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Platinum complex catalysts immobilized on epoxy resins cured with polythiourethane hardeners

Abstract: Some efficient polymer-supported platinum catalysts have been synthesized through the novel application of epoxy resin D.E.R.\textsuperscript{TM} 332 cured with polythiourethanes. Epoxide supports were obtained as a result of the use of polythiourethane hardeners. The activity, stability and selectivity during long-term use of the investigated catalytic systems were tested in a hydrogenation reaction of cinnamaldehyde. The results of this study indicate that polythiourethanes used to cure epoxy resin can also greatly affect the catalytic properties of the epoxide-supported platinum catalysts. To fully characterize both polymeric supports and heterogenized catalysts numerous research methods like time-of-flight secondary ion mass spectrometry (ToF-SIMS), infrared spectroscopy (IR), X-Ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM-EDX) and nitrogen BET surface area measurements were used.

Keywords: Catalysts, epoxy resins, polythiourethanes, heterogeneous catalysis, Heck reaction

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1 Introduction

Polymeric carriers used for the deposition of metal complex catalysts have many advantages. First of all, immobilization of a homogeneous catalyst can, in principle, facilitate its recovery and reuse. Over the past decades a number of approaches have been developed for this purpose, typically including using inert inorganic materials or organic polymers as supports or conducting the reactions in some unconventional media such as ionic liquids or supercritical CO\textsubscript{2} [1]. Epoxy resins are thermosetting materials widely used as adhesives, coatings and matrices in polymer composites because of the low viscosity of the formulations, good insulating properties of the final material, even at high temperatures, and also good chemical and thermal resistance. Epoxy carriers for complex catalysts are obtained by modification of epoxy networks where metal complexes are incorporated into the structure of the cured matrix. Although the concept has been known, there have been only a few reports on the use of epoxy resins as carriers for metal complex catalysts in organic synthesis [2]. One example, not widely reported, is their use in heterogeneous catalysis obtaining molybdenum-doped epoxy resin. An unquestionable advantage of such epoxy supports is the chemical, physical and morphological structure of polymer supports and their influence on the catalytic properties of the metal complex immobilized on it [3,4]. Epoxy resins doped with Mo, Pd, and Rh complexes have high catalytic stability in the processes of hydrogenation and hydroformylation. For the crosslinked macroporous resins it is relatively easy to generate a predetermined pore structure, including the pore size and surface area of the carrier. Additionally, use of insoluble systems allows easy separation of the catalyst from the reaction mixture for repeated use in the next reaction. Furthermore, as it was reported, the catalysts retain their specific properties, such as activity and selectivity when working under mild conditions of pressure and temperature [5]. Epoxy carriers seem to be almost ideal systems to develop very easy protocols for enzyme immobilization because epoxy groups can exhibit good reactivity under mild conditions and would be very stable at neutral pH values even in wet conditions [6]. Sun \textit{et al.} prepared PolyGMA resin with macroporous morphology and reactive epoxy groups. They used bulk polymerization of glycidyl methacrylate (GMA) using N, N'-methylene-2-bis (acylamide) as a crosslinking agent, a mixture of methanol aqueous solution as liquid pore-forming agents and nano-calcium carbonate as solid one. Under the optimum conditions, β-galactosidase was immobilized on this support, the basic property and the
kinetic data of all immobilized enzyme were determined, and satisfactory results were obtained in enzyme activity [7]. Grazu et al. described the synthetic approach for bi-functional epoxy-thiol carriers, in which the thiol groups were designed to speed up the process of physical adsorption while the epoxy groups were involved in the multipoint bonding of proteins [8]. Resins with amine and mercaptan as chelating groups were prepared by the suspended condensation polymerization of 2-chloroethoxymethyl thiirane and diamines. These resins showed high affinity for noble metal ions and Hg(II), and predominantly adsorbed Pd(II) or Hg(II) in the coexistence of Cu(II), Zn(II), and Mg(II) [9]. The results given by other authors showed that chelating resins with sulfur and nitrogen as donor atoms usually have excellent adsorption properties for mercury and noble metal ions [10-12].

Continuing the previous studies, herein we describe our approach to prepare the polymer-supported catalysts by immobilizing the platinum complex on the epoxy resin cured with thiol-terminated polythiourethane hardeners. These novel effective curing agents were synthesized from low-molecular-weight multifunctional mercaptan and diisocyanate precursors [13]. The efficiency of prepared catalysts was evaluated on the basis of their performance in the hydrogenation reaction. Our aim was to study the influence of the type of polythiourethane used as resin hardeners on the catalytic properties of the heterogenized catalysts. Test of catalyst stability during their prolonged use have also been described.

2 Experimental procedure

2.1 Materials

The high purity bisphenol A diglycidylether D.E.R.™332 epoxy resin (DER) with epoxy equivalent 170, (viscosity 4000–6000 mPas at 25°C), the Dow Chemical Company, USA was used. Polythiourethane hardeners were prepared by the reaction of hexamethylene diisocyanate (HDI) and pentaerythritol tetrakis (3-mercaptopropionate) and 3,6-dioxa-1,8-octanediethiol (SIGMA) in two molar excess by a previously reported method [13]. PtCl₂(PhCN)₂ was prepared from PtCl₂ (SIGMA, 98%) and benzonitrile (SIGMA, 99%) in petroleum ether (SIGMA) [14]. Toluene (POCH), trans-cinnamylaldehyde (Aldrich) and ethanol (POCH) were used for the hydrogenation reaction.

2.2 Support preparation

3 g of epoxy resin (DER) and 1.2 g of multifunctional polythiourethane (MPTU) or difunctional polythiourethane (DPTU) (Figs. 1a and 1b) were placed in flask and mixed until a homogeneous consistency was obtained. The mixture was transferred onto a Teflon® mold and cured at temperature 298 K over the period of 1 to 48 hours. The cured resin was frozen by immersion in liquid nitrogen and mechanically ground to a powder. The particle sizes were about 0.5 mm which was determined by sieve analysis.
2.3 Catalyst preparation

The platinum complex PtCl\(_2\)(PhCN)\(_2\) was immobilized on the prepared supports from toluene solution by ligand-exchange process.

To a known amount of the support (0.5 g) in a round-bottom flask, PtCl\(_2\)(PhCN)\(_2\) dissolved in 10 ml of toluene was added. The mixture was stirred at room temperature for 3 days when all Pt complex had reacted with the polymer. The yellow product was filtered off, extracted with toluene under nitrogen in order to remove complex that was non-chemically bound to the polymer and finally dried under vacuum. For all supported catalysts the Pt content was fixed below the metal uptake capacity for a polymer. Lower and higher concentrations of PtCl\(_2\)(PhCN)\(_2\) were also tested but the results are not discussed herein. Furthermore increased concentration of Pt complex did not lead to enhanced metal attachment to epoxides because there are steric restrictions imposed by the different microporosities of these supports and probably catalytic centers can be very different from of theirs homogeneous analogues.

2.4 Catalyst recycling

In the recycling tests, the catalyst was filtered off from the reaction products after a reaction, washed three times with 20 mL of hot toluene, dried under vacuum and used for the next reaction.

2.5 Spectroscopic characterization

To characterize physicochemical properties of the polymer matrices and polymer-supported catalyst we used a variety of analytical methods. The FTIR spectra were measured with a BIORAD FT-IR 175C spectrophotometer in an air atmosphere. The bonding nature at the surface of catalyst was performed by X-ray photoelectron spectroscopy (XPS). XPS measurements were made on a VG ESCALAB 210 spectrometer with Mg Ka (hn = 1253.6 eV) excitation from an X-ray tube (reduced power 10 kV, 10 mA). The pressure in the spectrometer chamber was about 10–9 mbar. Samples were pressed to pellets under a pressure of 100 kbar for 10 minutes before these measurements. The C 1s, N 1s, O 1s, Cl 2p and Pt 3d core level spectra were recorded. The analyzer pass energy was set at 20 eV. A take-off angle of 90° was used in all XPS studies. Curve fitting was performed using the ECLIPSE data system software. This software describes each of the components of a complex envelope as a Gaussian-Lorentzian sum function. The background was fitted using non-linear model function proportional to integral of the elastically scattered electrons. All binding energies (BEs) were referenced to the C 1s neutral carbon peak at 284.6 eV.

2.6 Morphology studies

The morphology of samples was investigated with a scanning electron microscope JEOL 5500 LV, working in high vacuum and accelerating voltage of 10 kV. Energy dispersive X-ray microscope (SEM–EDX), JEOL JSM 840A, Japan was used to observe the elemental distribution. Pore size distribution parameters were determined by application of the BET method on Sorptomatic 1900 FISON Instrument.

2.7 Study of Pt leaching

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was applied to study surface properties of catalysts. ToF-SIMS mass spectra and images of ions of studied catalyst surfaces were obtained using ToF-SIMS IV (ION-ToF, Germany) spectrometer with high mass resolution (9000 for m=29 u), equipped with the time-of-flight analyzer of reflection type and Bi\(_3^+\) gun working at 25 keV. At first, powder samples were tableted in order to obtain a plain surface, which allows achieving higher lateral and mass resolutions. The chemical composition of the catalyst was analyzed by acquiring secondary ion mass spectra of the catalyst’s surface.

2.8 Catalyst test

The hydrogenation reactions were carried out in 100 ml Parr reactor model 4593 with glass liner. The typical hydrogenation run was as follows. The reactor was charged with 0.2 g of supported platinum 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, 40 bar pressure and 75°C, respectively. 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).
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30 m × 0.63 mm × 1.0 μm film thickness. The products were identified by matching their retention times with those of authentic samples.

3 Results and discussion

3.1 Spectroscopic characterization of the support and platinum catalyst

Infrared spectroscopy was used to identify the mode of bonding of the metal species with the functional sites of the polymers. Spectroscopic characterization of epoxy resin cured with MPTU and DPTU polythiourethanes and their complexes with the PtCl₂(PhCN)₂ precursor is given in Fig. 2. The epoxy resin cross-linked with polythiourethanes has a few possible coordination centers namely oxygen, nitrogen and sulfur to which the metal ion can be bound (Fig. 3). Crystallographic characterization of the structure of low molecular model compounds are currently under way to obtain more information about the mode of metal coordination. It should be noted that although various concentrations of platinum complex were used, the amount of metal attached to epoxide supports remained the same, that is below the sorption capacity of the polymers. It is evident that the epoxy matrices were saturated with

Figure 2: FT-IR spectra of (a) DER/MPTU/Pt, (b) DER/MPTU, (c) DER/DPTU/Pt and (d) DER/DPTU.
the platinum complex and still retained a relatively large number of coordination sites. IR spectra of both epoxy supports have adsorption bands at 1704 cm⁻¹ and 1658 cm⁻¹, which are assigned to the C=O stretching vibration of urethane and thiourethane groups, respectively. Marked changes in the intensity of these bands, together with decreased absorption of thiourethane bands at 1507 cm⁻¹ (N-H bending) and 1104 cm⁻¹ (C-N stretching) after complexation, indicated that metal complex is attached to the epoxide support through oxygen and nitrogen atoms of thiourethane moiety introduced into epoxy network with hardener. The urethane absorptions at 1257 cm⁻¹, 1606 cm⁻¹ and 1548 cm⁻¹ provide the evidence for participation of urethane linkages in the crosslinking process (Fig. 3). The presence of urethane groups can be explained by the reaction of the free hydroxyl groups remaining in the condensed resin with the extremely reactive isocyanate groups released through dissociation of thiourethane moieties by heat of the curing reaction. The observed shifts in the intensity ratio of these bands, indicate an interaction between the urethane nitrogen and oxygen atoms and the transition metal respectively. The IR spectrum of DER/MPTU after immobilization of the platinum complex revealed the disappearance of the absorption bands of the oxirane ring at 915 cm⁻¹ and 825 cm⁻¹ (Fig. 2a) which indicates that oxygen atoms of the unreacted epoxy rings participate in the metal coordination to the epoxy matrix. Moreover, the changes in the intensity of ether absorption bands at 1232 cm⁻¹, 1085 cm⁻¹ and 1013 cm⁻¹, after catalyst immobilization, may suggest that ether linkage generated with opening of single epoxy ring or introduced with polythiourethane hardener, is one of the active centers of polymer network. From the infrared results it is not apparent that thiol and thiourethane groups bind the metal via sulfur atom as had been anticipated. The absence of the S–H vibration absorption at 2545 cm⁻¹ could indicate the quantitative conversion of thiol groups. However, the Pt-S interaction could not be detected because of the relatively low thiol concentration on the polymer beads together with the low extinction coefficient of the S-H and C-S vibrations. Nevertheless, sulfur-binding coordination by thiol groups was identified by the XPS method, that proved to be conclusive.

The XPS analysis was carried out to study the binding mechanism of Pt(II) to polythiourethane cured epoxy resin. Fig. 4a,b show S 2p XPS spectra before and after immobilization of platinum precursor on DER/MPTU sample. The major components of XPS spectra of the catalyst near 163.38 eV correspond to -CH₂-S-C(O)- sulfur atoms of thiourethane moiety, and –CH₂-S-CH₂ linkage generated with the opening of epoxy ring by the thiol group. The minor components at higher binding energy of the samples are assigned to thiol groups. Both peaks after Pt(II) immobilization were shifted to lower energy, which indicates the formation of S-Pt bonds. These observations suggest that the attachment of the Pt(II) catalyst to the epoxy substrate occurs through the two types of sulfur coordination centers. The concept of linkage to sulfur-containing groups, is also supported by data analysis of the Pt 4f spectrum. The shift of characteristic Pt(II) centers (not presented here) toward lower binding energy after linkage to sulfur-containing epoxy matrix, is in agreement with literature reports for platinum complexes with ligands bound to metal through Pt-S bonds [15,16].
Figure 4: S 2p XPS spectra of DER/MPTU: (a) before, (b) after immobilization of Pt(II) complex, O 1s spectra of: (c) DER/MPTU/Pt; (d) DER/DPTU/Pt, Pt 4f XPS spectra of DER/MPTU/Pt: (e) fresh catalyst; (f) after use in hydrogenation reaction and N 1s spectra of DER/MPTU/Pt: (g) fresh catalyst; (h) after use in hydrogenation reaction.
XPS results clearly show the differences in chemical structure between two research catalysts and show that oxygen based functional groups play a key role in chemical attachment of Pt(II) (Table 1). An additional peak observed in O 1s spectra of DER/DPTU/Pt catalyst (Fig. 4d), and its shift toward lower B.E. values, confirmed the immobilization of Pt(II) through interaction with unreacted epoxy rings, as revealed by IR measurements. Analysis of the Pt 4f signals could potentially be used for characterization of the electronic state of platinum in the supported catalyst. The Pt 4d<sub>5/2</sub> and Pt 4d<sub>7/2</sub> energy values for both catalysts are reported in Table 1. By means of curve-fitting analysis, each Pt 4f spin-orbit component of the experimental spectrum of catalysts results from the combination of two peaks associated to two platinum atoms involved in different chemical environments. This confirms the results of IR spectroscopy, indicating for presence of a few metal coordination groups in polymer support (Fig. 3). As expected, the platinum content, calculated from XPS, is larger for the DER/MPTU/Pt prepared using epoxy resins cured with multifunctional polythiourethane, that was also confirmed by ToF-SIMS measurements. Each catalyst was characterized using XPS both prior to and following its use in hydrogenation reaction. Figs. 4e,4f show the Pt 4f spectrum of DER/MPTU/Pt, before and after use in the reaction. Each Pt 4f<sub>5/2</sub> and Pt 4f<sub>7/2</sub> photoelectron line consist of two peaks due to Pt(II) and Pt(0). The smaller peaks at lower B.E. are associated with metallic Pt(0). For recovered catalyst these signals greatly increased indicating that metallic Pt is formed during subsequent catalyst use. A slight drop in platinum content after catalytic reaction, calculated from XPS data, is in agreement with ToF-SIMS data. Also, the analysis of N 1s spectrum of fresh and recovered catalysts, might be pointed as the confirmation for the changes in the electronic state of Pt during hydrogenation reaction. As shown in Figs. 4g,4h the N 1s level of the used DER/MPTU/Pt catalyst can be deconvoluted into three new bands. One peak is from Pt (II) and urethane and thiourethane nitrogen, one is from Pt (0) and urethane nitrogen and the next is from Pt (0) and thiourethane nitrogen. This can be explained by the interaction effect between Pt mixed valence species and nitrogen atoms of urethane and thiourethane moieties. The binding energy of Cl 2p<sub>3/2</sub> in the XPS spectra, in the region of 198.31–200.5 eV, indicates the presence of a PtCl<sub>2</sub> structure.

**Table 1: Binding energy (eV) values from XPS measurements.**

| Catalyst     | Element | Binding Energy (eV) | FWHM<sup>*</sup> (eV) | Relative Concentration (At, %) | Chemical States |
|--------------|---------|---------------------|------------------------|-------------------------------|-----------------|
|              | O 1s    | 531.89 2.01         | 2.99       | C=O                          |
|              | N 1s    | 400.53 2.46         | 3.41       | N-C(O)                        |
|              | S 2p    | 163.38 2.49         | 1.00       | S-H                          |
|              | Cl 2p   | 198.66 2.09         | 7.94       | PtCl<sub>2</sub>              |
|              | Pt 4f<sub>5/2</sub> | 74.66 2.03     | Pt(O)               |
|              |         | 76.63 2.29         | Pt(II)              |
|              |         | 71.24 1.55         | Pt(II)              |
|              |         | 73.32 2.26         | Pt(II)              |
|              | O 1s    | 531.07 1.94         | 1.41       | C=O                          |
|              | N 1s    | 400.63 2.40         | 1.20       | N-C(O)                        |
|              | S 2p    | 163.31 2.37         | 1.72       | S-H                          |
|              | Cl 2p   | 198.31 2.26         | 2.49       | PtCl<sub>2</sub>              |
|              | Pt 4f<sub>5/2</sub> | 74.86 1.90    | Pt(O)               |
|              |         | 76.13 1.97         | Pt(II)              |
|              |         | 71.56 1.97         | Pt(II)              |
|              |         | 72.83 1.90         | Pt(II)              |
3.2 Catalytic test

The effect of the structure of polymer support on the activity, selectivity and the stability of epoxy supported catalysts was examined in the hydrogenation reaction of cinnamaldehyde. The selective hydrogenation of α,β-unsaturated carbonyl compounds to their corresponding α,β-unsaturated alcohols is an important step in the preparation of various fine chemicals such as fragrances for the perfume industry [17]. The hydrogenation of cinnamaldehyde can give rise to three products, namely hydrocinnamaldehyde (HCALD), cinnamyl alcohol (CALC), and hydrocinnamyl alcohol (Scheme 1). The mostly desired product, α,β-unsaturated alcohol, is difficult to produce in a catalytic hydrogenation of α,β-unsaturated aldehydes because 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 2 shows results of the hydrogenation of cinnamaldehyde at 40 bar pressure and temperature of 75°C. It has been shown that the chemical structure of polymeric matrix influences the selectivity of this reaction that strongly depends on the type of binding groups presented in the polymer. For DER/MPTU/Pt catalyst selectivity towards HCALC increased after fifth run and it may be related to the reduction of the Pt(II) species to Pt(0). The catalyst selectivity depends on the size distribution of the metal immobilized on the carriers. Different metal particle size distribution influenced by the morphology of the support can be an explanation for unequal catalyst performances of the DER/DPTU/Pt catalyst, with the smallest size of nanopores. The steric effect exerted by the phenyl group of CALD prevents the close approach of the C=C to the surface of large metal particles so the molecule is tilted with C=O closer to the surface and therefore more easily activated. This barrier does not exist for the approach of phenyl group to a small particle, therefore the selectivity to CALC of the reduced DER/DPTU/Pt(II) catalyst is low. The stability of the supported catalyst was tested during repeated catalysis runs. Recycling the immobilized platinum catalysts five times demonstrated their high stability despite the changes that occur in their structure during the catalytic reaction. Selectively mercury poisoning was used to exclude the possibility of catalyzing the reaction by unbound platinum metal which appeared as result of elution of the complex from the surface of the carrier. This method is commonly used, which aims to define the nature of homogeneous or heterogeneous reaction [18-21]. The catalyst was poisoned with mercury and then the catalytic tests were done. The catalytic activity prepared samples were similar to activity for catalysts without mercury poisoning. This test was also prepared for the homogeneous complex PtCl₂(PhCN). In this case, the addition of Hg(0) to the homogeneous reaction mixture caused to stop the reaction. The mercury poisoning test shows that the metal complex elution did not affect the catalytic activity of the catalysts.

3.3 Study of Pt leaching

ToF-SIMS surface imaging provides information about the metal phase distribution on the surface of the catalyst in the micrometer range. The activity of investigated catalyst decreases with the subsequent usage which might be caused by platinum leaching. ToF-SIMS technique was used to study chemical composition of the catalyst surface. The time-of flight secondary ion mass spectrometry was applied to investigate deactivation process and to observe the deterioration of platinum distribution on the catalyst surface after fifth use in comparison with a fresh sample. ToF-SIMS method permits the evaluation of the chemical composition of the catalyst surface, nature of interactions between metallic phases and supports as well as the distribution of metal or other catalyst components on the surface. Owing to ToF-SIMS a considerable drop of the surface accessible Pt was observed for the DER/MPTU/Pt catalyst after the fifth run (Table 2). A small drop of the amount of surface accessible platinum was observed after fifth use however the drop of Pt content did not significantly affect the activity which can be another proof of higher activity of platinum nanoparticles generated in reused catalysts. It can be explained by the often reported enhancement of the activity for a catalyst containing mixed valence states of transition metal centres [22-24].
3.4 Morphology analysis

The morphology of a polymer support can greatly affect the activity and selectivity of the polymer attached complex catalysts. Conventional techniques have been used to study the porosity of the support and supported catalysts. The nitrogen adsorption method BET (Table 3) indicates that both investigated supports had similar pore size distribution. Such morphology probably arises from variances in cross-link densities. The catalyst DER/MPTU/Pt shows pore size distribution with the lower volume of micropores and this catalyst had micropores and greater volume of meso- and macropores. In addition a significant decrease in specific surface area after immobilization of metal for the both supports were observed (161 m² g⁻¹ before immobilization to 95 m² g⁻¹ after immobilization). Such a significant decrease in the specific surface area was caused by blocked metal complex on the DER/MPTU carrier.

The characterization of platinum distribution on the surface of the catalysts and the distribution of the size of the nanoparticles were performed by means of a scanning electron microscope (SEM-EDX). The dispersions of the supported platinum catalysts before use in hydrogenation reaction is presented in fig. 5a,c. The results reveal that the both catalysts exhibit almost identical dispersion in contrary to dispersion of palladium catalysts supported on epoxy resins reported previously [25,26]. A very homogeneous distribution of the platinum particles size was also observed on both catalysts recovered after reaction (Figs. 5b,5d). This indicates that conventional immobilization process is an effective method to prepare epoxy resin- supported platinum catalysts with high dispersion. This distribution demonstrates the chemical bonding the metal with polymer matrix. In the case of physical binding metal complex is bound in different places. Additionally, the high concentration and homogeneous distribution of metal on the catalyst grains would not be observed in the case of physical binding. A similar morphology of both carriers causes a regular distribution of platinum particles and size of the nanoparticles. However, even the slight

Table 2: The hydrogenation of cinnamaldehyde over the DER/MPTU/Pt and DER/DPTU/Pt.

| Catalyst     | Run | Intensity of ¹⁹⁵Pt⁺ | Conversion [%] | HCALD [%] | HCALC [%] | CALC [%] |
|--------------|-----|-------------------|---------------|-----------|-----------|----------|
| DER/MPTU/Pt  | 1   | 7.6 x 10⁻³        | 98            | 10        | 65        | 25       |
|              | 5   | 6.2 x 10⁻³        | 97            | 2         | 81        | 17       |
| DER/DPTU/Pt  | 1   | 4.3 x 10⁻³        | 97            | 7         | 63        | 30       |
|              | 5   | 2.5 x 10⁻³        | 95            | 3         | 95        | 2        |

Conditions: Temperature 80°C, time 4 h; [CALC]:[Pt]=18; solvent: 96% ethanol; the overall volume: 5.5 mL; unidentified reaction products are not shown.

Table 3: BET Data for the support and supported Pt catalysts.

| Polymer Supports And Supported Pt Catalysts | N₂ Surface Area [m² g⁻¹] | Average Pore Diameter [nm] |
|-------------------------------------------|--------------------------|----------------------------|
| DER/MPTU                                  | 161                      | 32                         |
| DER/MPTU/Pt                               | 95                       | 19                         |
| DER/DPTU                                  | 75                       | 12                         |
| DER/DPTU/Pt                               | 58                       | 8                          |

Figure 5: SEM-EDX micrographs of the surface of the (a) DER/MPTU/Pt/before hydrogenation reaction, (b) DER/MPTU/Pt/after hydrogenation reaction, (c) DER/DPTU/Pt/before hydrogenation reaction and (d) DER/DPTU/Pt/ after hydrogenation reaction.
differences between microporous structure of the DER/MPTU and DER/DPTU can influence the activity of catalyst by the steric demands of a catalytic center bound to this support.

4 Conclusion

Epoxy resins cured with multifunctional polythiourethane hardeners are very useful polymeric supports for the preparation of heterogenized platinum catalysts. The use of polythiouretanes as curing agents allow supports to be obtained that do not need any further functionalization. ToF-SIMS and SEM-EDX techniques could give complementary information about surface properties of supported catalyst subjected. On the basis of SEM-EDX analysis it appeared that for all tested catalysts, platinum was equally distributed on surface of the epoxy supports. Catalytic activity of prepared supports immobilized with platinum complex was tested in the hydrogenation reactions. It was demonstrated that the investigated catalyst showed good stability during prolonged use. The activity of the catalyst was comparable to that of homogeneous PtCl$_2$(PhCN) complex and maintained through five reaction cycles. The chemical structure of used polythiourethane hardeners can greatly affect activity of catalysts. Both heterogenized platinum catalysts showed good stability during prolonged use. Some differences in activity were caused by dissimilarity in chemical structure of supports, as well as the other effects of surface morphology of supports crosslinked with different type of polythiouretanes. The obtained results could help to get more information on the possible interaction modes of Pt(II) complexes with epoxy resin cured with polythiouretanes. The characteristic factors like matrix chemical structure and coordination surrounding of the metal centers have a significant effect on catalytic properties of heterogenized catalysts. Epoxy-metal complex is formed by interaction of a polymer containing coordinating groups with metal ions. Presented catalytic systems have a few possible coordination centers: oxygen, nitrogen and sulfur which can bound platinum complex. For MPTU catalyst the number of free S-containing functional groups is significantly higher than for DPTU catalyst which may affect the way of metal coordination. The diversity of coordination sites in polymer promote formation of active catalytic species mainly as finely dispersed metal particles with mixed valence states.

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