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Ionic liquid-initiated polymerization of epoxides: A useful strategy for the preparation of Pd-doped polyether catalysts

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ABSTRACT

Palladium compounds ($\text{Pd}(\text{OAc})_2$ and $\text{Pd}(\text{acac})_2$) were dissolved in commercially available epoxy resins (glycidyl derivatives of bisphenol A and *p*-aminophenol) and the formulations were polymerized employing the ionic liquid 1-ethyl-2-methylimidazolium acetate (EMIM acetate) as polymerization initiator. Thus, palladium species could be incorporated in the network of the resulting polyether materials. Polymerization reactions were investigated by DSC and the curing behavior of different formulations was compared. High polymerization enthalpies were observed indicating high crosslinking in the materials. Accordingly, the materials exhibited high glass transition temperatures and thermogravimetric data revealed high thermal stability. Due to the good solubility of the palladium compounds in the epoxy resins, a widely homogeneous dispersion of palladium species in the polyether matrix could be realized. This was confirmed by SEM-EDX and TEM measurements. XPS measurements revealed that reduction of Pd(II) to Pd(0) species occurred during catalyst preparation and this was also proven by XRD. The materials were ground and successfully employed as catalysts for the hydrogenation of several alkenes under mild reaction conditions. High conversions and selectivities could be reached within a few hours at room temperature and moderate hydrogen pressure of 2.5 bar. Palladium leaching from the catalysts to reaction solutions was investigated. To determine very low quantities, metal concentrations were enriched by removal of volatile components. Subsequent ICP-AES measurements revealed low palladium contents in the range of a few μg . These amounts correspond to values around 0.007% with respect to palladium originally loaded on the polymer. Catalyst recycling experiments were also carried out and it was shown that the catalysts can be employed in numerous consecutive reactions without any catalyst treatment and without loss of activity. Within a series of reactions, palladium leaching decreased while catalytic activity was not affected.

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1. Introduction

The development and use of polymer-supported catalysts offer several advantages such as commercial availability of numerous organic monomers and polymers, comparatively low costs, established polymerization techniques and convenient modification of polymers via common organic synthesis strategies. Thus, a broad flexibility is given and polymer-supported catalyst systems can be easily adjusted to the respective reactions and demands [1–3]. In the past, extensive work has been dedicated to this approach and the majority of such catalysts is based on polystyrene,

polymethacrylate, poly(ethylene glycol), polynorbornene, polybenzimidazole and polyimide [4]. Considering that these polymers represent only a small fraction from the extensive class of organic polymers, there is still an enormous potential for further developments.

However, one crucial obstacle in the field of polymer-supported catalysts is their limited stability and moderate long-term performance [5]. An outstanding long-term activity was observed employing metal-doped thermosetting resins such as epoxy or cyanate ester resins. These could be successfully used in a series of catalytic transformations, e.g., epoxidation, C–C-coupling, hydroformylation and hydrogenation reactions [6–8]. Such catalysts can be easily prepared by dissolving metal complexes in the respective resins or resin blends. Subsequent heating entails a release of ligands, i.e., Lewis bases, which initiate anionic resin polymerization.

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Thus, efficient metal incorporation into the resulting materials occurs.

In recent years, extensive research concentrated on the development of ionic liquids and remarkable progress was made regarding synthesis, characterization and understanding of their striking properties [9–12]. As a result, numerous applications have been reported, e.g., in the fields of alternative solvents [13–15], industrial processes [16–18], separation techniques [10,19] and catalysis [20–24]. A promising application of ionic liquids, particularly imidazolium salts, is their use as thermally latent initiators for the polymerization of epoxy resins [25,26]. Polymerization reactions as well as properties of the resulting polyethers can be largely influenced by choice of appropriate cation–anion combinations. In that way, resin formulations can be prepared that can be safely stored and processed at room temperature and elevated temperatures while polymerization can be started by increasing the temperature to a well-defined curing temperature. This temperature can be adjusted by the ionic liquid type and its concentration in the resin formulation. Imidazolium salts are highly efficient polymerization initiators and low amounts, typically in the range of a few percent, lead to high crosslinking with epoxide conversion above 90%. Further advantages are the good miscibility of imidazolium salts with epoxy resins and high compatibility with other components in the resin formulations [27–29].

Recently, this strategy was employed for the preparation of catalysts. A two-step procedure was described comprising epoxy resin polymerization in the first step and modification of the resulting materials with a palladium complex in the second step [30]. Polymerization was carried out using ammonium salt-based ionic liquids as polymerization initiators and the palladium complex was attached to the polyether matrices by an impregnation procedure. The resulting materials were employed as catalysts for the Heck coupling of iodobenzene with methyl acrylate and the hydrogenation of cinnamaldehyde [30,31].

Within this work, catalyst preparation by this approach was further developed and simplified. Two epoxy resins, the bifunctional glycidylether of bisphenol A (DGEBA) and the trifunctional glycidyl derivative of *p*-aminophenol (TGAP), a high-performance resin with several applications in the aerospace sector, were used [32–34]. It is shown that simple metal salts instead of metal complexes can be employed and a convenient one-step procedure for catalyst preparation is described. Palladium acetate ($\text{Pd}(\text{OAc})_2$) was employed and compared to palladium acetylacetonate ($\text{Pd}(\text{acac})_2$). Regarding the polymerization initiator, the ionic liquid 1-ethyl-3-methylimidazolium acetate (EMIM acetate) was employed, which is, among some related compounds, a highly efficient initiator for the anionic polymerization of epoxy resins. The palladium-doped polyether materials were tested as catalysts for the hydrogenation of different alkenes under mild conditions. Metal leaching from the catalysts to reaction solutions was investigated and catalyst recycling experiments were carried out.

2. Experimental

2.1. Materials and methods

The diglycidyl ether of bisphenol A (DGEBA) was obtained from LEUNA-Harze GmbH (Epilox A 18-00, epoxy equivalent weight: ~ 180 g/eq, viscosity at 25 °C: ~ 9000 mPa s) and the triglycidyl derivative of *p*-aminophenol (TGAP) was purchased from Aldrich (N,N-diglycidyl-4-glycidylxyaniline, epoxy equivalent weight: ~ 95 g/eq, viscosity at 25 °C: ~ 600 mPa s). The imidazolium salt 1-ethyl-3-methylimidazolium acetate (EMIM acetate, EA) and the analogous compounds with thiocyanate, dicyanamide and diethylphosphate anions were obtained from BASF SE. The

structures of the epoxy resins and EMIM acetate are shown in Fig. 1. Palladium acetate ($\text{Pd}(\text{OAc})_2$) and palladium acetylacetonate ($\text{Pd}(\text{acac})_2$) were obtained from Aldrich. Ethyl cinnamate was purchased from Alfa Aesar while cyclohexene and styrene were obtained from Fluka. All other substrates were purchased from Aldrich and hydrogen 5.0 was obtained from Basi. All chemicals were used as received without purification.

Polymerization of the resin formulations was monitored by differential scanning calorimetry (DSC) employing a Mettler Toledo DSC822° device. Typically, 3–10 mg resin samples were employed. The onset temperatures of the exothermic polymerization processes T_{onset} (tangent onset), peak maxima T_{peak} and polymerization enthalpies ΔH were recorded. Glass transition temperatures T_g of the polymerized materials were also determined by DSC according to DIN 53765. Thermogravimetric analyses (TGA) were carried out using a Mettler Toledo TGA/SDTA851° instrument employing 2–6 mg samples. DSC as well as TGA measurements were carried out under nitrogen atmosphere in the dynamic mode and the heating rate was 10 °C/min.

Palladium loadings of the materials were determined by SEM-EDX. SEM micrographs were recorded using a FESEM DSM 982 Gemini microscope from ZEISS equipped with a backscatter detector and coupled with an INCAPentaFET-x3 energy-dispersive X-ray unit (EDX) from Oxford Instruments.

To investigate the redox state of Pd particles, surface sensitive x-ray photoelectron spectroscopy (XPS) was applied. The dried samples were prepared for XPS analysis by pressing them onto an indium foil inside an anoxic glove box. The samples were conveyed into the XP spectrometer, ULVAC-PHI model VersaProbe II, without air contact by means of a vacuum transfer vessel. Monochromatic Al K_{α} X-rays (1486.6 eV) are used for excitation in conjunction with a dual-beam sample surface neutralization technique consisting of a beam of low energy electrons concurrently with a beam of low energy Ar^+ . The binding energy scale of the spectrometer was calibrated with the Cu $2p_{3/2}$ and Au $4f_{7/2}$ lines of pure and Ar^+ sputter cleaned metal foils [35]: the difference of binding energies between both lines is adjusted by the electronics to coincide with the reference value of 848.66 eV within ± 0.1 eV. Standard deviation of binding energies was within ± 0.2 eV. The C 1s line of adventitious hydrocarbon at 284.8 eV was used for charge referencing. Atomic concentrations are calculated from the areas of elemental lines (after Shirley background subtraction) of survey spectra using sensitivity factors of the elemental lines, asymmetry parameters, and transmission function of the analyzer. Narrow scans of elemental lines were recorded at 23.5 eV pass energy of the analyzer for determination of chemical shifts and spectral features. Data analysis was performed using ULVAC-PHI MultiPak Version 9.5.

Powder X-ray diffraction (XRD) studies were performed on the ground catalyst particles employing a PANalytical X'Pert Pro X-ray diffractometer operating with Cu K_{α} radiation.

Transmission electron microscopy (TEM, STEM-HAADF) was performed with a FEI Tecnai F20 ST TEM (operating voltage 200 kV) equipped with a field emission gun and EDAX EDS X-ray spectrometer. For TEM analysis, the ground powder of the catalyst before and after catalytic testing was suspended in isopropanol. A small drop of each suspension was then deposited onto amorphous carbon-coated 400 mesh copper grids and eventually air dried.

Palladium traces in the reaction solutions were quantified by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) employing a Varian Liberty 150 instrument. To reach maximum accuracy, palladium concentration was enriched before analysis by solvent evaporation and dissolving of the residues in small amounts of concentrated HNO_3 .

Conversions and selectivities were analyzed by GC-FID using an Agilent 6890 N gas chromatograph equipped with a J & W SCIENTIFIC DB5 column (30 m \times 0.25 mm, 0.25 μm film thickness).

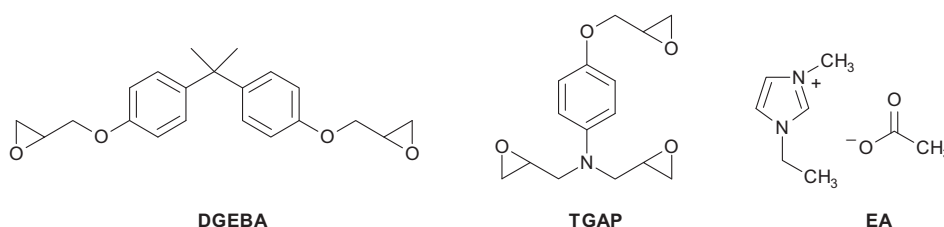


Fig. 1. Structures of epoxy resin monomers and the polymerization initiator.

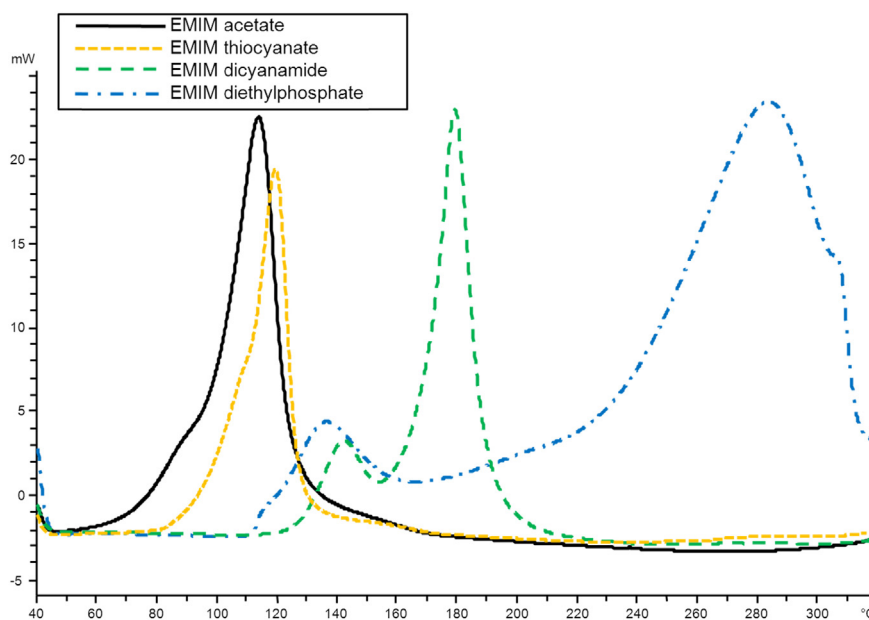


Fig. 2. DSC curves of DGEBA polymerization employing different EMIM-based imidazolium salts as polymerization initiators (3 wt.% initiator).

Products were quantified using calibration curves obtained with standard solutions. Unknown products were identified by GC–MS using a HP G1800A instrument (DB5 column from Agilent Technology, 30 m × 0.25 mm, 0.25 μm film thickness) coupled with a HP G1801 mass selective detector.

2.2. Catalyst preparation

The palladium compounds ($\text{Pd}(\text{OAc})_2$ or $\text{Pd}(\text{acac})_2$) were dissolved in the respective resin and EMIM acetate was added. Thereby, a palladium content of 5 wt.% and an initiator content of 3 wt.% was adjusted, respectively. Typically, the formulations were polymerized at the following temperatures: 0.5 h/40 °C, 0.5 h/60 °C, 0.5 h/80 °C, 0.5 h/100 °C, 0.5 h/120 °C, 0.5 h/140 °C, 0.5 h/160 °C,

0.5 h/180 °C and finally 3 h/200 °C. Polymerization was carried out in aluminum molds and thin plates were manufactured. These were ground in the next step employing an automated ceramic mortar and particle sizes were adjusted by sieving. Two fractions with particle diameters of 20–150 and 150–300 μm were obtained.

2.3. Hydrogenation reactions

A 100 ml glass autoclave was charged with the substrate (8.5 mmol), 50 ml methanol and the catalyst (0.5 g). After replacing the air and saturating the reaction solution with hydrogen, the pressure was raised to 2.5 bar. The mixture was magnetically stirred. After cooling to room temperature and expansion of the

Table 1
DSC and TGA data of Pd-doped polyether catalysts.

Catalyst	DSC data				TGA data
	T_{onset}^a (°C)	T_{peak}^b (°C)	ΔH^c (J/g)	T_g^d (°C)	$T_{5\%}^e$ (°C)
DGEBA-EA	99	118	595	141	388
DGEBA-Pd(OAc) ₂	112, 138	144, 172	54	Only partial crosslinking	
DGEBA-EA-Pd(OAc) ₂	101, 120, 154	122, 149, 168	589	79	327
TGAP-EA	96	110	737	169	336
TGAP-Pd(OAc) ₂	87, 281	112, 291	84, 686	Only partial crosslinking	
TGAP-EA-Pd(OAc) ₂	117	146	760	134	302
TGAP-Pd(acac) ₂	209	228, >300	10	Only partial crosslinking	
TGAP-EA-Pd(acac) ₂	103, 179	112, 185	738	113	277

^a Onset temperature of reaction peak.

^b Peak temperature.

^c Polymerization enthalpy.

^d Glass transition temperature of the resulting material.

^e Temperature at 5% weight loss; Values refer to particle sizes from 150 to 300 μm.

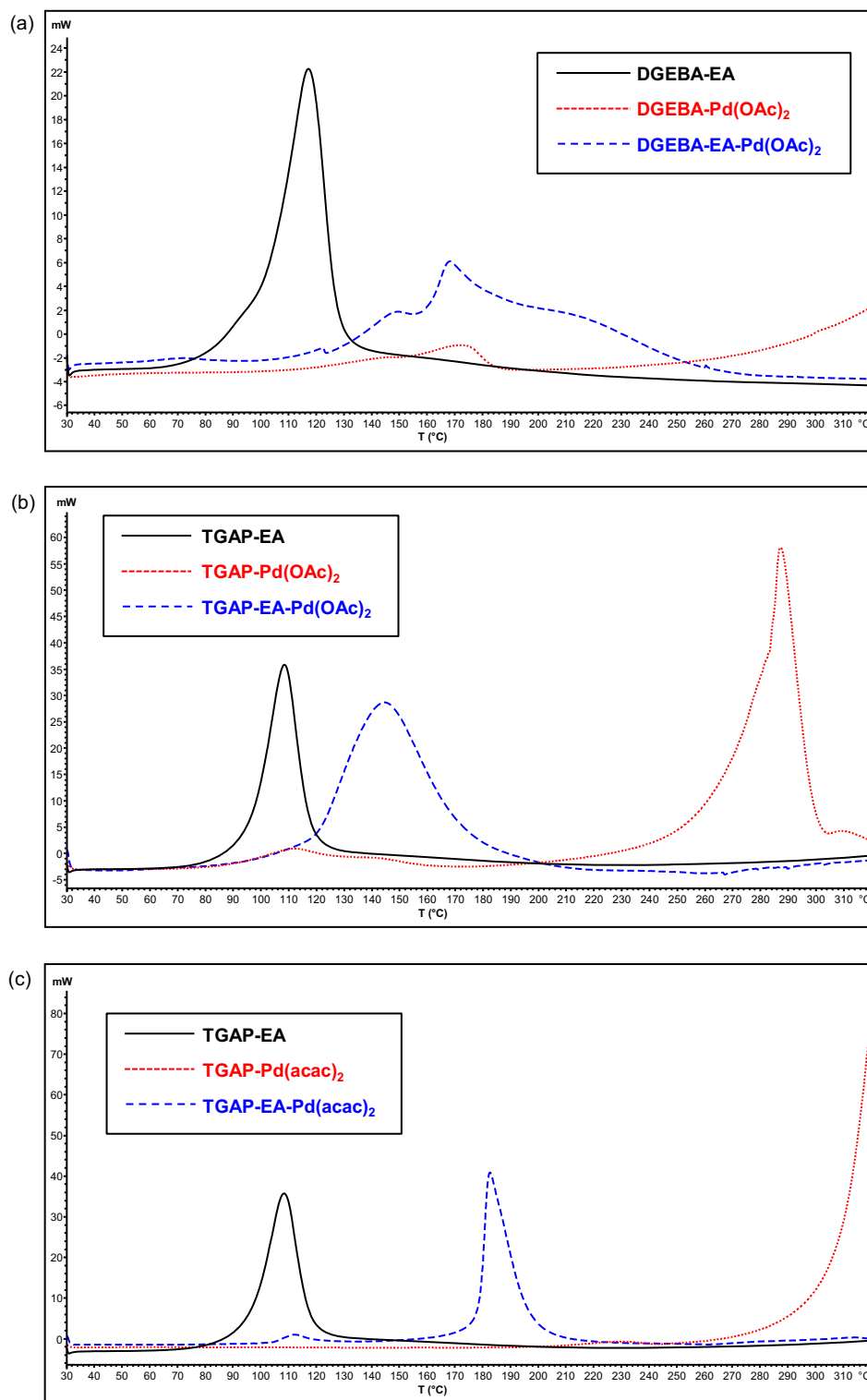


Fig. 3. DSC measurements of polymerization reactions (3 wt.% initiator).

system, the catalyst was separated by filtration and reused without reconditioning.

3. Results and discussion

3.1. Catalyst preparation and characterization

Initially, a screening on the use of imidazolium salts as polymerization initiators for the bifunctional DGEBA resin

was carried out. DSC measurements with different EMIM-based ionic liquids (EMIM acetate, thiocyanate, dicyanamide and diethylphosphate; 3 wt.% each) revealed high polymerization enthalpies and showed a remarkable influence of the anion on the reactivity of the formulations (Fig. 2). Thus, reactivity can be controlled to a large extent by choice of the imidazolium salt. Since EMIM acetate exhibited a high reactivity, this imidazolium salt was chosen for catalyst preparation.

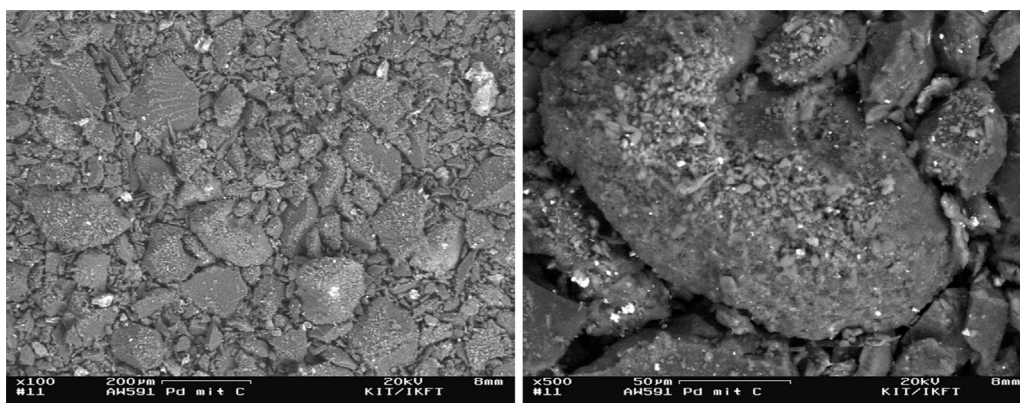


Fig. 4. SEM micrographs of TGAP-EA-Pd(OAc)₂.

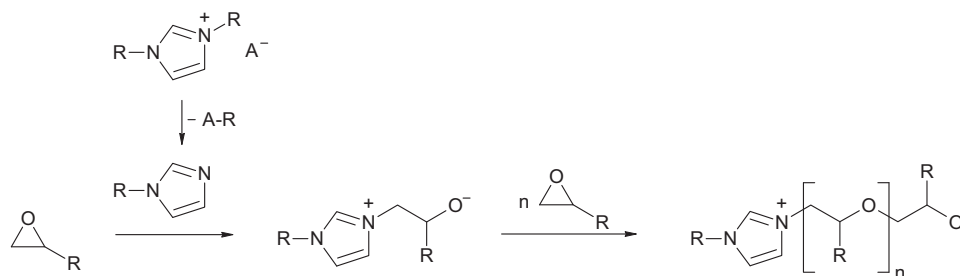


Fig. 5. Anionic polymerization of epoxides initiated by imidazolium salts.

With respect to catalyst preparation, not only DGEBA polymerization but also polymerization of the trifunctional TGAP resin (Fig. 1) were investigated by DSC (Table 1 and Fig. 3). Resin formulations containing only palladium compounds without polymerization initiator could not be polymerized sufficiently and remained viscous even after heating up to 200 °C. Thus, polymerization enthalpies of DGEBA-Pd(OAc)₂ and TGAP-Pd(acac)₂ are very low in the temperature range up to 300 °C. In the case of TGAP-Pd(OAc)₂ polymerization enthalpy is high ($\Delta H = 770 \text{ J g}^{-1}$) but the main reaction takes place at high temperatures ($T_{\text{onset}} = 281 \text{ °C}$ and $T_{\text{peak}} = 291 \text{ °C}$) and decomposition of the formulation already starts in this temperature range. Regarding TGAP-Pd(acac)₂, a similar behavior was observed. T_{onset} is at 309 °C and T_{peak} was not recorded since it is above 320 °C. The exothermic peaks at such high

temperatures are not only due to decomposition processes but also due to reactions of amine groups with epoxide groups of the TGAP monomer.

If EMIM acetate is used, polymerization enthalpies of all formulations are very high and those of the catalyst formulations are similar to those of the corresponding formulations without palladium (DGEBA-EA and TGAP-EA). Furthermore, main reaction peaks of the catalyst formulations are shifted to remarkably higher temperatures compared to the palladium-free systems. This temperature shift increases in the order TGAP-EA-Pd(OAc)₂ < DGEBA-EA-Pd(OAc)₂ < TGAP-EA-Pd(acac)₂. In the case of the DGEBA-based catalyst three peaks were detected indicating a multistep curing process over a broad temperature range.

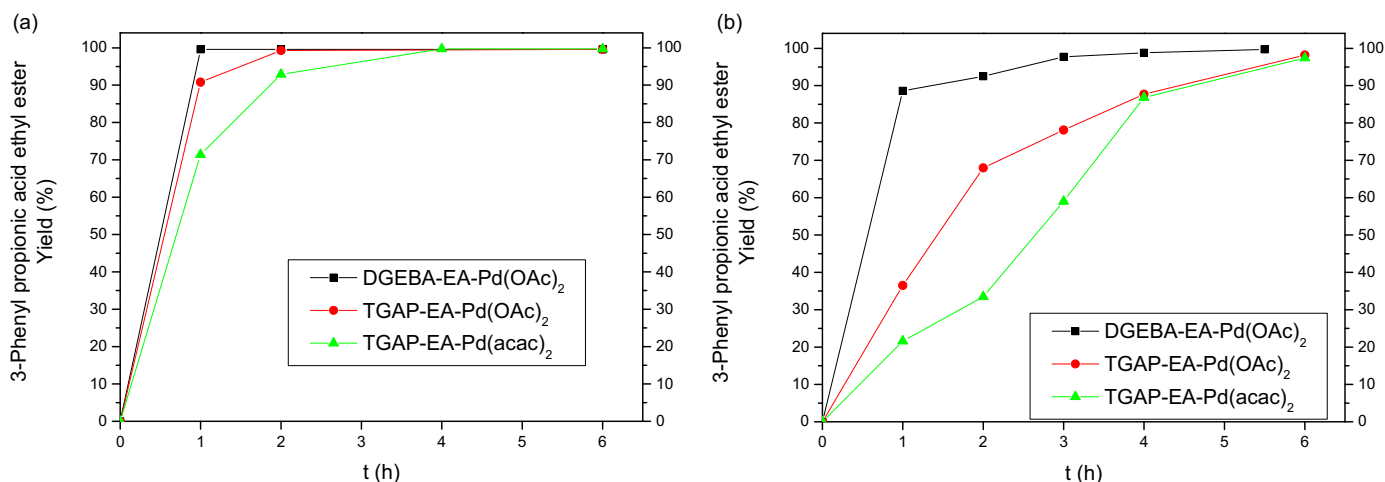


Fig. 6. Hydrogenation of ethyl cinnamate employing palladium-doped polyether catalysts. Catalyst particle sizes: (a) 20–150 and (b) 150–300 µm. Reaction conditions: 8.5 mmol ethyl cinnamate, 2.5 bar H₂, 50 ml MeOH, 0.5 g catalyst (3 mol% Pd), room temperature.

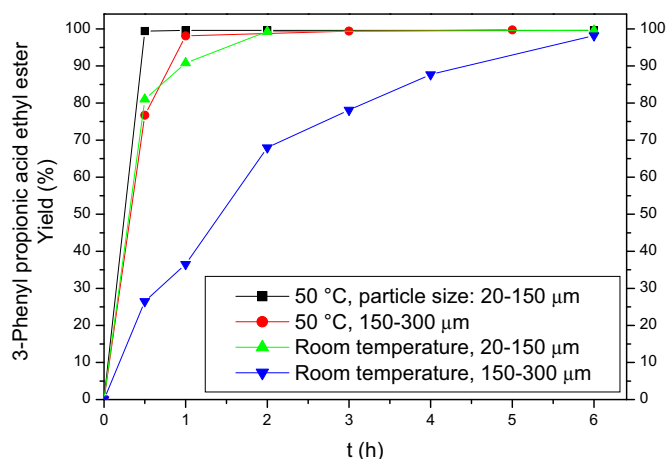


Fig. 7. Influence of temperature on the hydrogenation of ethyl cinnamate employing TGAP-EA-Pd(OAc)₂ as catalyst. Reaction conditions: 8.5 mmol ethyl cinnamate, 2.5 bar H₂, 50 ml MeOH, 0.5 g catalyst (3 mol% Pd; particle sizes: 20–150 and 150–300 μm).

Regarding glass transition temperatures, T_g -values of all catalysts are lower compared to the reference systems without palladium (DGEBA-EA and TGAP-EA). This phenomenon is pronounced in the case of the DGEBA-based catalysts and the glass transition temperature of DGEBA-EA-Pd(OAc)₂ is 79 °C whereas DGEBA-EA exhibits a T_g -value of 141 °C. This could be due to the high concentration of Pd(OAc)₂ in the formulation. Its content is 10.3 wt.% and it seems to affect the resulting material properties. The Pd(acac)₂ loading in TGAP-EA-Pd(acac)₂ is even higher (13.9 wt.%) but this could be partially compensated by the higher crosslinking of the trifunctional resin.

Overall, best results in terms of polymerization temperature, enthalpy and glass transition temperature were obtained in the case of TGAP-EA-Pd(OAc)₂. Polymerization occurs readily at comparatively low temperatures ($T_{\text{peak}} = 146$ °C) and the polymerization enthalpy is very high ($\Delta H = 760 \text{ Jg}^{-1}$). As a result, a high glass transition temperature is reached ($T_g = 134$ °C).

Concerning TGA data, performance of TGAP-EA-Pd(OAc)₂ ($T_{5\%} = 302$ °C) is between DGEBA-EA-Pd(OAc)₂ ($T_{5\%} = 327$ °C) and TGAP-EA-Pd(acac)₂ ($T_{5\%} = 277$ °C). It is remarkable that $T_{5\%}$ values of the DGEBA-based materials are higher than the corresponding values of the TGAP-based systems. One would expect a higher crosslinking and thus a higher thermal stability in the case of the trifunctional TGAP resin. This phenomenon could be due to a release of components, possibly impurities or byproducts formed during the curing process, which are not present in the DGEBA-based systems.

SEM-EDX measurements showed a homogeneous palladium dispersion in the polyether matrix (Fig. 4). However, a few bright spots with high palladium contents were also detected. Since resin solubility of the employed palladium compounds is high, palladium agglomeration could be due to partial segregation of palladium species during the curing reaction.

Regarding the mechanism of polymerization initiation, a multistep process was proposed [36]. It comprises dealkylation of the imidazolium salt and imidazole formation in the initial step, followed by nucleophilic attack of the imidazole at the epoxide ring, epoxide ring opening and anionic polymerization (Fig. 5). Polymerization reactions of the catalyst formulations are somewhat retarded compared to those of the palladium-free formulations (Table 1 and Fig. 3). This could be due to temporary coordination of intermediate imidazole species to palladium species and palladium-imidazole complexes are well-known [37,38]. Palladium incorporation into the materials could occur via coordinative

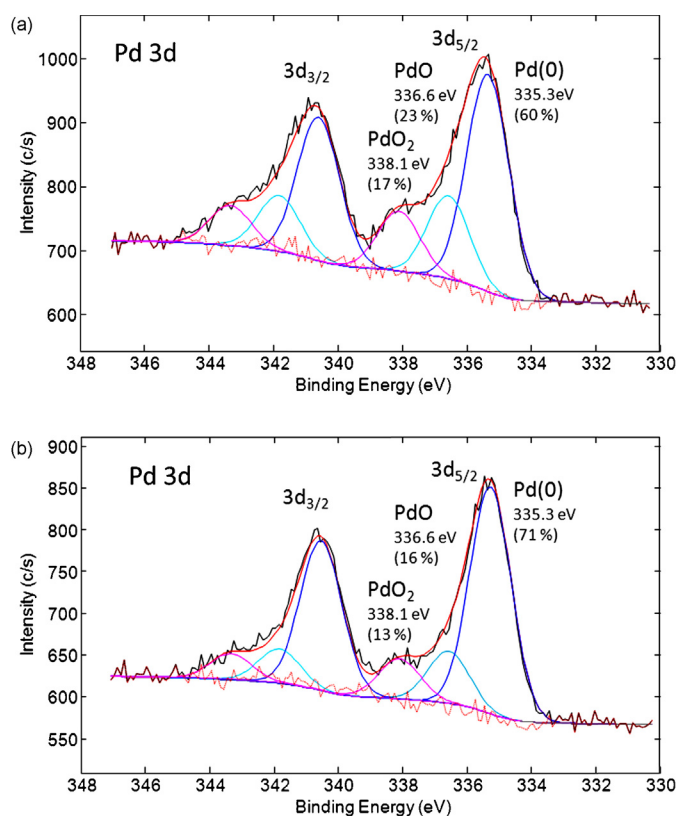


Fig. 8. XPS spectra of TGAP-EA-Pd(OAc)₂ (a) before and (b) after use in the hydrogenation of ethyl cinnamate.

interaction of palladium centers with oxo species from the polyether matrix.

3.2. Catalyst testing

At first, the catalysts were tested in the hydrogenation of ethyl cinnamate. Reactions were carried out in methanol at a hydrogen pressure of 2.5 bar and at room temperature. Reference experiments without catalyst and with the palladium-free materials DGEBA-EA and TGAP-EA were carried out and no alkene conversion was observed. The influence of reaction time and catalyst particle size was investigated (Fig. 6). Particle sizes between 20 and 150 μm (Fig. 6a) as well as fractions with particle sizes between 150 and 300 μm (Fig. 6b) were employed and reactions are significantly faster in the case of smaller particle sizes. Regarding particle sizes between 20 and 150 μm, performances of the different catalysts were similar and full conversion was reached after 1 h (DGEBA-EA-Pd(OAc)₂), 2 h (TGAP-EA-Pd(OAc)₂) and 4 h (TGAP-EA-Pd(acac)₂). Employing larger particles, several hours are needed to reach full conversion under the same reaction conditions. The influence of particle size is in accordance with results obtained in earlier work [7] and can be explained by the nature of the materials. After curing, highly crosslinked and compact materials are obtained, especially in the case of epoxy monomers with more than two functional groups. The materials are nonporous, and catalytic performance depends to a large extent on the swelling behavior of the surface. Swelling itself depends mainly on the resin type, the solvent, reactants, temperature and operating time. Usually, swelling of TGAP-based resins is, in comparison with DGEBA-resins, lower. Thus, a fraction of catalytically active centers is not accessible, at least in initial reactions with the fresh catalyst. Naturally, this is directly reflected in the catalytic performance and the use of small particles with high surface area is favorable.

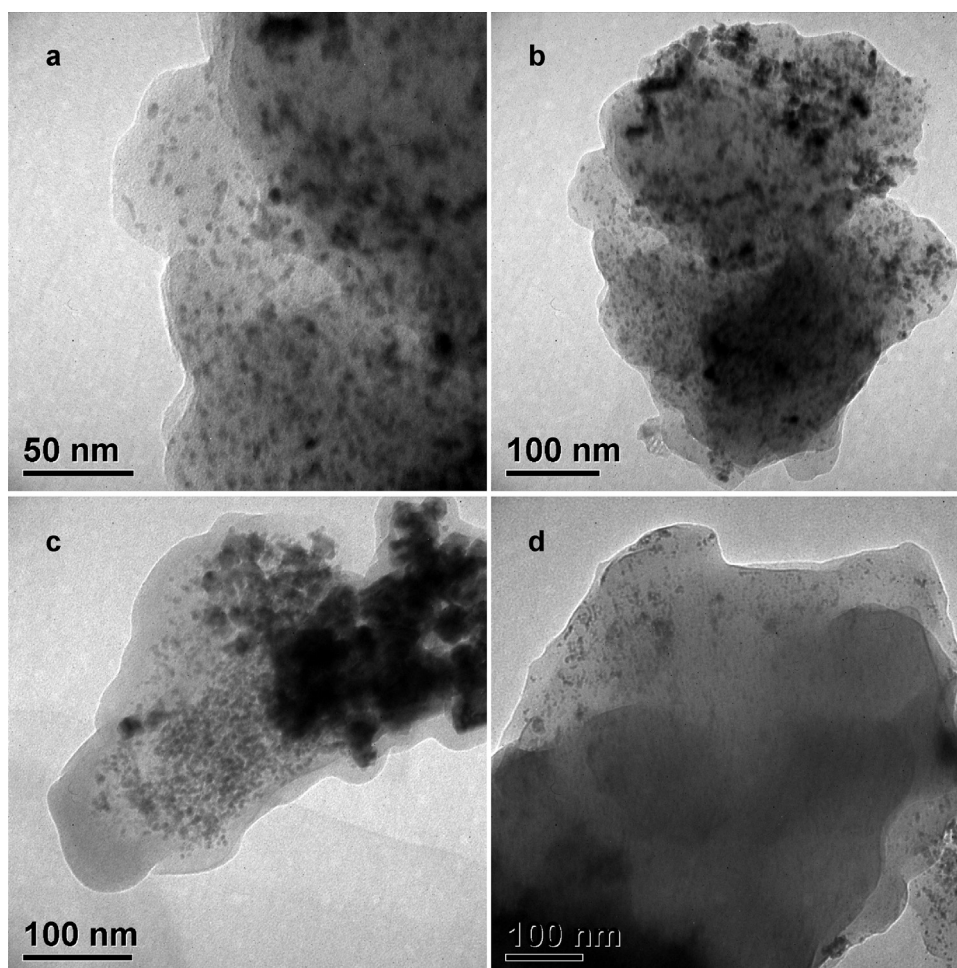


Fig. 9. TEM images of TGAP-EA-Pd(OAc)₂ (a and b) before and (c and d) after use in the hydrogenation of ethyl cinnamate.

Within the scope of these comparative tests, catalyst DGEBA-EA-Pd(OAc)₂ exhibited the best catalytic performance. However, it is known from previous experiments that DGEBA-based catalysts exhibit only moderate long-term stability and metal leaching from the polyether matrix can be rather high [6]. Thus, TGAP-EA-Pd(OAc)₂ was chosen for further investigations since this catalyst exhibits both, good material characteristics (Table 1) and good hydrogenation activity (Fig. 6). At first, the influence of reaction temperature was investigated. Increasing the reaction temperature to 50 °C and using particle sizes between 20 and 150 μm, full conversion is reached within 0.5 h. Using the fraction with particle sizes from 150 to 300 μm, almost full conversion is reached after 1 h (Fig. 7).

The nature of palladium species was investigated more in detail by recording XPS spectra of catalyst TGAP-EA-Pd(OAc)₂ before and after use in the hydrogenation of ethyl cinnamate (Fig. 8). Given that no reduction step was carried out before the reaction, the Pd(0) content is fairly high (Fig. 8a). However, this is in accordance with investigations on the thermal decomposition of neat Pd(OAc)₂. In this case, Pd(0) formation occurred in the temperature range from 200 to 300 °C [39]. The Pd(0) content after reaction is, as expected, significantly higher while the percentage of oxidic Pd species decreased (Fig. 8b). The XRD patterns of the catalyst before and after catalytic testing revealed the (1 1 1), (2 0 0), (3 1 1), and (2 2 2) reflections of metallic Pd(0) particles at 40.10°, 68.09°, 81.98° and 86.46° for 2θ, respectively.

TEM investigations revealed small Pd nanoparticles which were homogeneously distributed over the polymer matrix (Fig. 9). TEM

images of the unused catalyst (Fig. 9a and b) are very similar to those recorded after reaction (Fig. 9c and d). In agreement with SEM analysis at lower magnification (Fig. 4), some large Pd agglomerates were also observed by TEM analysis.

To investigate recyclability, catalyst TGAP-EA-Pd(OAc)₂ was employed repeatedly in 10 consecutive reactions. The reaction solution was completely removed after each reaction and the catalyst was reused without any washing or reactivation step. In all reactions, almost 100% yield of 3-phenyl propionic acid ethyl ester was obtained (Table 2). Palladium leaching from the polyether

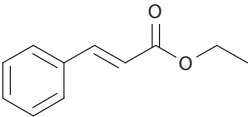
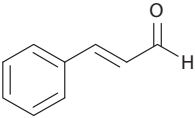

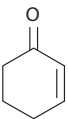
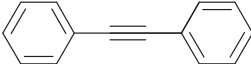
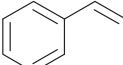
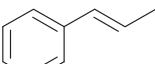
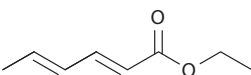
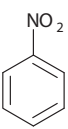
Table 2
Performance of TGAP-EA-Pd(OAc)₂ in 10 consecutive reactions.^a

Run no.	Yield (%)	Pd loss	
		(μg)	(%) ^b
1	99	2.1	0.009
2	>99	2.2	0.009
3	>99	1.8	0.007
4	>99	2.9	0.012
5	>99	1.9	0.008
6	99	1.5	0.006
7	>99	0.7	0.003
8	99	0.8	0.003
9	>99	0.7	0.003
10	>99	0.7	0.003

^a Reaction conditions: 8.5 mmol ethyl cinnamate, 2.5 bar H₂, 50 ml MeOH, 0.5 g catalyst (3 mol% Pd; particle sizes: 20–150 μm), room temperature, reaction time: 2 h.

^b Percentage of Pd originally loaded on the polymer.

Table 3
Hydrogenation of different substrates employing TGAP-EA-Pd(OAc)₂ as catalyst.^a

Entry	Substrate	Conversion (%)	Selectivity (%)
1		>99	>99 (hydrocinnamic acid ethyl ester)
2		83	63 (hydrocinnamic aldehyde) 33 (hydrocinnamic alcohol) 1 (cinnamic alcohol) 3 (others) ^b
3		>99	>99 (cyclohexane)
4		82 ^c	96 (cyclohexanone) 4 (others)
5		67 ^c	98 (Z-stilbene) 2 (E-stilbene)
6		>99	>99 (ethylbenzene)
7		>99	>99 (propylbenzene)
8		81	73 (ethyl hexenoate) 27 (ethyl hexanoate)
9		19 (>99) ^d	>99 (aniline) (>99) ^d

^a Reaction conditions: 8.5 mmol substrate, 2.5 bar H₂, 50 ml MeOH, 0.5 g catalyst (3 mol% Pd; particle sizes: 20–150 μm), room temperature, reaction time: 2 h.

^b Byproducts: coupling products and acetals.

^c Reaction in THF instead of methanol.

^d Values in parentheses: reaction at 60 °C.

support to the reaction solutions was also investigated in this series of reactions (Table 2). To ensure high accuracy, volatile components were removed from the reaction mixtures by evaporation. The residues were dissolved in small amounts of concentrated HNO₃ and the solutions were subjected to ICP-AES measurements. Metal leaching is decreasing from around 2 μg in the initial reactions to around 0.7 μg in the last reactions. The average leaching from these 10 reactions is 1.5 μg per reaction, which corresponds to 0.006% of palladium originally loaded on the polymer. Thus, metal leaching is very low and in the same range as leaching previously observed. Similar catalysts could be used in more than 100 reactions while remaining highly active and exhibiting very low metal losses [6,7].

In the next step, hydrogenation reactions were extended to other substrates. The same reaction conditions as mentioned above were employed and almost quantitative yields were obtained in the case of ethyl cinnamate (Table 3, entry 1), cyclohexene (entry 3), styrene (entry 6) and *trans*-β-methylstyrene (entry 7).

In the case of cinnamaldehyde (entry 2), conversion was 83% and the product spectrum comprised hydrocinnamic aldehyde, hydrocinnamic alcohol and cinnamic alcohol with 63, 33 and 1% selectivity, respectively. Low amounts of byproducts were detected (3% selectivity) and these were stemming from coupling reactions of cinnamaldehyde and acetalization reactions with the solvent. Results obtained with TGAP-EA-Pd(OAc)₂ differ from recently reported results obtained with other epoxy resin catalysts [31]. These catalysts were tested at 80 °C and 50 bar hydrogen pressure. Depending on the catalyst, hydrocinnamic alcohol or cinnamic alcohol were the main products. Regarding cyclohexenone (entry 4), conversion was 82% with a cyclohexanone selectivity of 96%. The reaction was carried out in THF. If methanol is used as solvent, conversion is 100% but a series of byproducts is observed, stemming from reactions with the solvent. In the hydrogenation of diphenylacetylene (entry 5) and sorbic acid ethyl ester (entry 8) only partial hydrogenation was observed. Employing the former

substrate, conversion was 67% and stilbene was formed selectively (98% of (Z)-stilbene and 2% of (E)-stilbene). Employing sorbic acid ethyl ester (entry 8), a mixture of ethyl hexanoate and monohydrogenated ethyl hexenoate was obtained. The products were formed in a ratio of 1:2.7 at a conversion of 81%. In the case of nitrobenzene (entry 9), only 19% conversion was obtained at room temperature but almost quantitative conversion to aniline was reached at 60 °C. Thus, yields can be easily improved by running the reactions at somewhat elevated temperatures. On the whole, catalyst TGAP-EA-Pd(OAc)₂ is, in terms of activity, recyclability and stability, comparable to polymer-incarcerated or polysilane-supported palladium catalysts [40–43]. These are prepared by reaction of Pd(PPh₃)₄ with epoxide-containing copolymers and exhibit very good hydrogenation performances under mild reaction conditions. However, preparation of catalysts like TGAP-EA-Pd(OAc)₂ is much easier and more cost-efficient.

4. Conclusions

A convenient and highly efficient one-step procedure was developed to incorporate palladium species in the network of polyethers. Simple metal salts like Pd(OAc)₂ can be dissolved in commercially available epoxy resins and epoxide monomers can be crosslinked via anionic polymerization employing ionic liquids, e.g., EMIM acetate, as polymerization initiators. Thus, the use of costlier metal complexes can be circumvented and promising catalysts can be obtained just as well. The resulting polyether materials exhibit high catalytic activity in a series of hydrogenation reactions, even under mild reaction conditions. The catalysts can easily be recycled and reused while maintaining high catalytic activity. Since palladium leaching to reaction solutions is very low, catalysts can be employed over an extended period, depending on the reaction conditions. Ongoing research concentrates on the long-term performance of such catalysts, variation of reaction conditions, hydrogenation of other substrates and extension of the concept to other metal salts and catalytic reactions. Current activities also focus on the characterization of catalytically active centers for a deeper understanding of the catalytic processes and rational optimization.

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