

# Hydrogenation of cinnamaldehyde over supported palladium catalysts

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The selective hydrogenation of cinnamaldehyde has been studied using palladium catalysts based on epoxy resin cured with ionic liquids. Characterization of palladium catalysts has involved the following methods: IR spectroscopy, X-ray photoelectron spectroscopy (XPS), AAS spectroscopy and time-of-flight secondary ion mass spectrometry (TOF-SIMS). The investigated catalysts showed high stability and good recycling efficiency what makes them useful for a prolonged use. The factors influencing the selectivity of the supported catalysts were discussed.

**Keywords:** selective hydrogenation, supported catalyst, epoxy resin, ionic liquids.

## INTRODUCTION

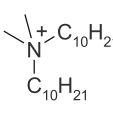
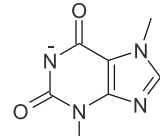
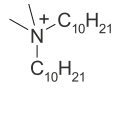
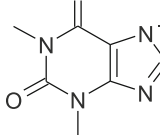
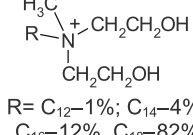
The great importance of the catalytic hydrogenation of unsaturated aldehydes to unsaturated alcohols is caused by several applications of unsaturated alcohols in the flavour and fragrance industry<sup>1,2</sup> as well as in the pharmaceutical manufacturing<sup>3</sup>. However, the hydrogenation of the C=C bond is thermodynamically more favourable than the C=O hydrogenation, and the low yields of the desired product are obtained with the conventional hydrogenation catalysts. Many factors such as: the presence of catalytic activators or poisons, temperature, pressure, solvent agitation and other conditions specific to the particular process, are influencing the catalytic hydrogenation reactions<sup>4</sup>. The choice of a proper metal and carrier is one of the most important steps while creating the catalyst. The carrier is able to disperse the metal to smaller particles as compared to bulk metal enhancing the specific metal surface area. Additionally, smaller metal particles partially behave as non-metals, e.g. have higher electron densities, leading to higher hydrogenation rates compared to larger particles. In addition to electronic effects, which are different for different metals, the geometric properties of the metal particles can affect the hydrogenation rate and selectivity if the size of the reacting molecule is close to the size of metal crystallites<sup>5</sup>.

Hydrogenation reaction often relies on the use of transition metal catalysts in order to increase the efficiency of the reaction. In addition, the ligands required to effect asymmetric versions of these reactions can be expensive to purchase or to produce. Thus, the recycling ability of a catalyst is of great importance. Polymer – supported catalysts that can be potentially recycled have been prepared by attachment of a ligand to the polymer followed by incubation of the supported ligand with an appropriate metal source<sup>6</sup>. A number of attempts have been made to prepare low molecular palladium complexes immobilized on polymeric supports. Several reports describe the synthesis and characterisation of palladium complexes such as: Pd(Cl)<sub>2</sub>(IPA)<sub>2</sub> (IPA = 3-isocyanopropylacrylate) copolymerized with N,N-dimethylacrylamide (DMAA) and N,N'-methyleneacrylamide (MBAA)<sup>7</sup> and Pd(II) complex of L-2-amino butanol anchored on styrene-divinylbenzene copolymer<sup>8,9</sup>. Also the catalytic activity of palladium supported on heterocyclic polyamides<sup>10</sup>,

carbon nanomaterials (nanotubes and nanofibres)<sup>11</sup> has been reported. Benvenuti et al. reports the use of the cross-linked styrene/divinylbenzene resin functionalized with bis(diphenylphosphino)methane ligands which yield a supported palladium complex. The obtained heterogenized catalysts were employed for the hydrogenation of nitrocompounds and  $\alpha,\beta$ -unsaturated aldehydes under mild conditions. While nitrobenzene is converted only into aniline, cinnamaldehyde is selectively converted into hydrocinnamaldehyde<sup>12</sup>.

In this paper we present the synthesis of novel heterogenized palladium catalysts based on epoxy resin cured with ammonium ionic liquid. The palladium complex PdCl<sub>2</sub>(PhCN)<sub>2</sub> was introduced to the polymer matrix via ligand exchange. The selectivity and stability during the prolonged use was tested in the hydrogenation of cinnamaldehyde. Our aim was to study the influence of the selected ionic liquid on the stability and selectivity of the investigated catalysts. In our work we investigated 3 supports based on epoxy resin cured with ionic liquids whose structures are presented in Table 1.

**Table 1.** Description of used ionic liquids

Cation	Anion	Acronym
		[d <sub>2</sub> m <sub>2</sub> am][thb] 125
		[d <sub>2</sub> m <sub>2</sub> am][thp] 126
 R = C <sub>12</sub> -1%; C <sub>14</sub> -4%, C <sub>16</sub> -12%, C <sub>18</sub> -82%	BF <sub>4</sub> <sup>-</sup>	[h <sub>2</sub> emam][BF <sub>4</sub> ] 142

## EXPERIMENTAL

### Materials

Epoxy resin bisphenol A epichlorohydrin medium molecular weight  $\leq 700$  Epidian 5 (EP5), epoxy equivalent 200, (viscosity 20 000–30 000 mPas at 23°C), Organika

Sarzyna, Poland was used. Toluene (POCH), *trans*-cinnamylaldehyde (Aldrich), etanol (POCH) were used for the hydrogenation reaction.

### Support preparation

The epoxy resin (3 g) and the relevant ionic liquid (1,2 g) were placed in a flask and mixed until a homogenous consistency was obtained. The mixture was transferred onto a Teflon® mold and cured at temperature from 298 to 423 K over a period of 1 h to 48 h. The cured resin was frozen by immersion in liquid nitrogen and mechanically ground to powder.

### Catalyst preparation

For all the catalysts a typical procedure was followed. In a round-bottom flask a known amount of cured epoxy resin (1.0 g) and a known amount of PdCl<sub>2</sub>(PhCN)<sub>2</sub> (0.2 g) were placed and dissolved in 10 ml of toluene. The progress of this reaction was determined by the disappearance of the red colour of the mixture. The yellow precipitation was filtered off and washed with toluene (3 x 20 ml) in order to remove the palladium complex non-chemically bound to the polymer. For all the catalysts the Pd content was fixed below the metal uptake capacity.

### Catalytic tests

The reactions were carried out in a 100 ml Parr microreactor model 4593 with glass liner. The typical hydrogenation run was as follows. The reactor was charged with 0.2 g of supported palladium catalyst, 5 ml of 96% ethanol, 0.25 ml of toluene and 0.25 ml of cinnamaldehyde. The reactor was flushed several times with pure hydrogen and then the hydrogen pressure and temperature were adjusted to the required level, 50 bar and 80°C, respectively. The composition of the samples was analyzed by GC. The reaction products were quantitatively analyzed by gas chromatography (GC) on a Hewlett-Packard 5990 II gas chromatograph equipped with a thermal conductivity detector. The GC column was HP-50+ (crosslinked 50% Ph Me silicone) 30 m x 0.63 mm x 1.0 µm film thickness. The products were identified by matching their retention times with those of authentic samples.

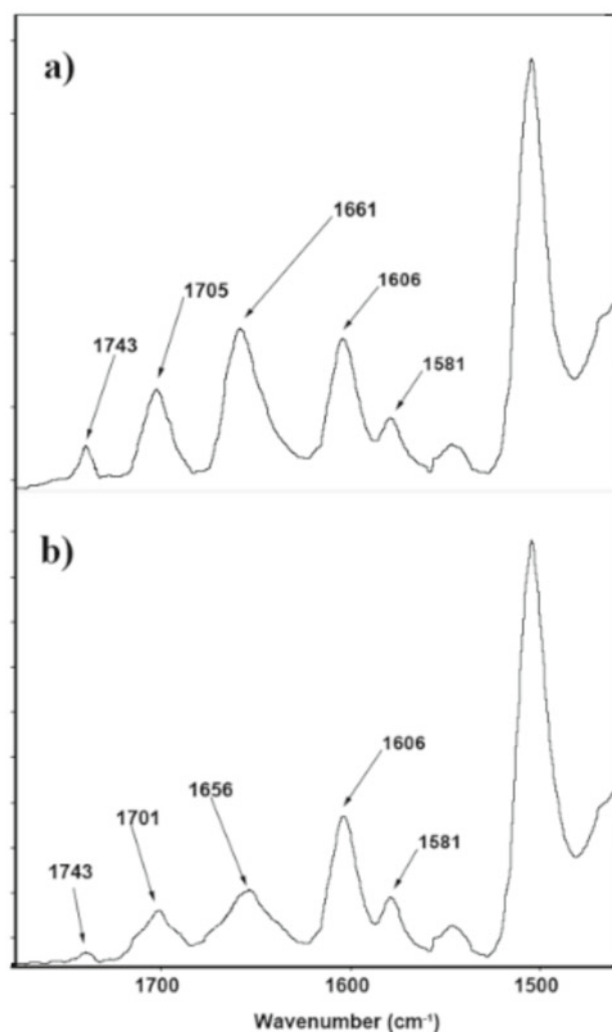
### Catalyst recycling

In the recycling tests, when the reaction was complete, the catalyst was filtered off from the reaction mixture, washed with 3 x 25 ml of toluene, dried vacuum and used for the next reaction.

## RESULTS DISCUSSION

### Spectroscopic characterization of the support and palladium catalyst

Due to the capacity of this article we decided to focus on the EP5/[d<sub>2</sub>m<sub>2</sub>am][thp] support and the EP5/[d<sub>2</sub>m<sub>2</sub>am][thp]-Pd catalyst which serve as an example of spectroscopic characterization (Fig. 1). Table 2 lists the characteristic absorption bands for the EP5/[d<sub>2</sub>m<sub>2</sub>am][thp] support and the EP5/[d<sub>2</sub>m<sub>2</sub>am][thp]-Pd catalyst and ascribed corresponding groups.

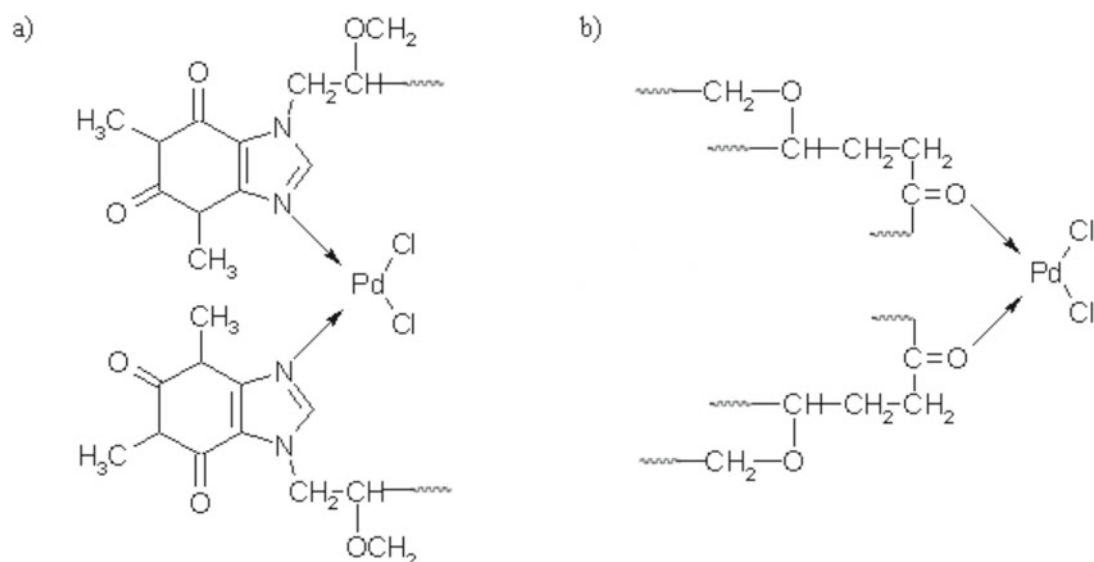


**Figure 1.** FT-IR spectra of: a) EP5/[d<sub>2</sub>m<sub>2</sub>am][thp] support; b) EP5/[d<sub>2</sub>m<sub>2</sub>am][thp]-Pd catalyst

The absorption band at 1743 cm<sup>-1</sup> corresponds to the C=O group of the epoxide chain resulted presumably from the polymerization of the epoxy resin. This band in the spectrum of EP5/[d<sub>2</sub>m<sub>2</sub>am][thp]-Pd shows a weak intensity what indicates the metal bonding by the O atom. The shifts and decrease of absorption bands from 1661 cm<sup>-1</sup> to 1656 cm<sup>-1</sup> and 1705 cm<sup>-1</sup> to 1701 cm<sup>-1</sup> may be related to the disorientation of the purine ring. This indicates the possibility of palladium coordination of the -N= atom. No changes observed for strong bands at 1581 cm<sup>-1</sup> and 1606 cm<sup>-1</sup>, considered to be due to asymmetric and symmetric stretching vibrations of two

**Table 2.** Characteristic absorption bands and corresponding groups received from the FTIR analysis for the EP5/[d<sub>2</sub>m<sub>2</sub>am][thp] support and the EP5/[d<sub>2</sub>m<sub>2</sub>am][thp]-Pd catalyst

Characteristic absorption band [cm <sup>-1</sup> ]		
Support EP5/[d <sub>2</sub> m <sub>2</sub> am][thp]	Catalyst EP5/[d <sub>2</sub> m <sub>2</sub> am][thp]-Pd	
1743	1743	C=O
1705	1705	-C=N-
1661	1656	-C=N-
1606	1606	C=O
1581	1581	C=O



**Scheme 1.** Mode of coordination of Pd(II) complex by the EP5/[d<sub>2</sub>m<sub>2</sub>am][thp] support

carbonyl groups of theophylline moiety, indicate that the metal complex is not bonded to epoxide-support through theophylline carbonyl groups (Scheme 1).

The results received from the XPS spectroscopy (Table 3) showed that on the freshly prepared catalyst EP5/[d<sub>2</sub>m<sub>2</sub>am][thp]-Pd palladium appears dominantly in the form of Pd(II) with minor fractions of Pd<sup>δ+</sup> nanoclusters. The recovered catalyst after 2<sup>nd</sup> hydrogenation reaction contained also zero-valent palladiumPd(0).

### Thermal studies

The differential scanning calorimetry (DSC) was used in order to observe the structural rearrangements of the polymer network that takes place during the complexation. No differences between the pure supports and the palladium immobilized supports were observed what indicates the lack of changes in the polymeric structure after metal introduction. The DSC analysis has shown that the pure polymeric supports are stable to about 210°C and the introduction of palladium species does not change their thermal stability. The DSC method was also applied to determine the curing temperature which was about 90°C for the [d<sub>2</sub>m<sub>2</sub>am][thb] and [d<sub>2</sub>m<sub>2</sub>am][thp] ILs and about 140°C for the [h<sub>2</sub>emam][BF<sub>4</sub>] IL. This results show that the curing temperature strongly depends on the structure of the used ionic liquids.

### Catalytic test

The influence of the structure of the polymer support on the reaction selectivity was studied in the hydrogenation of cinnamaldehyde. The hydrogenation of cinnamaldehyde can give rise to three products, namely hydrocin-

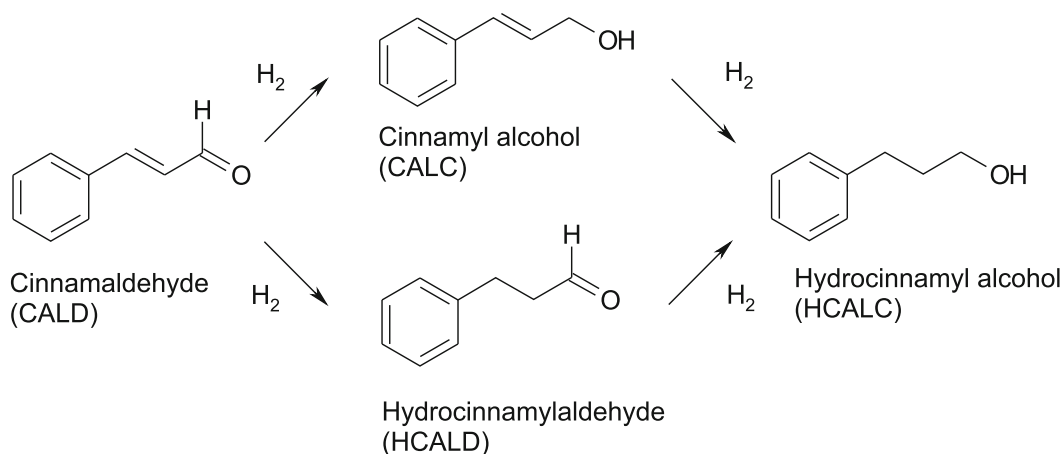
namaldehyde (HCALD), cinnamyl alcohol (CALC), and hydrocinnamyl alcohol (Scheme 2). The mostly desired product – unsaturated alcohol – is difficult to produce in a catalytic hydrogenation of α,β-unsaturated aldehydes because the hydrogenation of C=C bonds in the presence of noble metals is thermodynamically and kinetically favoured over the hydrogenation of the C=O bonds.

Table 4 lists results of the hydrogenation of cinnamaldehyde at 50 bar pressure and temperature 80°C. It has been shown that the morphology and the chemical structure of the polymeric matrix influence the selectivity of this reaction. The selectivity of this reaction strongly depends on the types of binding groups presented in the polymer. Hydrocinnamyl alcohol (HCALC) is formed predominantly by the consecutive hydrogenation of cinnamaldehyde (CALD) and hydrocinnamaldehyde (HCALD) in the presence of EP/125-Pd and after the 1<sup>st</sup> run in the presence of EP5/142-Pd, whereas after the 2<sup>nd</sup> run the main product in the presence of this catalyst is the cinnamyl alcohol (CALC). Cinnamyl alcohol (CALC) is also the main product obtained in the presence of EP5/126-Pd catalyst.

For the EP5/142-Pd catalyst selectivity towards CALC increased after the 2<sup>nd</sup> run. This may be related to the reduction of the Pd(II) species to Pd(0). It is known that the catalyst selectivity depends on the size distribution of the metal<sup>13</sup>. Larger palladium nanoparticles created on EP5/142-Pd(0) after reduction were found to give higher selectivity towards cinnamyl alcohol (CALC). The steric effect exerted by the phenyl group prevents the close approach of the C=C to the surface of large particles so the molecule is tilted with C=O closer to

**Table 3.** Binding energy values from XPS measurements

Sample	Binding energy (eV)						
	N 1s		O 1s	Pd 3d <sub>5/2</sub>			Cl 2p <sub>3/2</sub>
	-N=	N-C(=O) N		Pd <sup>δ+</sup>	Pd(0)	Pd(II)	
EP5/[d <sub>2</sub> m <sub>2</sub> am][thp]	403.4	401.3	532.0	–	–	–	–
EP5/[d <sub>2</sub> m <sub>2</sub> am][thp]-Pd before use	406.3	403.7	536.1	339.7	–	341.5	201.9
EP5/[d <sub>2</sub> m <sub>2</sub> am][thp]-Pd after 2 <sup>nd</sup> run	406.1	403.4	536.4	339.6	335.8	341.3	201.8



**Scheme 2.** Hydrogenation of cinnamaldehyde

**Table 4.** Product distribution in the hydrogenation of cinnamaldehyde over palladium supported catalysts

Catalyst	Run	Conversion [%]	Product distribution [%]		
			HCALD	CALC	HCALC
EP5/125-Pd	1	98	9	23	68
	2	97	2	1	97
EP5/126-Pd	1	95	14	83	3
	2	96	15	84	1
EP5/142-Pd	1	98	0	1	99
	2	94	14	59	27

Conditions: Temperature 80°C ; Time 2 h ; solvent: 96% ethanol; the overall volume: 5.5 ml; unidentified reaction products are not shown.

the surface and therefore more easily activated. This barrier does not exist by the approach of phenyl group to a small particle, therefore the selectivity to CALC of the not reduced catalyst EP5/142-Pd(II) is low<sup>14</sup>. The presence of the palladium nanocluster were confirmed by XPS spectroscopy (Table 3).

The results presented in table 4 show that for catalysts EP5/125-Pd and EP5/142-Pd there is a significant difference in the product distribution between 1<sup>st</sup> run and 2<sup>nd</sup> run. This is probably caused by the increasing volume of the sample (swelling), hence allowing for an easier access to the active spots in the open pores of the catalyst.

The activity of the investigated catalysts decreases with the subsequent usage which might be caused by palladium leaching. The time-of flight secondary ion mass spectrometry (TOF-SIMS) was applied to investigate the deactivation process and to observe the deterioration of palladium distribution on the catalyst surface after 2<sup>nd</sup> use in comparison with a fresh sample. Owing to TOF-SIMS a considerable drop of the surface accessible Pd was observed for the EP5/142-Pd catalyst after 2<sup>nd</sup> run (Table 5). The drop of Pd was at a safe level and slightly affects the catalyst activity within acceptable limits.

**Table 5.** Normalized intensity of <sup>106</sup>Pd<sup>+</sup> selected from the mass spectra of palladium catalysts

Catalyst	Run	Intensity of <sup>106</sup> Pd <sup>+</sup>
EP5/142-Pd	0	7.9 × 10 <sup>-3</sup>
	2	5.8 × 10 <sup>-3</sup>

## CONCLUSIONS

The results demonstrated that the prepared supports meet the requirements for organic carriers in that they

can be readily received in a form suitable for heterogenization of the metal complex without any previous functionalization. The used ionic liquid greatly affects the selectivity of the polymer supported complex catalyst. The studied catalysts appeared to be highly effective for the hydrogenation of cinnamaldehyde reaction.

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