so that the substrates can not access to the active species.

Table 39: Cyclohexene epoxidation using Novolac$^{64\%}$/Fe$^{29\%}$-Mo(EH)$_n^{1.00\%Mo}$ and TBHP[a].

Run no[b].	Conv. [c] (%)	Sel.[d] (%)	Mo[e] leached (µg)	Mo[f] content (%)	Byproduct selectivity (%)			
					Cyclohexenol	Cyclohexenone	Diol	Others
1	64	94	5.49	99.89	2	2	2	<1
2	67	94	3.46	99.82	2	2	2	<1
3	68	93	2.55	99.77	2	2	2	<1
4	63	92	2.03	99.73	3	2	2	<1
5	60	95	4.73	99.64	2	2	1	<1
6	82	94	12.32	99.39	2	1	3	<1
7	66	95	11.24	99.17	2	1	2	<1
8	74	95	11.08	98.95	2	1	2	<1
9	61	93	10.51	98.74	3	2	2	<1
10	62	94	9.77	98.55	2	2	2	<1

[a] Reaction conditions: 500 mg catalyst (particle size: 300-500 µm), 10 mmol cyclohexene, 12 mmol TBHP (36 wt.% TBHP/toluene). [b] The catalyst was used with a reaction time of 7 h in runs 1-5, and 24 h in the following 5 runs. [c] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [d] Byproducts are cyclohexenol, cyclohexenone and diol. [e] Determined by ICP-AES by dissolving the reaction residues in concentrated 65% HNO_3. [f] Percentage of Mo initially loaded on the catalyst.

2.8.2.2 Suzuki coupling of 4-iodoanisole with phenylboronic acid using TGAP$^{44\%}$/Fe$^{50\%}$-Pd(PPh$_3$)$_4^{0.50\%Pd}$

TGAP$^{44\%}$/Fe$^{50\%}$-Pd(PPh$_3$)$_4^{0.50\%Pd}$ was investigated in the Suzuki coupling of 4-iodoanisole with phenylboronic acid using a dioxane/water mixture as solvent. The reactions were carried out at 90 °C with a reaction time of 4 h. The results are summarized in Table 40.

It can be seen that the conversion of 4-iodoanisole varies between 52 and 76%. This is lower than in the case of TGAP-Pd(PPh$_3$)$_4^{1.00\%Pd}$ under identical reaction conditions. No byproducts were detected by GC-MS and GC-FID. Palladium species leaching is high and the amount of palladium in the reaction solutions is between 23 and 29 µg correponding to 1 ppm. Maybe iron particles interfere with the resin crosslinking giving a higher metal species leaching.

Table 40: Suzuki coupling of 4-iodoanisole with phenylboronic acid using TGAP$^{44\%}$/Fe$^{50\%}$-Pd(PPh$_3$)$_4$$^{0.50\%Pd[a]}$.

Run no.	Conversion[b] (%)	Selectivity[c] (%)	Pd[d] leached (µg)
1	76	>99	28.77
2	65	>99	26.34
3	63	>99	24.42
4	55	>99	24.55
5	52	>99	22.77

[a] Reaction conditions: 0.50 g catalyst (particle size: 300-500 µm), 10 mmol 4-iodoanisole, 12 mmol phenylboronic acid, 20 mmol K_2CO_3, 10 ml dioxane, 10 ml distilled water, 90 ^{o}C, 4 h. [b] Determined by GC-MS and GC-FID using calibration curves obtained with standard solutions and dodecane as external standard. [c] Determined by GC-MS and GC-FID. [d] Determined by ICP-AES.

2.8.2.3 Hydrogenation of unsaturated esters and aldehydes using TGAP$^{44\%}$/Fe$^{50\%}$-Pd(PPh$_3$)$_4$$^{0.50\%Pd}$

TGAP$^{44\%}$/Fe$^{50\%}$-Pd(PPh$_3$)$_4$$^{0.50\%Pd}$ was also investigated in the hydrogenation of *trans*-ethylcrotonate and crotonaldehyde. The reactions were carried out at 60 ^{o}C with a reaction time of 4 h in the hydrogenation of *trans*-ethylcrotonate and with a reaction time of 24 h in the hydrogenation of crotonaldehyde. The results are summarized in Table 41.

In the hydrogenation of *trans*-ethylcrotonate using methanol as solvent, TGAP$^{44\%}$/Fe$^{50\%}$-Pd(PPh$_3$)$_4$$^{0.50\%Pd}$ can be recycled by magnetic decantation and reused in the following runs without any treatments. In five consecutive runs, n-butyric acid ethyl ester was obtained quantitatively. There is no loss in activity using this catalyst. Obtained AAS data show that the amount of palladium in the reaction solutions is below 170 ng except for the first run and beyond 99.96% of initially loaded Pd are saved on the catalyst. This shows that the catalyst is recyclable and could be reused without any loss of activity.

In the hydrogenation of crotonaldehyde using toluene as solvent, TGAP$^{44\%}$/Fe$^{50\%}$-Pd(PPh$_3$)$_4$$^{0.50\%Pd}$ can be recycled by magnetic decantation and reused without loss of activity. Only butyraldehyde was formed in the reaction solution and crotonaldehyde can be converted to butyraldehyde quantitatively using this catalyst. The metal leaching was determined by AAS analysis of the reaction solutions. Leaching is high in the first run (550 ng) and decreases significantly to values below 150 ng in the fifth run. After five consecutive runs, beyond 99.94% of initially loaded Pd are saved. This shows that the magnetic catalyst TGAP$^{44\%}$/Fe$^{50\%}$-Pd(PPh$_3$)$_4$$^{0.50\%Pd}$ possesses highly catalytic activity and long-term stability in the hydrogenation of crotonaldehyde and can be easily separated from the reaction solutions by magnetic decantation.

Table 41: Catalytic performance of the magnetic catalyst TGAP$^{44\%}$/Fe$^{50\%}$-Pd(PPh$_3$)$_4$$^{0.50\%Pd}$ in the hydrogenation of *trans*-ethylcrotonate and crotonaldehyde[a].

Run no.	*trans*-Ethylcrotonate (60 °C, 4 h)				Crotonaldehyde (60 °C, 24 h)			
	Conv.[b] (%)	Sel.[c] (%)	Pd[d] leached (ng)	Pd[e] content (%)	Conv. (%)	Sel. (%)	Pd leached (ng)	Pd content (%)
1	100	>99	220	>99.99	100	>99	550	>99.98
2	100	>99	<170	>99.99	100	>99	260	>99.97
3	100	>99	<170	>99.98	100	>99	240	>99.96
4	100	>99	<170	>99.97	100	>99	170	>99.95
5	100	>99	<170	>99.96	100	>99	<150	>99.94

[a] Reaction conditions: 0.50 g catalyst (particle size: 300-500 µm), 10 mmol substrate, 20 ml toluene used as solvent in the hydrogenation of crotonaldehyde or 20 ml methanol used as solvent in the hydrogenation of *trans*-ethylcrotonate, 2.5 bar H_2. [b] Determined by GC-FID (external standard: dodecane). [c] Determined by GC-MS and GC-FID. [d] Determined by AAS by dissolving the reaction residues in concentrated HNO_3. [e] Percentage of palladium initially loaded on the catalyst.

2.8.3 Summary

Magnetic catalysts are attractive due to the possibility of magnetic separation and recyclability. Novolac$^{64\%}$/Fe$^{29\%}$-Mo(EH)$_n$$^{1.00\%Mo}$ and TGAP$^{44\%}$/Fe$^{50\%}$-Pd(PPh$_3$)$_4$$^{0.50\%Pd}$ were prepared via epoxy resin homopolymerization in the presence of iron particles and evaluated in the epoxidation of cyclohexene with TBHP, Suzuki coupling of 4-iodoanisole with phenylboronic acid, and hydrogenation of *trans*-ethylcrotonate and crotonaldehyde. In the epoxidation of cyclohexene, the presence of iron on Novolac$^{64\%}$/Fe$^{29\%}$-Mo(EH)$_n$$^{1.00\%Mo}$ maybe accelerates the decomposition of TBHP. Conversions are lower compared with similar catalysts without iron and leaching is higher. Moderate conversions were obtained in the Suzuki coupling of iodoanisole associated with higher palladium species leaching compared to iron-free catalysts. When the hydrogenation of *trans*-ethylcrotonate and crotonaldehyde was investigated with the magnetic catalyst TGAP$^{44\%}$/Fe$^{50\%}$-Pd(PPh$_3$)$_4^{0.50\%Pd}$, the substrates can be quantitatively hydrogenated at the C=C double bonds. The amount of palladium in the reaction solutions is low and below 550 ng corresponding to 0.03 ppm per run. After five recycling reaction runs, beyond 99.94% of palladium initially loaded on the catalyst are retained.

3 Conclusions and outlook

Epoxy resins are excellent supports for the immobilization of *d*-block metal species and can be cured by homopolymerization of the epoxy resins or polyaddition of the epoxy resins and anhydrides using *d*-block metal complexes as initiators. Transition metal complexes can release ligands at elevated temperatures that promote anionic epoxy resin polymerization. TGA data of the metal species-containing epoxy resins TGMDA-$Mo(OEt)_5^{1.50\%Mo}$, TGAP-$Mo(EH)_n^{1.50\%Mo}$, Novolac-$Mo(EH)_n^{1.50\%Mo}$ and TGAP-$Pd(PPh_3)_4^{1.00\%Pd}$ show that these materials possess high thermostability and can be used up to 300 °C. SEM-EDX images show that transition metal species are highly dispersed on the supports that effectively suppress their agglomeration and aggregation. Obtained materials were used as catalysts in the epoxidation of liquid alkenes and propene, Suzuki and Heck coupling reactions, and hydrogenation of unsaturated esters and aldehydes.

In the epoxidation of liquid alkenes with TBHP or CHP as oxidant, epoxy resins containing molybdenum species prepared via homopolymerization show better long-term stability than those prepared via polyaddition. Among the supported molybdenum catalysts investigated, TGMDA-$Mo(OEt)_5^{1.50\%Mo}$, TGAP-$Mo(EH)_n^{1.50\%Mo}$ and Novolac-$Mo(EH)_n^{1.50\%Mo}$ exhibit the best catalytic activities and long-term stabilities. Epoxy resins containing titanium and tungsten species do not display the desired activity. In the epoxidation of allylic alcohols, TGMDA-$VO(OPr)_3^{1.50\%V}$ and TGAP-$V(NAPH)_n^{1.00\%V}$ show good catalytic activity but comparatively high metal species leaching. Using TGMDA-$Mo(OEt)_5^{1.50\%Mo}$ as catalyst, metal species leaching depends on the nature of alkene. Among the investigated liquid alkenes, 1-octene is more difficult to be epoxidized by TBHP than other alkenes. The byproducts in cyclohexene epoxidation are due to allylic oxidation and epoxide ring-opening. In the epoxidation of (R)-(+)-limonene, the double bond in the ring is mainly epoxidized and byproducts are the dioxirane and products arising from isomerization processes and allylic oxidation. Using other alkenes such as 1-octene, *trans*-2-octene and styrene, the selectivities to their oxiranes are all beyond 99%. ICP-AES analyses show that metal species leaching from the polymers is extremely low. A long-term test in the epoxidation of cyclohexene exhibits that TGAP-Mo(EH)$_n$$^{1.50\%Mo}$ is highly stable with respect to the thermal and oxidative decomposition and can be used over at least 875 h. Hot filtration test shows that homogeneous catalysis mainly takes place in combination with surface catalysis. In most cases, the conversions of liquid alkenes correlate to metal leaching. The higher the metal species leaching, the higher the alkene conversion.

Propene epoxidation with TBHP was investigated using molybdenum catalysts based on epoxy resins such as single metal species catalysts (TGMDA-Mo(OEt)$_5$$^{1.50\%Mo}$, Novolac-Mo(EH)$_n$$^{1.50\%Mo}$ and TGAP-Mo(EH)$_n$$^{1.50\%Mo}$), a double metal species catalyst (TGAP-Mo(OEt)$_5$$^{1.42\%Mo}$-Pd(PPh$_3$)$_4$$^{0.50\%Pd}$) and an epoxy/cyanate ester blend containing molybdenum species (TGAP/PT30-Mo(OEt)$_5$$^{0.75\%Mo}$). Usually, the propene oxide yield and molybdenum species leaching strongly depend on reaction conditions and decrease with the decrease of reaction temperature and reaction time. In some cases, propene oxide yields are high while molybdenum species leaching is comparatively low. Among the investigated catalysts, Novolac-Mo(EH)$_n$$^{1.50\%Mo}$ exhibits comparatively low stability. In most cases, the propene oxide yields decrease slightly after some reactions. The catalysts can be isolated from the reaction solutions by simple filtration and reused without any treatments. In the investigation of catalyst recycling, the epoxy resins containing molybdenum species all show high long-term activities and stabilities in the epoxidation of propene using TBHP as oxidant. In comparison with other reported polymer-supported molybdenum epoxidation catalysts, the performance of epoxy resins containing molybdenum species is superior.

In the Suzuki coupling of haloarenes with arylboronic acids, TGAP containing palladium species (0.50 or 1.00% Pd) was investigated. The investigation of different solvents shows that the activity of catalysts is closely related to the solvents used and dioxane/water mixtures are particularly suitable. There is also an important impact from the used bases and K_2CO_3 promotes the reaction rate of Suzuki coupling. The presence of water is very important for the desired conversion of haloarene. It is suggested that polar water leads to more palladium species leaching from the support and then promotes the reaction in the homogeneous phase. Sufficient water is necessary and the best dioxane/water ratio is 1:1. TGAP containing palladium species can be applied in a wide range of haloarenes. The catalysts can be easily isolated by simple filtration and reused without any treatments and without loss of activity. A competition reaction shows that functional groups at the haloarenes have an important influence on the reaction rate and the reaction rate decreases in the order: electron-withdrawing > neutral > electron-donating substituents. The reaction rates of haloarenes decrease in the order: aryl iodides > aryl bromides > aryl chlorides. A hot filtration test shows only around 30% conversion of 2-iodoanisole due to dissolved palladium species. Hg(0) and PVPy poisoning tests show that exclusively dissolved palladium species are responsible for the activity. A redeposition test shows that the amount of dissolved but redeposited palladium species on the support after the completion of the reaction is high, and there is an equilibrium between the dissolving and redeposition process. It is suggested that leaching of palladium species from the support is induced by oxidative addition of haloarenes. In summary, TGAP containing palladium species acts as a reservoir of catalytically active species and Suzuki coupling occurs via homogeneous catalysis. Although a homogeneous catalysis mechanism was confirmed, TGAP containing palladium species could be a promising catalyst system for technological applications due to the slow release of active palladium species and the existence of dissolving/redeposition process so that the catalysts can be used over a long period without loss in activity.

TGAP-$Pd(PPh_3)_4^{1.00\%Pd}$ was investigated in the Heck coupling of iodobenzene, 2-iodoanisole and 4-iodoanisole with butyl acrylate or styrene. Three reaction systems were used and dioxane/water mixtures as solvent gave promising results. Sufficient water is needed to accelerate the reaction rate. Using NMP as solvent, a high reaction temperature and the addition of TBAB is needed for the desired aryl iodide conversions. Using TEA as both solvent and base, the catalyst can be easily separated from the reaction solutions. However, lower conversions of aryl iodides were obtained compared to dioxane/water/K_2CO_3 system. TGAP-$Pd(PPh_3)_4^{1.00\%Pd}$ can be recovered by simple filtration and aryl iodides can be quantitatively converted under mild reaction conditions. The leached, dissolved palladium species are probably responsible for the catalytic activity as shown for Suzuki coupling reactions.

In the hydrogenation of unsaturated esters and aldehydes such as *trans*-ethylcrotonate, *trans*-ethylcinnamate, crotonaldehyde and *trans*-cinnamaldehyde, three TGAP supported catalysts TGAP-$Mo(OEt)_5^{1.42\%Mo}$-$Pd(PPh_3)_4^{0.50\%Pd}$, TGAP-$Pd(PPh_3)_4^{1.00\%Pd}$ and TGAP-$Nb(OEt)_5^{1.00\%Nb}$ were investigated. TGAP-$Nb(OEt)_5^{1.00\%Nb}$ exhibits low catalytic activity. However, TGAP-$Mo(OEt)_5^{1.42\%Mo}$-$Pd(PPh_3)_4^{0.50\%Pd}$ and TGAP-$Pd(PPh_3)_4^{1.00\%Pd}$ show good activity and selectivity. *trans*-Ethylcrotonate and *trans*-ethylcinnamate can be almost quantitatively converted to the corresponding hydrogenation products n-butyric acid ethyl ester and ethyl 3-phenylpropionate at 60 ^{o}C with a reaction time of 4 h using TGAP-$Mo(OEt)_5^{1.42\%Mo}$-$Pd(PPh_3)_4^{0.50\%Pd}$ as catalyst, respectively. Using TGAP-$Pd(PPh_3)_4^{1.00\%Pd}$ as catalyst, the unsaturated substrates except *trans*-cinnamaldehyde (80%) can also be hydrogenated at the C=C bonds quantitatively. The catalysts can be separated and recovered by filtration and reused without any treatments. The amount of palladium in the reaction solutions is extremely low and below 330 ng corresponding to 0.02 ppm per run. After five consecutive runs, beyond 99.97% of palladium initially loaded on the catalyst are retained and make a long-term application possible.

Magnetic catalysts are attractive due to the possibility of magnetic separation and recyclability. $Novolac^{64\%}/Fe^{29\%}$-$Mo(EH)_n^{1.00\%Mo}$ and $TGAP^{44\%}/Fe^{50\%}$-$Pd(PPh_3)_4^{0.50\%Pd}$ were prepared via epoxy resin homopolymerization in the presence of iron particles and evaluated in the epoxidation of cyclohexene with TBHP, Suzuki coupling of 4-iodoanisole with phenylboronic acid, and hydrogenation of *trans*-ethylcrotonate and crotonaldehyde. In the Suzuki coupling and epoxidation reactions, no promising results were obtained due to either high metal species leaching or low activity arising from the formation of inactive species. In the epoxidation of cyclohexene, the presence of iron on $Novolac^{64\%}/Fe^{29\%}$-$Mo(EH)_n^{1.00\%Mo}$ maybe accelerates the non-productive decomposition of TBHP. Another possibility is that active metal sites are blocked by iron particles so that the substrates can not access to the active species. However, when the hydrogenation of *trans*-ethylcrotonate and crotonaldehyde was investigated with a magnetic catalyst TGAP$^{44\%}$/Fe$^{50\%}$-Pd(PPh$_3$)$_4^{0.50\%Pd}$, the substrates can be quantitatively hydrogenated at the C=C double bonds. The amount of palladium in the reaction solutions is very low and below 550 ng corresponding to 0.03 ppm per run. After five consecutive reactions, beyond 99.94% of palladium initially loaded on the catalyst are retained.

Epoxy resins containing transition metal species can be used directly as catalysts and do not need any activation or other treatments. The catalysts can be easily separated from the reaction mixtures by simple filtration and reused without reactivation. Thus, the contamination of reaction products by metal species can be minimized. This shows that the immobilization of catalytically active metal species on epoxy resins via homopolymerization is a reliable and feasible method and obtained materials are highly active and long-term stable in several catalytic reactions. Furthermore, considering the potential for use under more severe temperature and pressure conditions, transition metal catalysts based on epoxy resins offer a promising prospect for technological applications and a great potential for further optimization.

4 Experimental section

4.1 Materials

The employed materials are listed in Table 42 and were used as received.

Table 42: Suppliers of materials used in the study.

Material	Supplier
Acetonitrile	Merck
4-Acetylbiphenyl	Aldrich
Allyl alcohol	Aldrich
Biphenyl	Aldrich
Bis-(diethyldithiocarbamato)-dioxomolybdenum (VI) ($MoO_2(DEDC)_2$)	Strem
4-Bromoacetophenone	Aldrich
4-Bromoanisole	Aldrich
Bromobenzene	Aldrich
ß-Bromostyrene	Aldrich
4-Bromotoluene	Aldrich
5-Bromo-*m*-xylene	Aldrich
3-Butene-2-ol	Aldrich
tert-Butyl hydroperoxide in water (TBHP)	Aldrich
Cesium carbonate (Cs_2CO_3)	Aldrich
Chlorobenzene	Aldrich
Chromyl chloride (CrO_2Cl_2)	Gelest
trans-Cinnamaldehyde	Aldrich
Crotonaldehyde	Aldrich
Cumyl hydroperoxide (CHP)	Aldrich
Cyanate ester based on phenol novolac (Primaset PT30)	Lonza
Cyclohexene	Aldrich
Cyclohexene oxide	Aldrich
Diethyl ether	Fluka
Diglycidylaniline	Aldrich
N,N’-Diglycidyl-4-glycidyloxyaniline (TGAP)	Aldrich
1,2-Dihydronaphthalene (DHNT)	Aldrich
Dimethylformamide (DMF)	Fluka
1,4-Dioxane	Fluka
3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (ERL4221)	Aldrich
Epoxy phenol novolac (Bakelite® EPR600) (Novolac)	Bakelite
Ethanol	Fluka
trans-Ethylcinnamate	Aldrich
trans-Ethylcrotonate	Aldrich
Glacial acetic acid	Merck

Hexahydro-4-methylphthalic anhydride (HMPA)	Aldrich
Hydrogen (purity: > 99.99%)	Basi
4-Iodoacetophenone	Aldrich
2-Iodoanisole	Aldrich
4-Iodoanisole	Aldrich
Iodobenzene	Aldrich
4-Iodotoluene	Aldrich
Iron powder (particle size: < 10 μm)	Merck
(R)-(+)-Limonene	Aldrich
Methanol (CH_3OH)	Fluka
N-Methyl-2-pyrrolidone (NMP)	Aldrich
4,4'-Methylene-bis-(N,N-diglycidylaniline) (TGMDA)	Aldrich
Molybdenum(VI) dioxide bis(acetylacetonate) ($MoO_2(acac)_2$)	Strem
Molybdenum(VI) dioxide bis(2,2,6,6-tetramethyl-3,5-heptanedionate) ($MoO_2(TMHD)_2$)	Strem
Molybdenum(V) ethoxide ($Mo(OEt)_5$)	Gelest
Molybdenum 2-ethylhexanoate (15% Mo) ($Mo(EH)_n$)	Strem
Niobium(V) ethoxide ($Nb(OEt)_5$)	Gelest
1-Octene	Aldrich
1-Octene oxide	Aldrich
trans-2-Octene	Aldrich
Phenylboronic acid	Strem
trans-2-Phenylvinylboronic acid	Aldrich
Phosphomolybdic acid hydrate ($H_3Mo_{12}O_{40}P \cdot xH_2O$)	Aldrich
Poly(vinylpyridine) (PVPy)	Aldrich
Potassium acetate (KOAc)	Aldrich
Potassium *tert*-butoxide (KO^tBu)	Aldrich
Potassium carbonate (K_2CO_3)	Merck
2-Propanol	Aldrich
Propene (purity: > 99.99%)	Messer
Sodium carbonate (Na_2CO_3)	Gelest
Sodium iodide (NaI)	Fluka
Sodium thiosulphate ($Na_2S_2O_3$)	Merck
trans-2-Stilbene	Aldrich
Styrene	Aldrich
Styrene oxide	Aldrich
Tetrabutylammonium bromide (TBAB)	Aldrich
Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$)	Strem
Toluene	Fluka
Titanium(IV) 2-ethylhexanoate ($Ti(EH)_4$)	Strem
Triethylamine ($N(Et)_3$) (TEA)	Fluka
Triphenylolmethane triglycidyl ether (TPMTGE)	Aldrich
Tungsten(V) ethoxide ($W(OEt)_5$)	Gelest
Vanadium(V) oxytripropoxide ($VO(OPr)_3$)	Gelest
Vanadyl naphthenate (2.8% V) ($V(NAPH)_n$)	Strem
p-Xylene	Fluka

4.2 General considerations

DSC experiments (differential scanning calorimetry) were conducted with a Mettler Toledo DSC 822^e with a heating rate of 10 ^{o}C/min. Typically, an amount between 3 and 20 mg was used for the investigation of curing behavior of epoxy resins.

TGA analyses (thermogravimetric analysis) were carried out on a Mettler Toledo TGA/SDIA 851^e instrument.

SEM-EDX analyses (scanning electron microscopy-energy dispersive X-ray analysis) were performed on a Leo SEM 982 coupled with an Oxford instrument ISIS 300 EDX unit.

Rotilabo® (PTFE, 0.45 μm pore width) syringe filters were used for catalyst separation.

Products were analyzed by GC-FID using an Agilent 6890N gas chromatograph equipped with a Phenomenex ZB-1 capillary column (60 m × 0.32 mm, 1 μm film thickness) and a flame ionization detector and quantified using calibration curves obtained with standard samples and dodecane as external standard. Unknown products were identified by GC-MS using an Agilent 6890N instrument (J & W Scientific DB-5 column, 30 m × 0.25 mm, 0.25 μm film thickness) coupled with an Agilent 5973 mass selective detector.

ICP-AES (inductively coupled plasma-atomic emission spectroscopy) or AAS (atomic adsorption spectroscopy) analyses were carried out on a Varian Liberty 150 machine and a Varian SpectrAA 800 instrument.

4.3 Preparation of epoxy resins containing *d*-block metal species

In a typical procedure, the *d*-block metal complex was added to the epoxy resin monomer and the mixture was stirred, then transferred to an aluminum mold to form a thin layer of around 1 mm thickness. The epoxy resin was cured by heating successively and obtained solid plates were cut and ground with an analytical mill. Obtained grained particles were annealed and sieved. Details are listed in Table 43.

Table 43: Preparation of epoxy resins containing *d*-block metal species.

Catalyst	Epoxy resin (+ additives)	Metal complex (+ Solvent)	Curing	Annealing
TGMDA-$Mo(OEt)_5^{1.50\%Mo}$	TGMDA (12.4763 g)	$Mo(OEt)_5$ (0.6635 g)	120 °C-1 h, 160 °C-1 h, 200 °C-1 h, 230 °C-4 h	230 °C-6 h
TGMDA-$MoO_2(TMHD)_2^{0.50\%Mo}$	TGMDA (11.5360 g)	$MoO_2(TMHD)_2$ (0.2291 g)	120 °C-1 h, 160 °C-1 h, 200 °C-1 h, 230 °C-4 h	230 °C-6 h
TGMDA-$H_3Mo_{12}O_{40}P{\bullet}xH_2O^{3.00\%Mo}$	TGMDA (5.4918 g)	$H_3Mo_{12}O_{40}P{\bullet}xH_2O$ (0.2624 g) Methanol (0.8565 g)	120 °C-1 h, 160 °C-1 h, 200 °C-1 h, 230 °C-4 h	230 °C-6 h
TGMDA-$W(OEt)_5^{1.50\%W}$	TGMDA (11.8715 g)	$W(OEt)_5$ (0.4152 g)	120 °C-1 h, 160 °C-1 h, 200 °C-1 h, 230 °C-4 h	230 °C-6 h
TGMDA-$Mo(OEt)_5^{0.50\%Mo}$-$W(OEt)_5^{0.50\%W}$	TGMDA (11.3292 g)	$Mo(OEt)_5$ (0.1884 g) $W(OEt)_5$ (0.1318 g)	120 °C-1 h, 160 °C-1 h, 200 °C-1 h, 230 °C-4 h	230 °C-6 h
TGMDA-$Ti(EH)_4^{3.00\%Ti}$	TGMDA (8.3992 g)	$Ti(EH)_4$ (3.6280 g)	120 °C-1 h, 160 °C-1 h, 200 °C-1 h, 230 °C-4 h	230 °C-6 h
TGAP-$Mo(EH)_n^{1.50\%Mo}$	TGAP (12.2385 g)	$Mo(EH)_n$ (1.2284 g)	120 °C-1 h, 160 °C-1 h, 180 °C-1 h, 200 °C-4 h	200 °C-6 h
Novolac-$Mo(EH)_n^{1.50\%Mo}$	Novolac (11.3211 g)	$Mo(EH)_n$ (1.2224 g)	120 °C-1 h, 160 °C-1 h, 200 °C-1 h, 230 °C-4 h	230 °C-6 h
TGMDA-$VO(OPr)_3^{1.50\%V}$	TGMDA (9.5737 g)	$VO(OPr)_3$ (0.7070 g)	120 °C-1 h, 160 °C-1 h, 200 °C-1 h, 230 °C-4 h	230 °C-6 h

TGAP-V(NAPH)$_n^{1.00\%\mathrm{V}}$	TGAP (8.2839 g)	V(NAPH)$_n$ (4.6020 g)	120 °C-1 h, 140 °C-1 h, 1600 °C-1 h	160 °C-6 h
ERL4221/HMPA-Mo(EH)$_n^{1.50\%\mathrm{Mo}}$	ERL4221 (5.0083 g) HMPA (5.0123 g)	Mo(EH)$_n$ (0.9932 g)	120 °C-1 h, 140 °C-1 h, 160 °C-4 h	160 °C-6 h
TGAP-Mo(OEt)$_5^{1.42\%\mathrm{Mo}}$-Pd(PPh$_3$)$_4^{0.50\%\mathrm{Pd}}$	TGAP (8.0700 g)	Mo(OEt)$_5$ (0.4270 g) Pd(PPh$_3$)$_4$ (0.4880 g)	120 °C-1 h, 160 °C-1 h, 200 °C-1 h, 220 °C-4 h	220 °C-6 h
TGAP/PT30-Mo(OEt)$_5^{0.75\%\mathrm{Mo}}$	TGAP (5.00 g) PT30 (cyanate ester) (5.00 g)	Mo(OEt)$_5$ (0.2576 g)	80 °C-1 h, 100 °C-1 h, 120 °C-1 h, 140 °C-1h 160 °C-1 h, 180 °C-1 h, 200 °C-1 h, 230 °C-1 h	230 °C-6 h
TGAP-Pd(PPh$_3$)$_4^{1.00\%\mathrm{Pd}}$	TGAP (3.0256 g)	Pd(PPh$_3$)$_4$ (0.3746 g)	120 °C-1 h, 160 °C-1 h, 200 °C-1 h, 220 °C-4 h	220 °C-6 h
TGAP-Pd(PPh$_3$)$_4^{0.50\%\mathrm{Pd}}$	TGAP (22.9930 g)	Pd(PPh$_3$)$_4$ (1.3526 g)	120 °C-1 h, 160 °C-1 h, 200 °C-1 h, 220 °C-4 h	220 °C-6 h
TGAP-Nb(OEt)$_5^{1.00\%\mathrm{Nb}}$	TGAP (8.6298 g)	Nb(OEt)$_5$ (0.2581 g)	120 °C-1 h, 140 °C-1 h, 160 °C-1 h, 180 °C-4 h	180 °C-6 h
Novolac$^{64\%}$/Fe$^{29\%}$-Mo(EH)$_n^{1.00\%\mathrm{Mo}}$	Novolac (5.1095 g) Iron powder (particle size: < 10 μm) (2.3249 g)	Mo(EH)$_n$ (0.5335 g)	120 °C-1 h, 160 °C-1 h, 200 °C-1 h, 230 °C-4 h	230 °C-6 h
TGAP$^{44\%}$/Fe$^{50\%}$-Pd(PPh$_3$)$_4^{0.50\%\mathrm{Pd}}$	TGAP (4.8420 g) Iron powder (particle size: < 10 μm) (5.4854 g)	Pd(PPh$_3$)$_4$ (0.5923 g)	120 °C-1 h, 160 °C-1 h, 200 °C-1 h, 220 °C-4 h	220 °C-6 h

4.4 Catalytic reactions

The epoxidation of liquid alkenes and Suzuki and Heck coupling reactions were carried out in glass flasks with a reflux condenser and an airtight septum cap, and heated using a thermostatic oil bath under magnetic stirring. The epoxidation of propene and hydrogenation reactions were conducted in 80 ml steel autoclaves.

Typical procedure for the epoxidation of liquid alkenes using TBHP as oxidant: the catalyst (0.50 g), oxidant (12 mmol TBHP, 36 wt.% TBHP solution in toluene) and alkene (10 mmol) were charged in a glass flask equipped with a reflux condenser and an airtight septum cap and heated to the desired temperature. The catalyst was separated after the reaction by filtration and used in the next cycle without any treatments. The catalytic activity was evaluated in terms of alkene consumed (GC determination). The filtrate (2 g) was evaporated and the reaction residue was dissolved in 2 g of 65% HNO_3. Metal traces in these solutions were quantified by ICP-AES or AAS.

Typical procedure for the epoxidation of propene using TBHP as oxidant: the catalyst (1.00 g) and oxidant (50 mmol TBHP, 34.5 wt.% TBHP solution in toluene and dodecane; dodecane serves as internal standard for GC analyses) were added to the autoclave and the reactor was flushed three times with propene. After the solution was saturated, the autoclave was heated to the desired temperature. Normally, the reaction was operated at 90 ^{o}C with a reaction time of 24 h. The initial pressure of propene in the autoclave was 8 bar and the highest operating pressure can reach 25 bar during the reaction at elevated temperature. After the reaction, the reactor was cooled to room temperature and the solution was filtered. The filtrate was analyzed by GC-FID. The yield of propene epoxide is expressed in terms of the consumption of TBHP (determined by iodometric titration). The amount of leached metal from the support was measured by ICP-AES. For this purpose, the filtrate (5 g) was evaporated and the residue was dissolved in 2 g of 65% HNO_3. The recycled catalyst was subjected to the next run under identical reaction conditions without any treatments.

Typical procedure for Suzuki coupling: the catalyst (0.50 g), haloarene (5 mmol), arylboronic acid (6 mmol), K_2CO_3 (20 mmol), dioxane (10 ml) and distilled water (10 ml) were added to a 25 ml glass flask with above-mentioned instruments and heated to the desired temperature. In most cases, the reactions were conducted at 90 ^oC with a reaction time of 24 h. After the reaction, two phases were formed and the catalyst particles were located in the interphase between organic and water phase. The organic phase solution and water phase solution were separated after the addition of 10 ml diethyl ether. The organic phase was analyzed by GC-FID and the water phase solution (2 ml) was used for ICP-AES analysis. In addition, the organic phase (5 g) was also used by evaporating the solvent and dissolving the residue in 5 g 65% HNO_3.

Typical procedure for Heck coupling: the catalyst (0.50 g), aryl iodide (5 mmol), unsaturated substrate (6 mmol), base (20 mmol), solvent (10 or 20 ml) were added to a 25 ml glass flask and heated to the desired temperature. After the completion of the reaction, the filtrate was analyzed by GC-FID.

Typical procedure for the hydrogenation of unsaturated esters and aldehydes: substrate (10 mmol) was dissolved in the solvent (20 ml) and added to the reactor together with the catalyst (0.50 g). The reactor was flushed three times by hydrogen. The reactor was heated to the desired temperature and the mixture was magnetically stirred for 4 h or 24 h. After the completion of the reaction, the reactor content was cooled and the reaction solution was filtered. The filtrate was analyzed by GC-FID. The amount of leached metal from the support was measured by ICP-AES. For this purpose, the filtrate (5 g) was evaporated and the residue was dissolved in 2 g of 65% HNO_3. The recycled catalyst was subjected to the next run under identical reaction conditions without any treatments.

4.5 Hot filtration test

After the completion of the reaction, the hot reaction solution was separated by filtration. Equivalent amounts of fresh reactants were added to the filtrate in a new glass flask. The composition of obtained solution was measured by GC-FID and then a new reaction was carried out under identical reaction conditions using this solution. After the completion of the reaction, the composition of the reaction solution was measured by GC-FID again. The difference between the two obtained results gave quantitative information about the catalytic activity from leached, dissolved metal species.

4.6 Poisoning test

Typical procedure in Hg(0) poisoning: A mixture consisting of 2-iodoanisole (5 mmol, 1.17 g), phenylboronic acid (6 mmol, 0.74 g), K_2CO_3 (20 mmol, 2.76 g), Hg(0) (3 mmol, 0.60 g), dioxane (10 ml, 10.34 g), distilled water (10 ml, 10.00 g) and TGAP-Pd$(PPh_3)_4{}^{1.00\%Pd}$ (0.50 g) was added to a glass flask and the reaction was carried out at 90 ^{o}C with a reaction time of 24 h. After the completion of the reaction, the reaction solution was separated by filtration and then the organic phase was isolated after the addition of 10 ml diethyl ether and analyzed by GC-FID.

Typical procedure in PVPy poisoning: A mixture consisting of 2-iodoanisole (5 mmol, 1.17 g), phenylboronic acid (6 mmol, 0.74 g), K_2CO_3 (20 mmol, 2.76 g), PVPy (1.18 g), dioxane (10 ml, 10.34 g), distilled water (10 ml, 10.00 g) and TGAP-Pd$(PPh_3)_4{}^{1.00\%Pd}$ (0.50 g) was added to a glass flask and the reaction was carried out at 90 ^{o}C with a reaction time of 24 h. After the completion of the reaction, the reaction solution was separated by filtration and then the organic phase was isolated after the addition of 10 ml diethyl ether and analyzed by GC-FID.

4.7 Dissolving/redeposition test

A mixture consisting of 2-iodoanisole (5 mmol, 1.17 g), phenylboronic acid (6 mmol, 0.74 g), K_2CO_3 (20 mmol, 2.76 g), $Pd(PPh_3)_4$ (0.08 g), dioxane (10 ml, 10.34 g), distilled water (10 ml, 10.00 g) and $TGAP\text{-}Mo(EH)_n^{1.50\%Mo}$ (0.50 g) were added to a glass flask and the reaction was carried out at 90 °C with a reaction time of 24 h. After the completion of the reaction, $TGAP\text{-}Mo(EH)_n^{1.50\%Mo}$ was separated by filtration. The solid particles were marinated and washed using water and dioxane for two days and then dried. After this, the obtained $TGAP\text{-}Mo(EH)_n^{1.50\%Mo}$ was used as catalyst in five consecutive reactions at 90 °C with a reaction time of 24 h. The reaction solutions were separated by filtration and then the organic phase was isolated after the addition of 10 ml diethyl ether and analyzed by GC-FID.

4.8 Competition reaction

Phenylboronic acid (6 mmol), K_2CO_3 (20 mmol), dioxane (10 g), distilled water (10 g), bromobenzene (1 mmol), 4-bromoanisole (1 mmol), 4-bromoacetophenone (1 mmol), 5-bromo-*m*-xylene (1 mmol), 4-bromotoluene (1 mmol) and $TGAP\text{-}Pd(PPh_3)_4^{0.50\%Pd}$ were added to a glass flask and the reaction was carried out at 90 °C with a reaction time of 24 h. After the completion of the reaction, the reaction solution was separated by filtration and then the organic phase was isolated after the addition of 10 ml diethyl ether and analyzed by GC-FID.

5 Appendix

DSC measurements of epoxy resins mixed with *d*-block metal complexes:

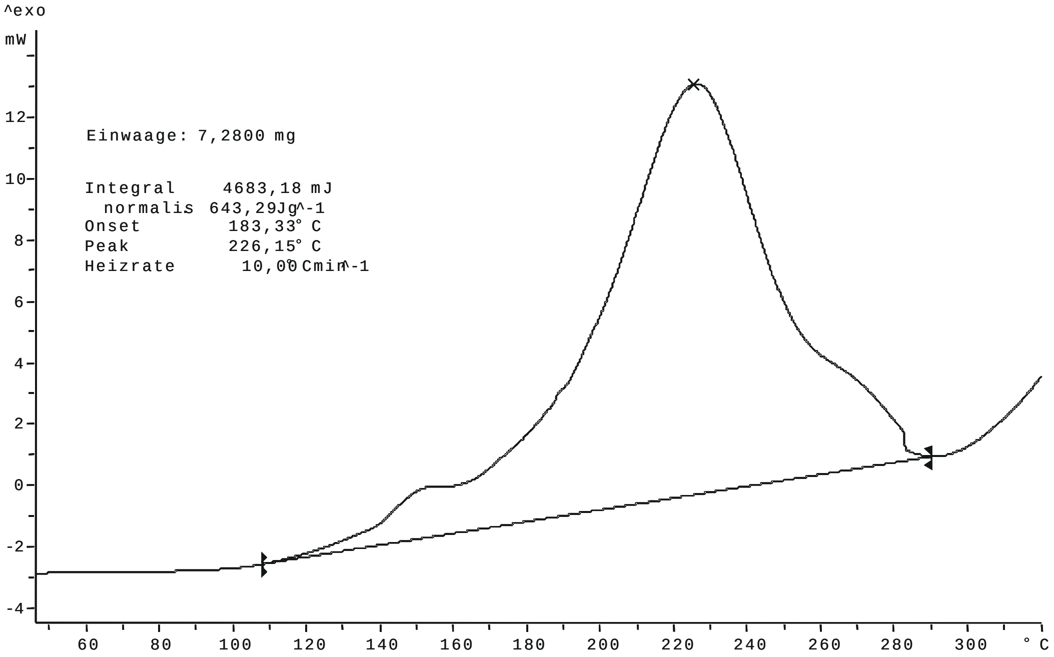


Figure 30: TGMDA (7.882 g), $Mo(EH)_n$ (0.8215 g).

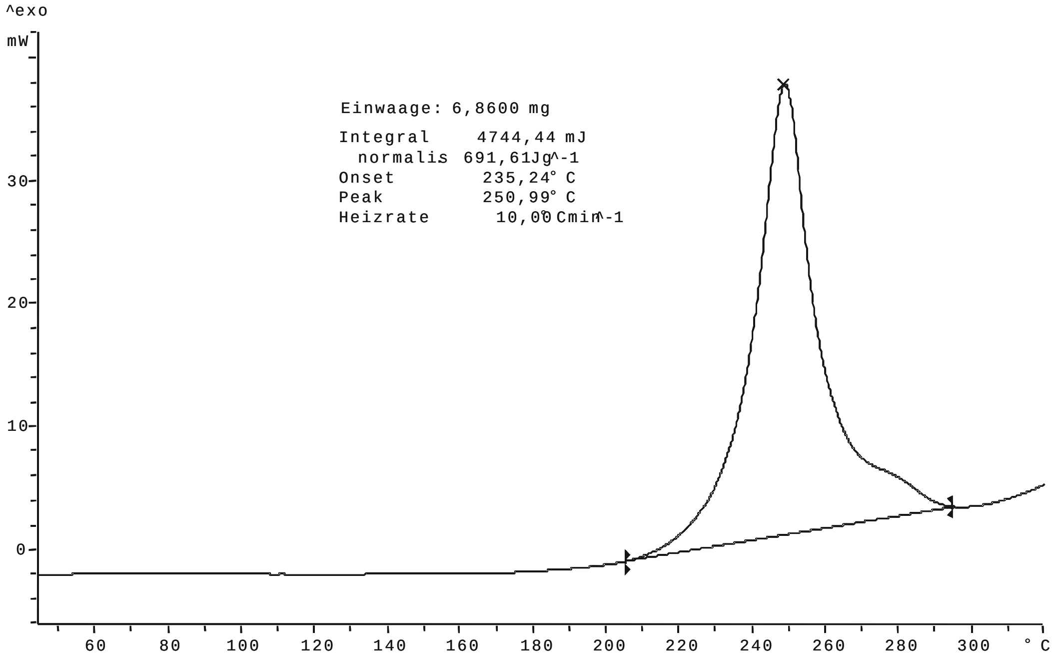


Figure 31: TGMDA (11.5922 g), methanol (4.7238 g), $H_3Mo_{12}O_{40}P{\cdot}xH_2O$ (0.1097 g).

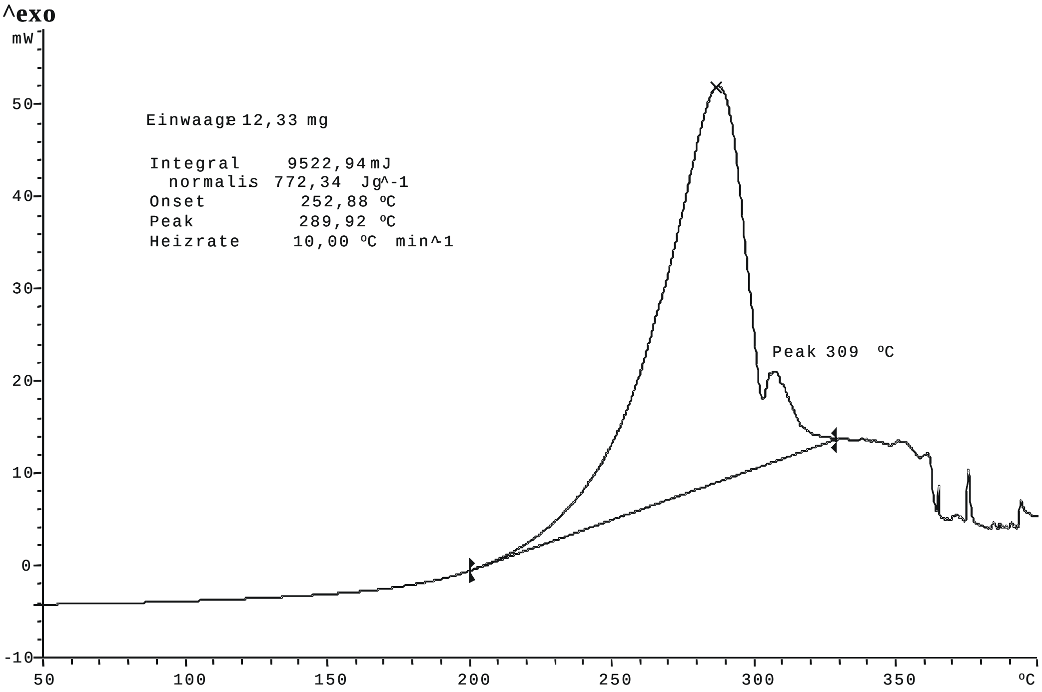


Figure 32: TGAP (9.7037 g), CrO_2Cl_2 (0.3028 g).

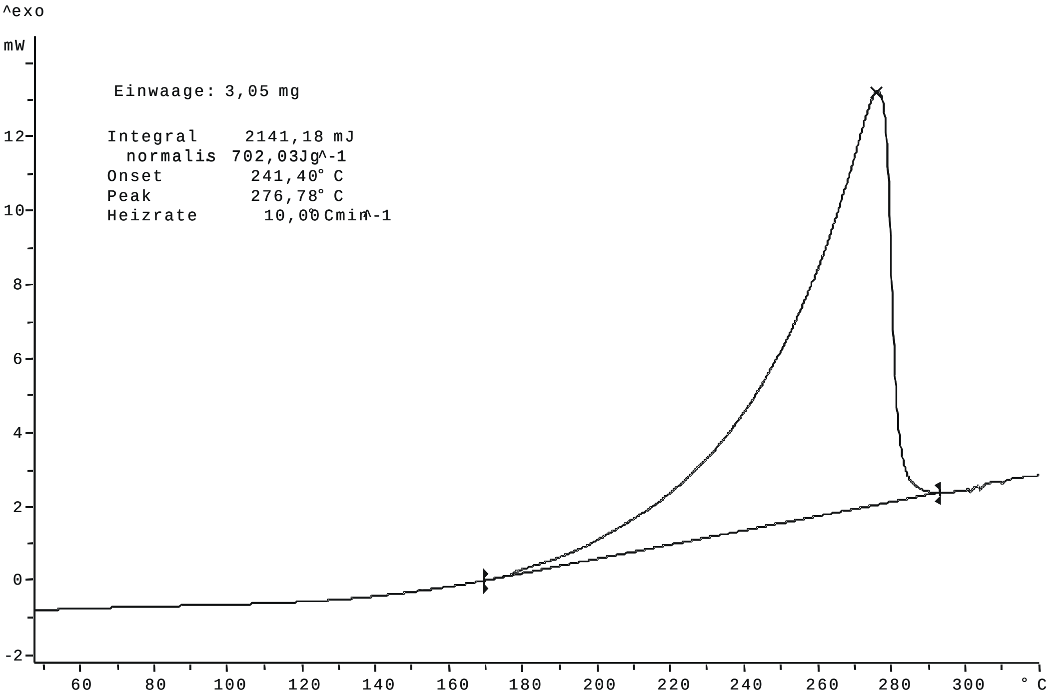


Figure 33: TGMDA (9.9817 g), CrO_2Cl_2 (0.2617 g).

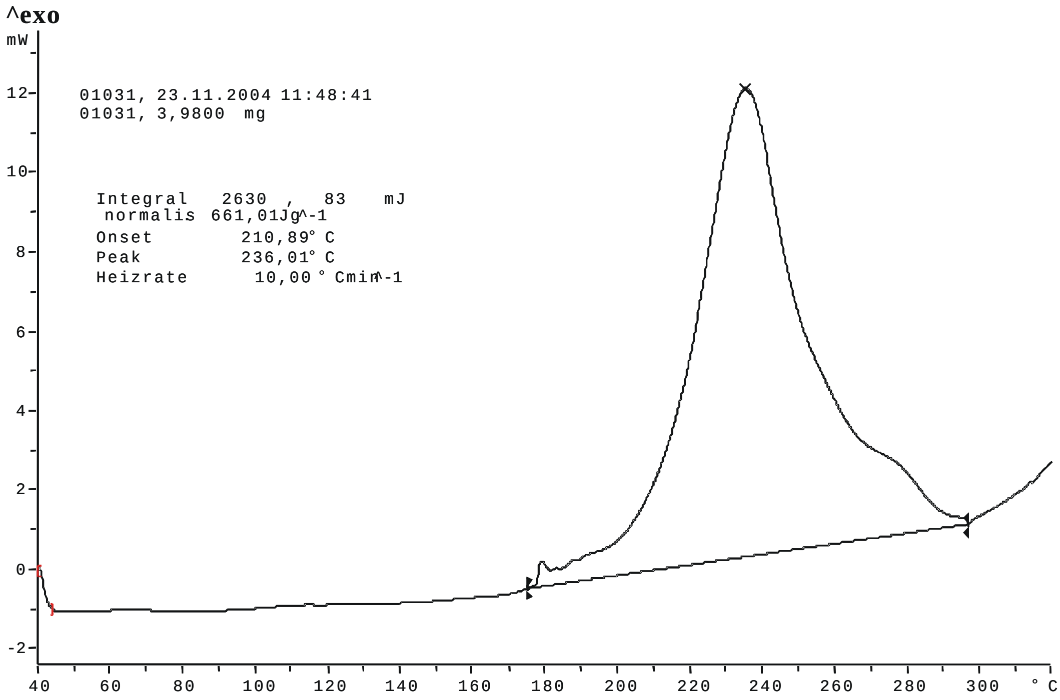


Figure 34: TGMDA (11.5360 g), $MoO_2(TMHD)_2$ (0.2291 g).

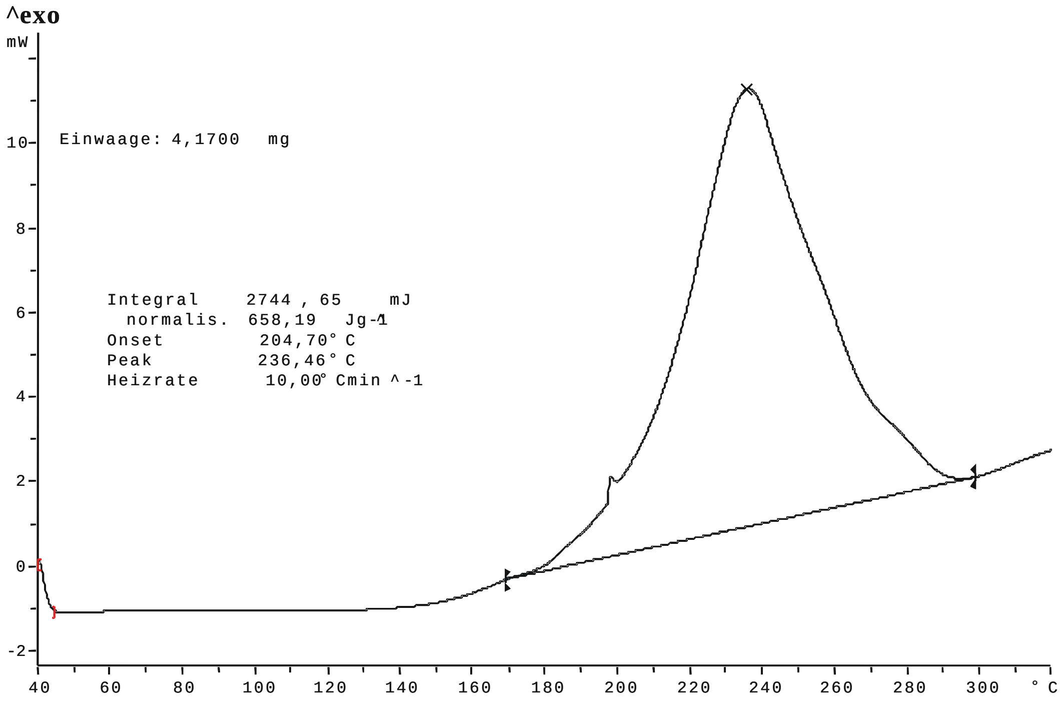


Figure 35: TGMDA (8.3135 g), $MoO_2(DEDC)_2$ (0.2389 g).

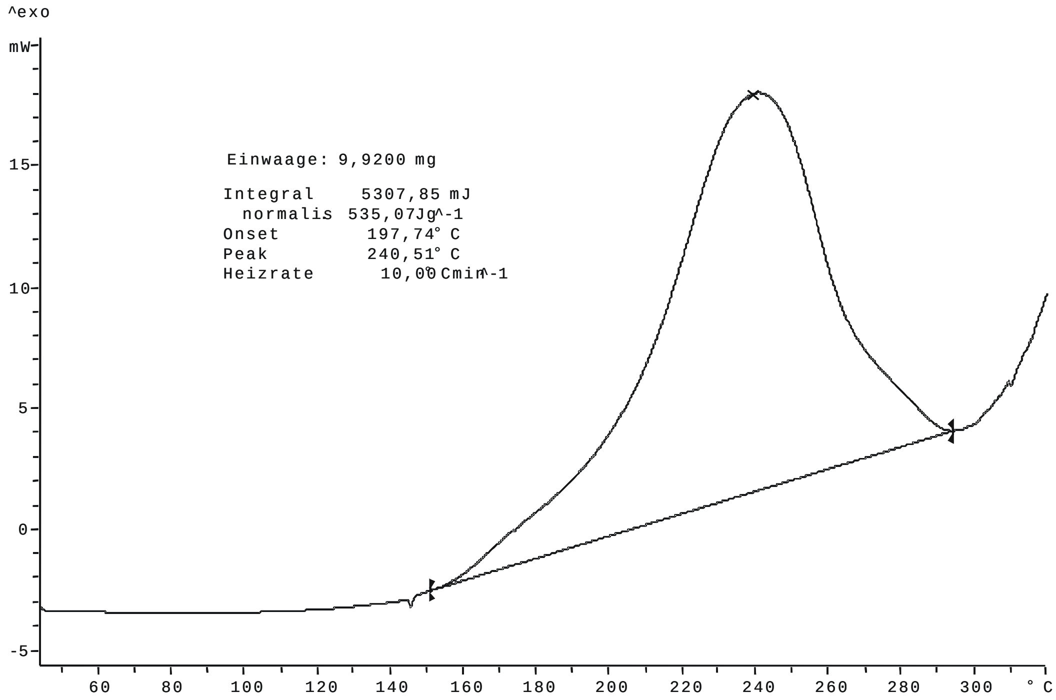


Figure 36: TGAP (5.8665 g), TGMDA (5.9655 g), Mo(OEt)$_5$ (0.4321 g).

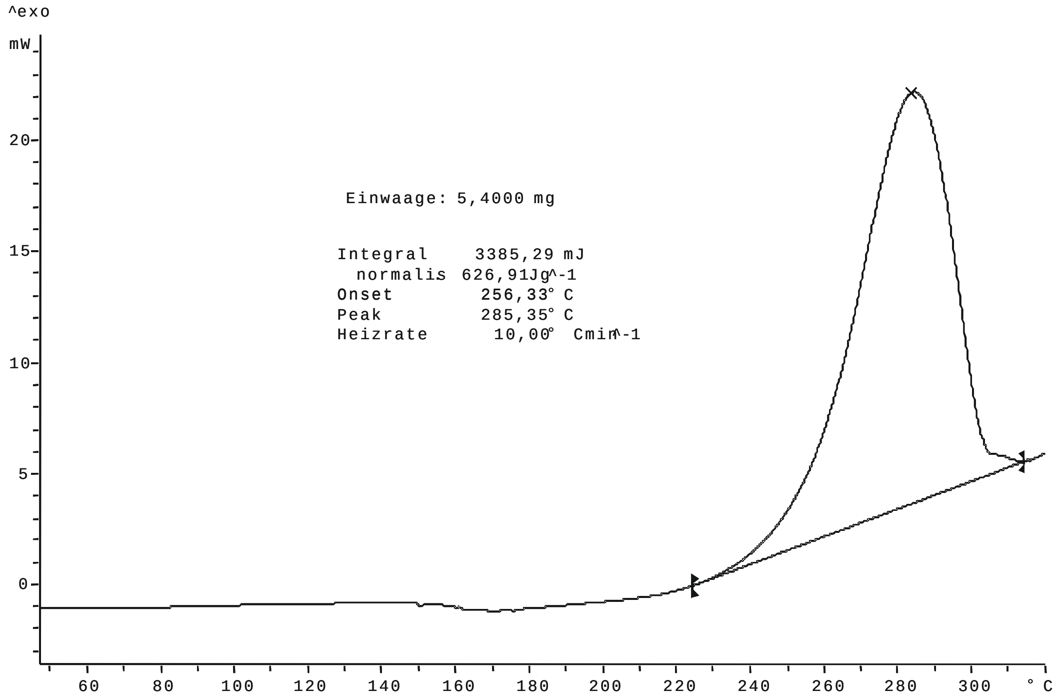


Figure 37: TGAP (5.6378 g), TGMDA (5.7815 g), W(OEt)$_5$ (0.1317 g), Mo(OEt)$_5$ (0.1034 g).

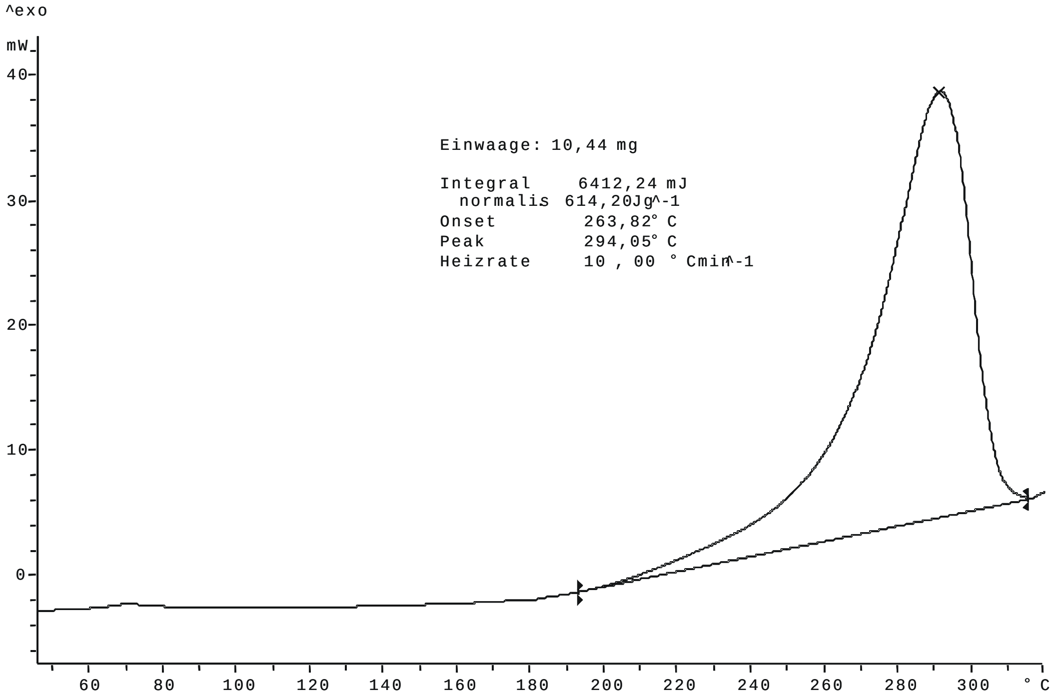


Figure 38: TGMDA (11.8715 g), W(OEt)$_5$ (0.4152 g).

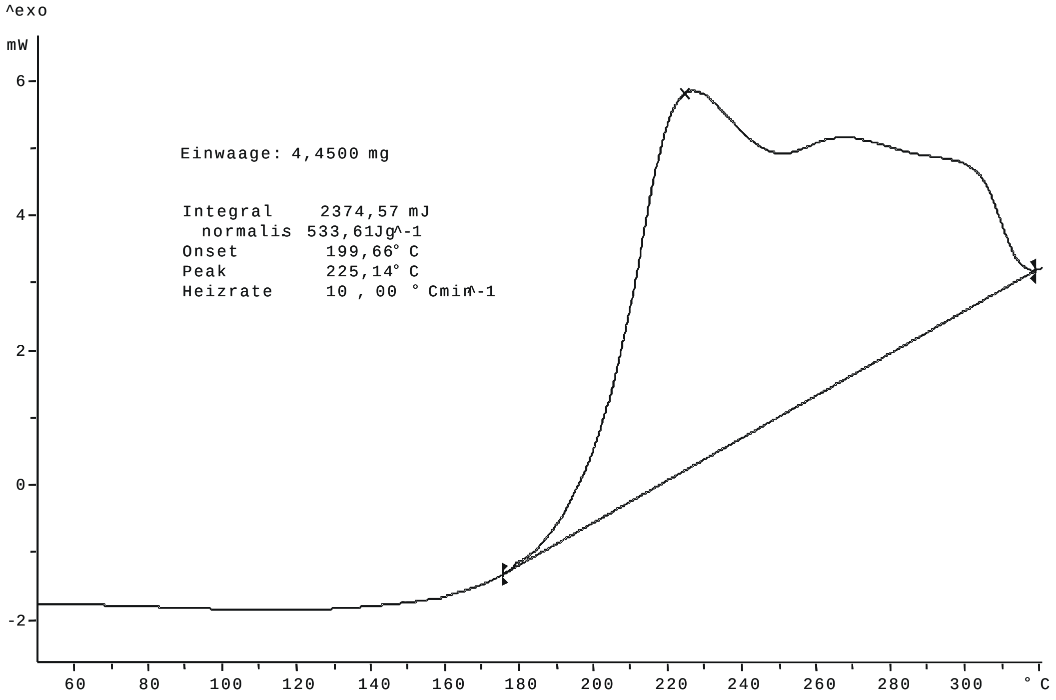


Figure 39: TGMDA (10.8643 g), Nb(OEt)$_5$ (0.3548 g).

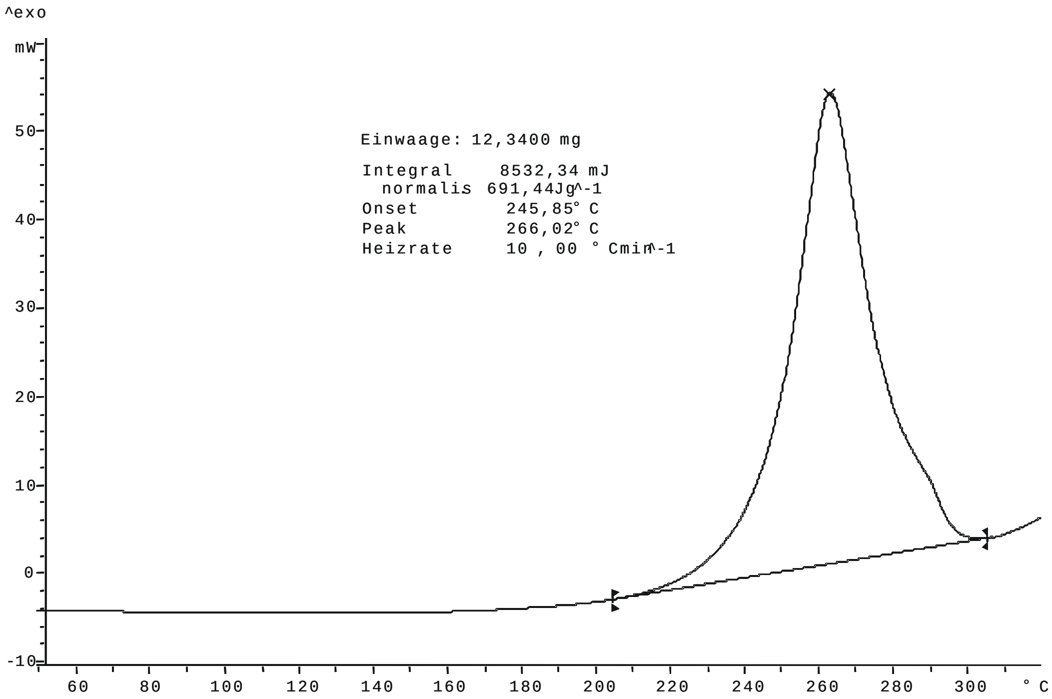


Figure 40: TGMDA (11.3292 g), W(OEt)$_5$ (0.1318 g), Mo(OEt)$_5$ (0.1884 g).

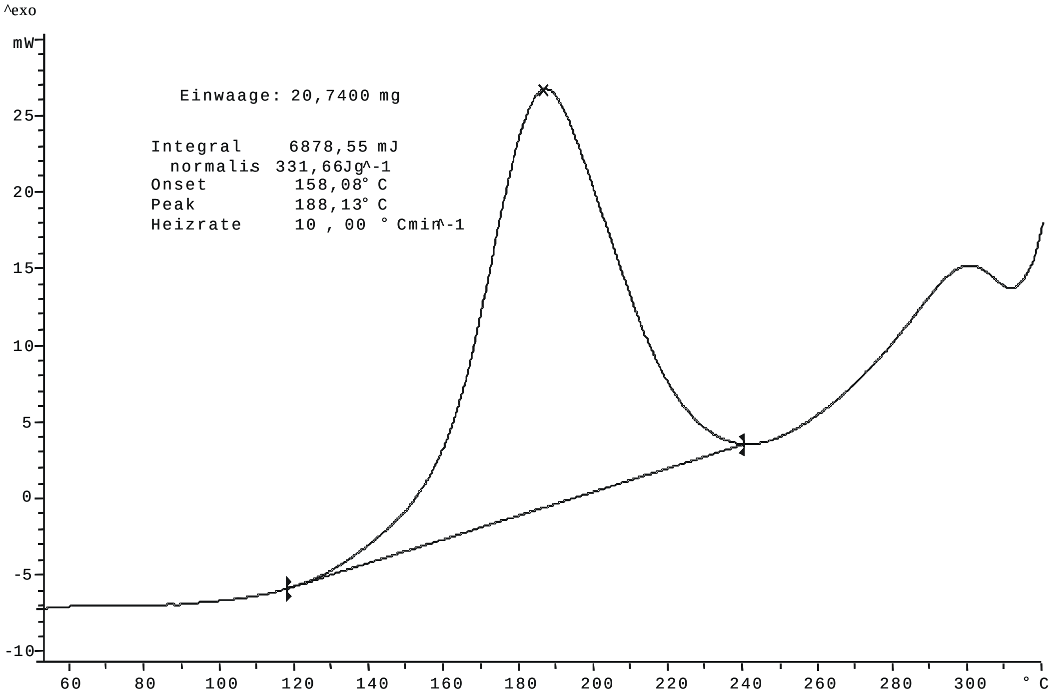


Figure 41: TGAP (8.6298 g), Nb(OEt)$_5$ (0.2581 g).

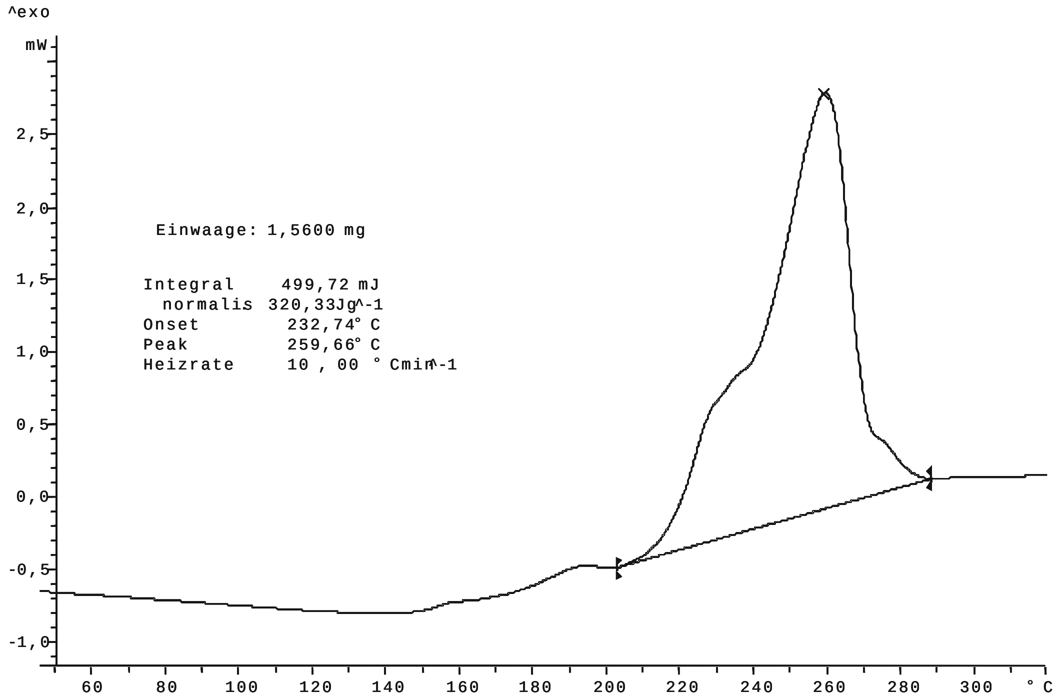


Figure 42: Novolac (10.8292 g), Mo(EH)$_n$ (1.2029 g).

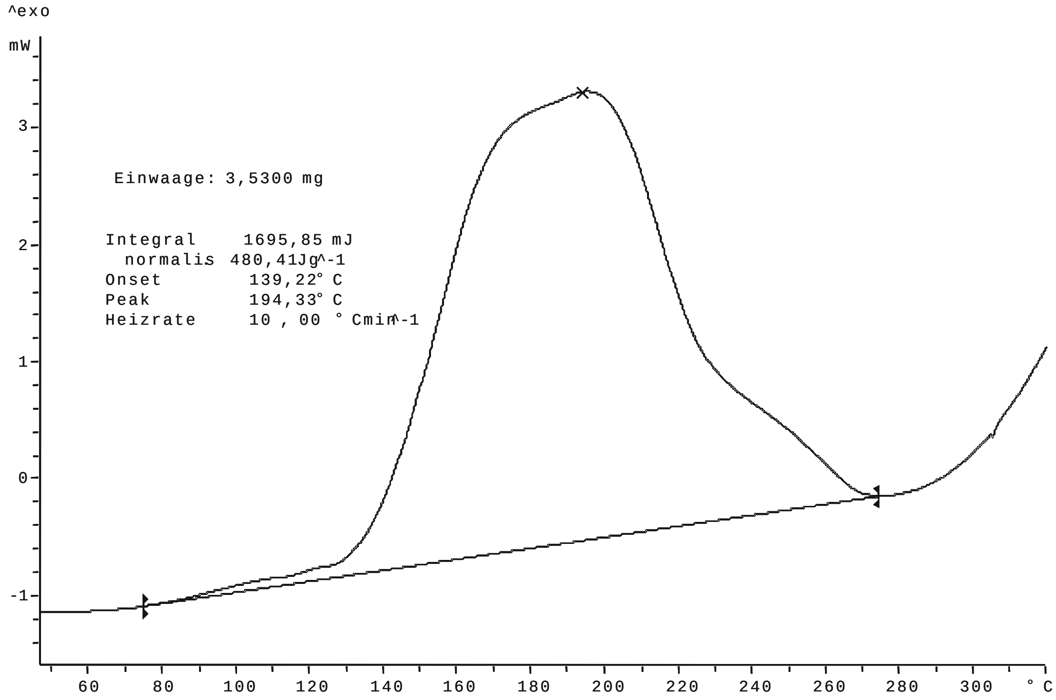


Figure 43: TGMDA (8.9264 g), Mo(EH)$_n$ (2.0631 g).

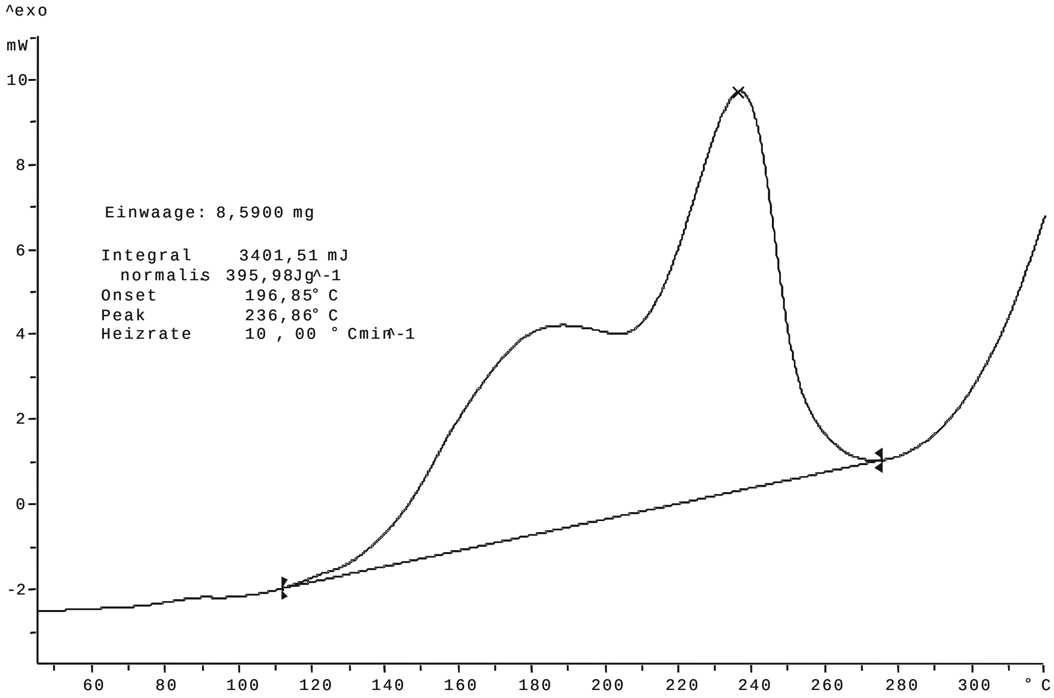


Figure 44: TGAP (3.4511 g), Novolac (3.5415 g), Mo(EH)$_n$ (1.1225 g).

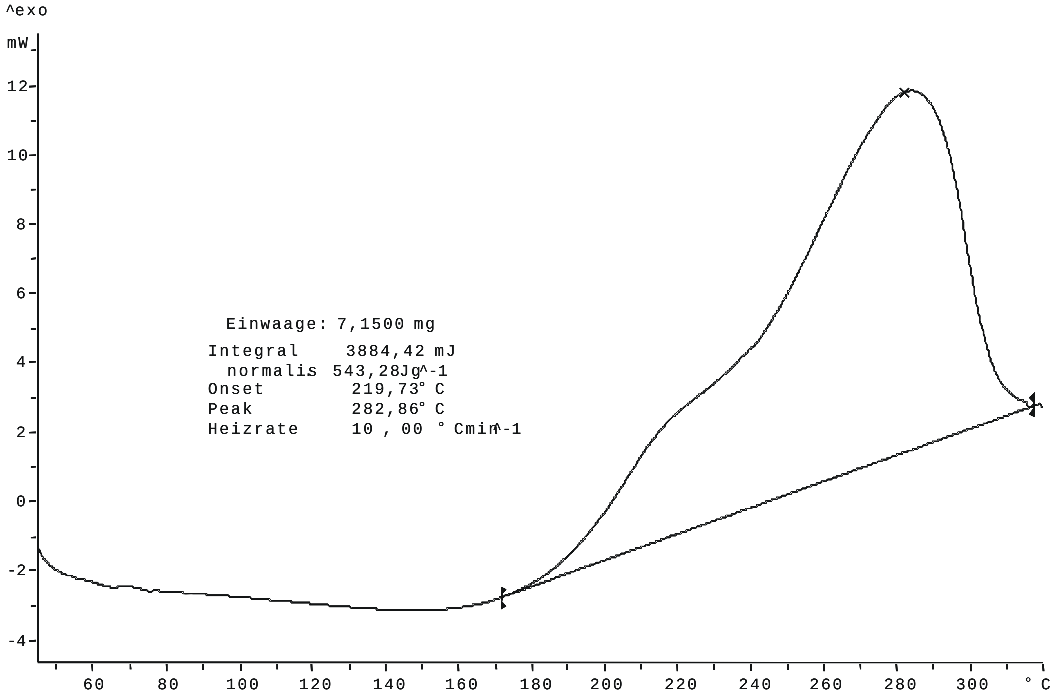


Figure 45: TGMDA (8.3992 g), Ti(EH)$_4$ (1.8190 g).

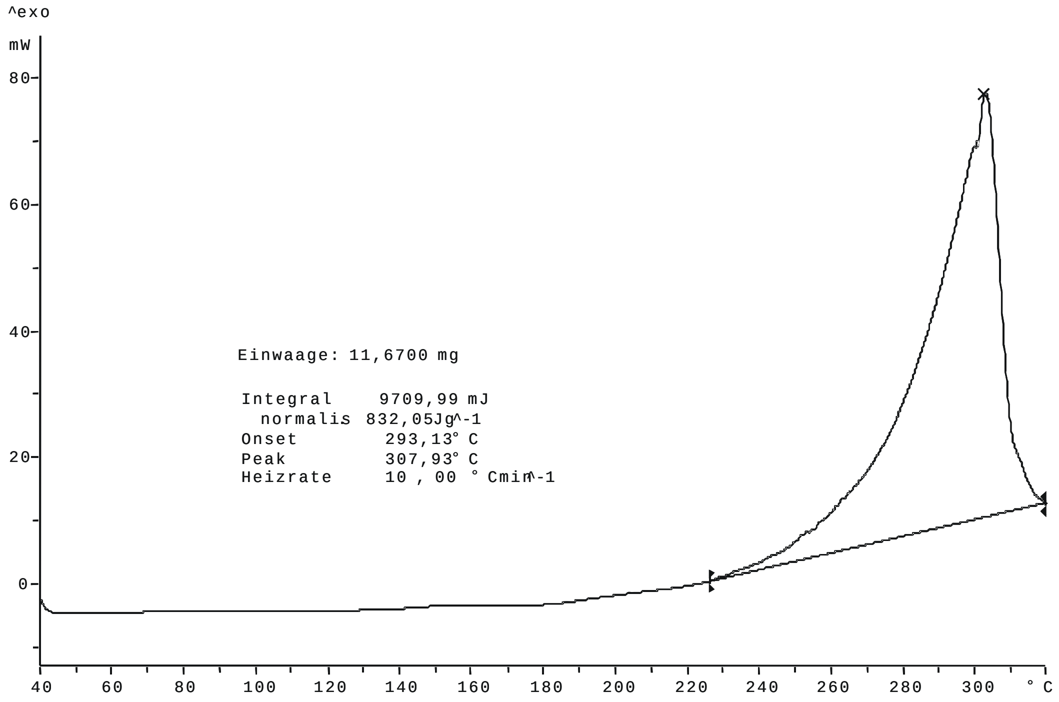


Figure 46: TGAP (3.0256 g), $Pd(PPh_3)_4$ (0.3746 g).

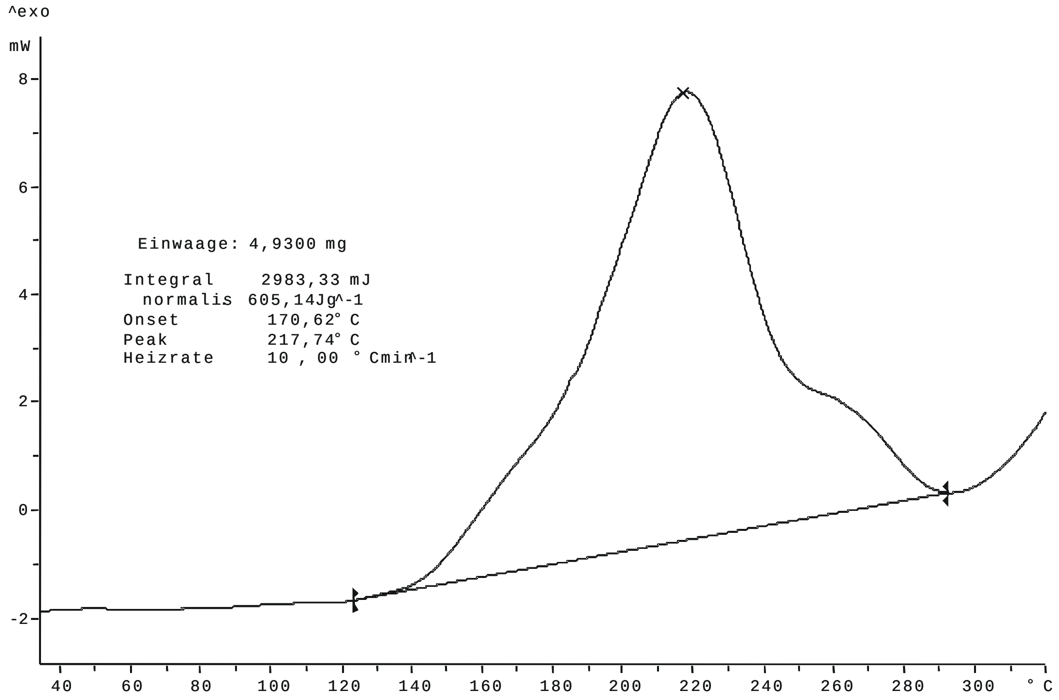


Figure 47: TGMDA (9.7011 g), $Mo(EH)_n$ (1.0116 g).

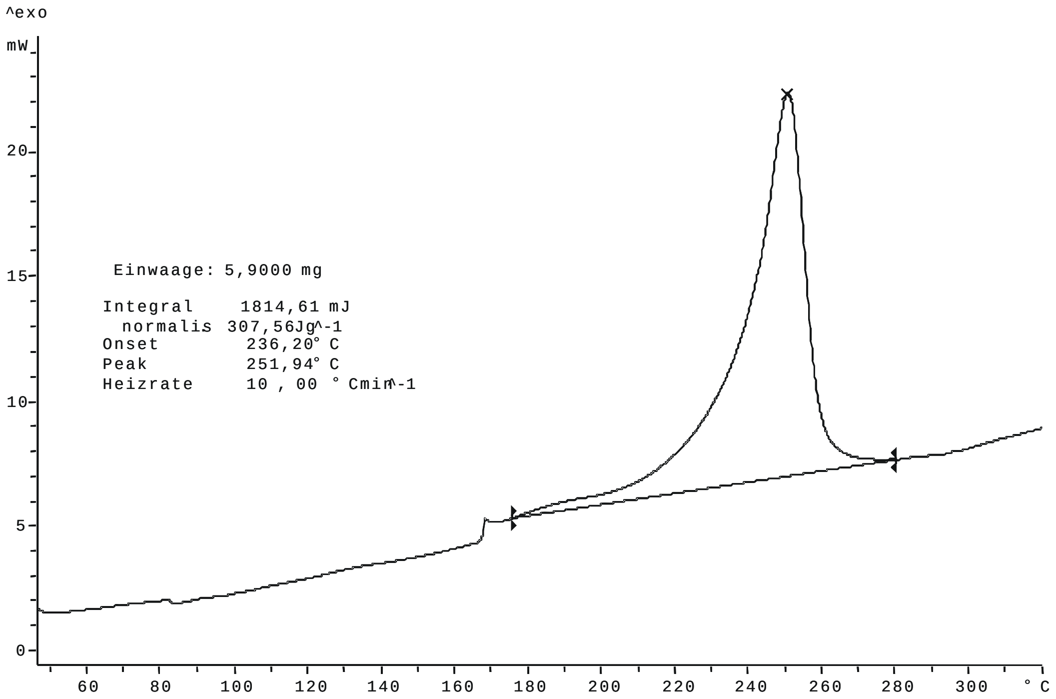


Figure 48: TGMDA (9.5737 g), VO(OPr)$_3$ (0.7070 g).

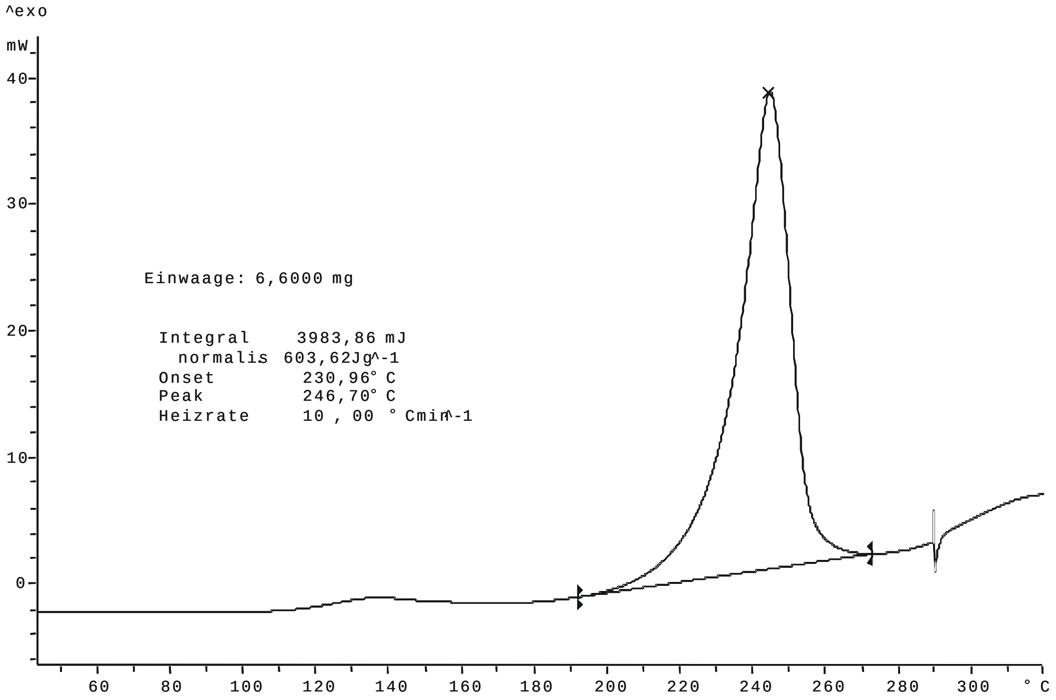


Figure 49: TGAP (6.0721 g), VO(OPr)$_3$ (0.5774 g).

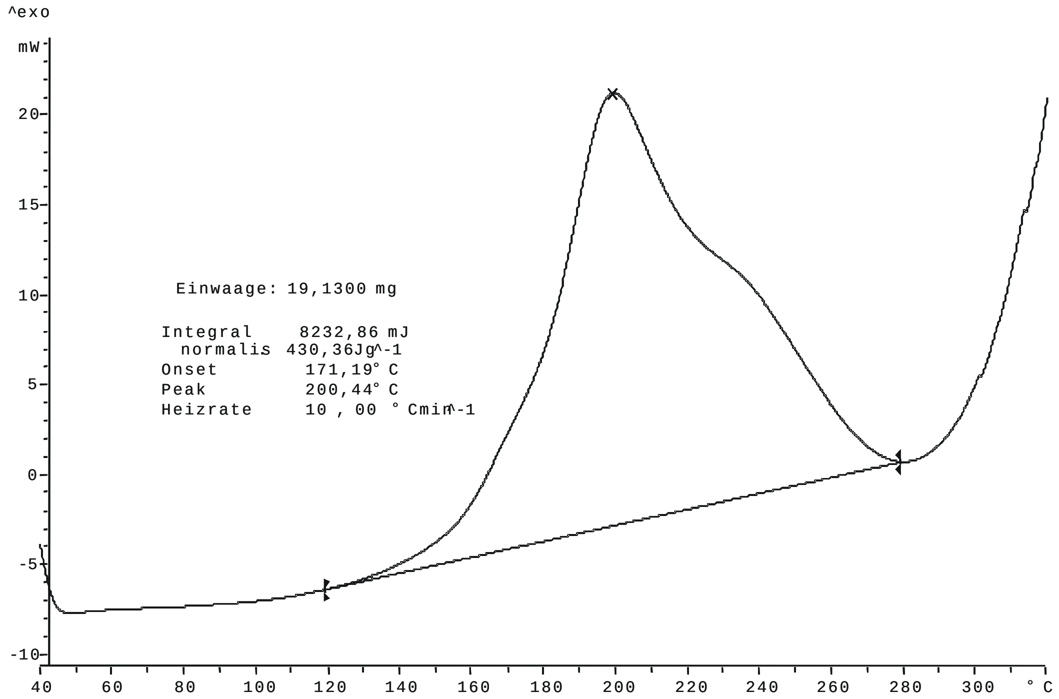


Figure 50: TGAP (12.2385 g), Mo(EH)$_n$ (1.2284 g).

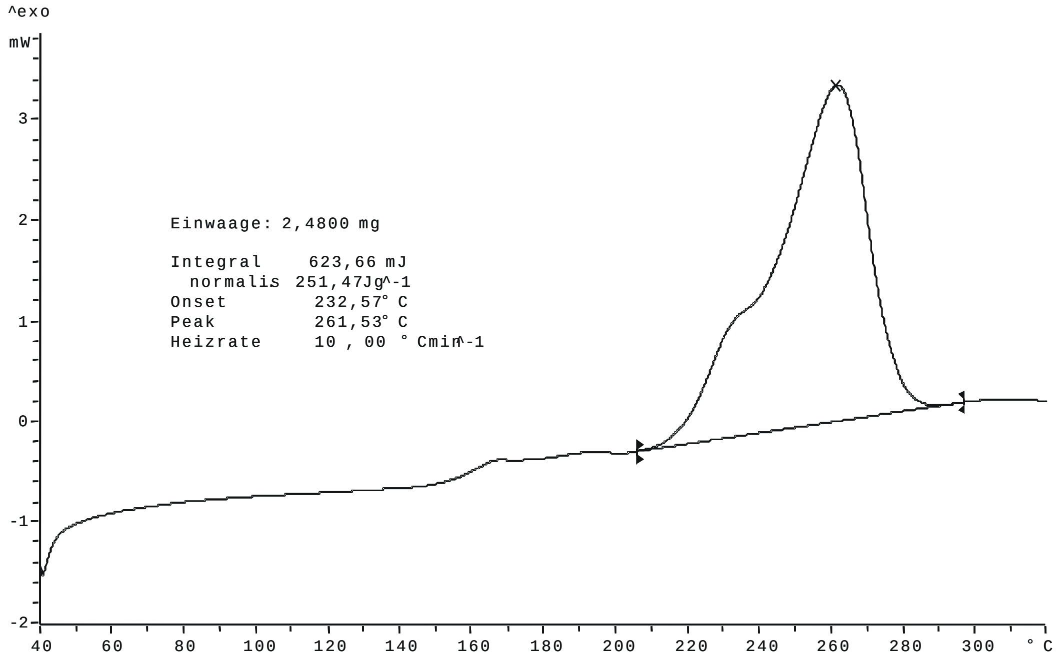


Figure 51: Novolac (5.1095 g), Mo(EH)$_n$ (0.5335 g), Iron powder (particle size: <10 µm) (2.3249 g).

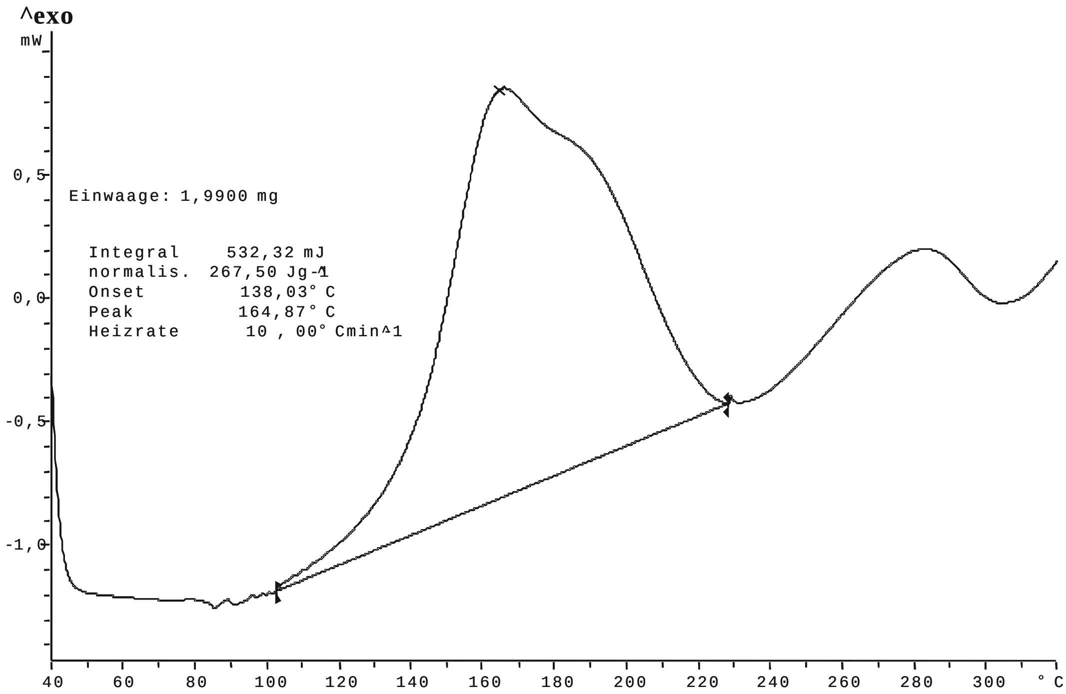


Figure 52: TGMDA (8.5833 g), Nb(OEt)$_5$ (0.9404 g).

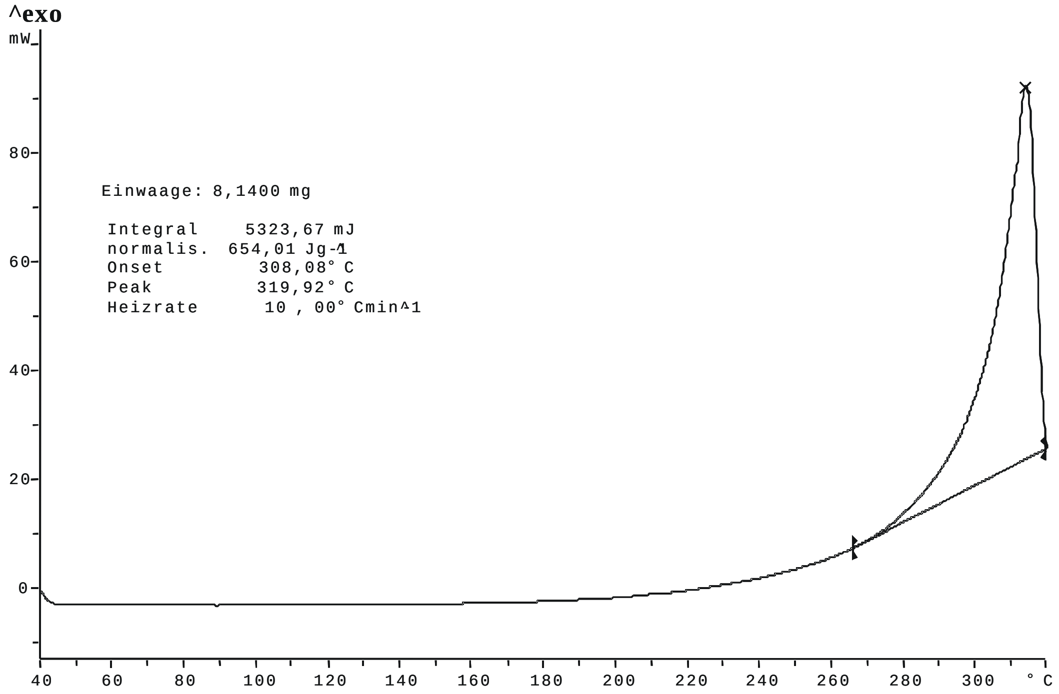


Figure 53: TGAP (4.8420 g), Pd(PPh$_3$)$_4$ (0.5923 g), Iron powder (particle size: <10 µm) (5.4854 g).

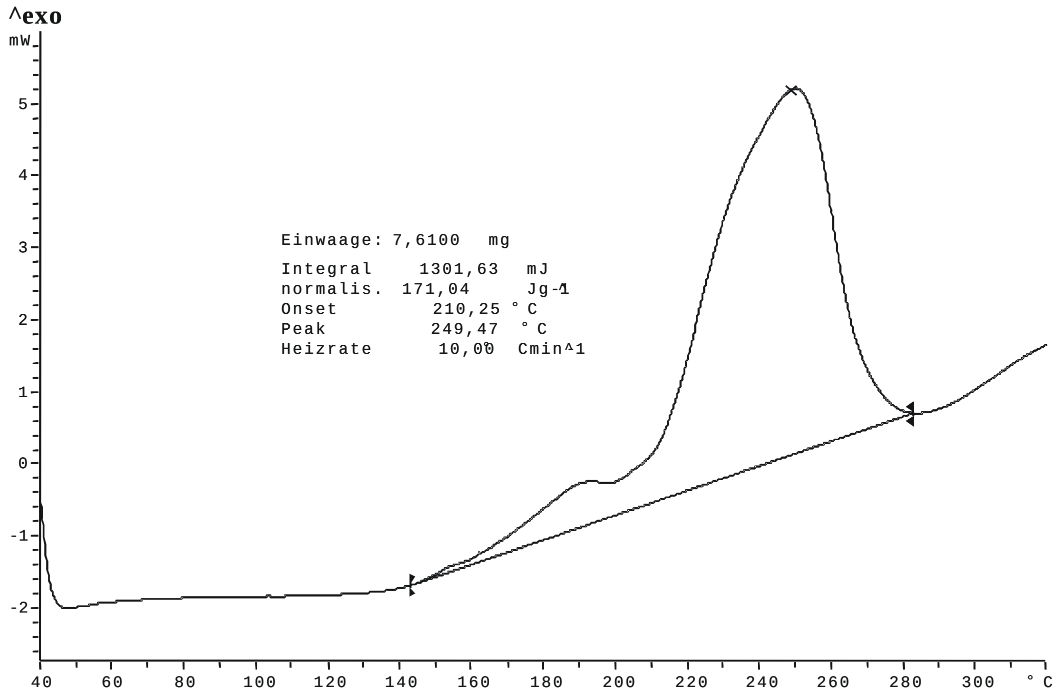


Figure 54: Novolac (5.9419 g), Mo(EH)$_n$ (1.5118 g), Iron powder (particle size: <10 µm) (7.4587 g).

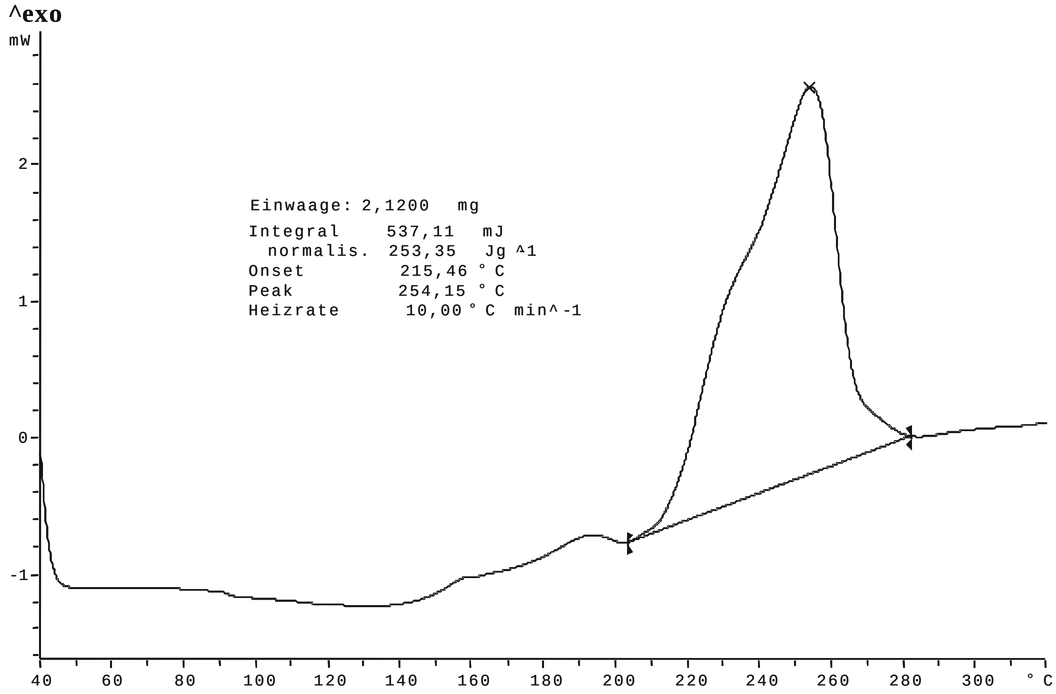


Figure 55: Novolac (5.7629 g), TPMTGE (5.8317 g), Mo(EH)$_n$ (1.3288 g).

6 References and notes

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