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Application of Conjugated Polymer–Platinum Group Metal Composites as Heterogeneous Catalysts

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Abstract Composites of polyaniline (PANI) or polypyrrole (PPy) doped with chloride ions and Pt or Rh particles were prepared by chemical reduction of metal ions conducted in the presence of the polymers. Based on X-ray diffraction studies it was established that the composites contained metal nanoparticles (5–9 in size). However, according to SEM investigations metal particles were agglomerated (40 nm–1.1 µm in size). Redox activity of the composites in the catalytic isopropyl alcohol conversion was ca. ten times higher than the acid–base one. Pt dispersed in polymer matrices showed higher catalytic activity than Rh. PPy doped with chloride ions had a promoting effect on the activity of Pt catalysts.

Keywords Platinum · Rhodium · Polyaniline · Polypyrrole · Isopropyl alcohol conversion

1 Introduction

Conjugated polymers have been intensively studied for the last three decades, i.e., since the discovery of the conductive form of polyacetylene [1]. New generations of these materials are presently applied as sensors, anticorrosion and antistatic coatings, elements of organic electronic devices and heterogeneous catalysts [2–5].

Polypyrrole (PPy) and polyaniline (PANI) are two conjugated polymers often investigated nowadays. They are stable in air, can be easily prepared and can serve as hosts for incorporation of various species showing interesting properties. In particular, PPy and PANI have been found to be suitable supports for heterogeneous catalysts, such as, e.g., heteropolyacids [6, 7] or noble metals. Of the latter, platinum and palladium have received a great deal of attention. In most cases, these metals have been introduced into PPy and PANI by electrodeposition and their electrocatalytic properties in, e.g., methanol [8–10] or formic acid [11, 12] oxidation investigated. There are markedly less reports in the literature on the catalytic activity of the composites which have been synthesized chemically. They deal mainly with palladium catalysts [13–16]. Thus, it has been found that PANI–Pd composite obtained by polymerization of aniline-stabilized Pd nanoparticles using ammonium persulfate has contained small metal particles (average diameter of 4.9 nm) and has been an active catalyst in Suzuki-Miyaura and Heck reactions of aryl iodides [13]. Reductions of PANI–Pd(II) complex with ethanol or $NaBH_4$ have led to the systems differing in the sizes of Pd particles (3.1 and 9.2 nm, respectively) and selectivity in the oxidative coupling of 2,6-di-*t*-butylphenol [14]. It has been also demonstrated that performance of PANI–Pd and PPy–Pd composites in the removal of nitrite ions from water is better than that of Pd dispersed on a classical

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support (Al_2O_3); this has been attributed to the ion-exchange and redox properties of the polymers [15]. Pd nanoparticles incorporated into PANI nanofibers serving as the matrix have been exceptionally active catalysts in Suzuki coupling of aryl chlorides with arylboronic acids as well as phenol formation from aryl halides and potassium hydroxide in water [16].

Although, as has been already mentioned, application of chemically prepared PANI–Pt or PPy–Pt composites as heterogeneous catalysts has been scarcely studied, catalytic properties of PANI–Pt system in hydrogenation of α,β-unsaturated aldehyde (citral) have been reported recently [17]. Of the two reactions possible in this process, i.e., carbonyl groups and carbon–carbon double bonds hydrogenation, this catalyst has shown enhanced selectivity towards carbonyl groups hydrogenation products when compared with PtO_2 dispersed on PANI [17].

In the present work, particles of platinum group metals (Pt and Rh) have been incorporated into PANI and PPy doped with chloride ions by a simple chemical reduction of the metal ions carried out in the presence of the polymers. Catalytic activity of the composites thus obtained has been determined using isopropyl alcohol conversion as the test reaction. The aim of the investigations has been to evaluate the influence of the type of the polymer matrix and the type of the metal on catalytic properties of the composites. It is worth noting that up to our knowledge, there have been no reports on conjugated polymer–Rh composites so far, with our work on PANI–Rh composites [18] being the exception.

2 Experimental

2.1 Materials

The monomers for polymer preparation, i.e., pyrrole and aniline were purchased from Fluka (Germany) and POCh (Poland), respectively. They were distilled under atmospheric pressure before use. The oxidant, ammonium peroxydisulfate was obtained from POCh (Poland) and used as received. $RhCl_3 \times 3\ H_2O$ and $PtCl_4$ were supplied by Alfa Aesar (Germany). They were dissolved in distilled water and the exact concentrations of metal ions in the resulting solutions were verified by colorimetric method according to the procedures described in [19] for Pt and in [20] for Rh. Sodium borohydride was obtained from Alfa Aesar (Germany) and used in the experiments without any additional purification.

2.2 Methods

For the incorporation of metallic particles, PPy doped with chloride ions and PANI in the emeraldine base form were used. They were prepared by oxidative polymerization of the monomers, i.e., pyrrole or aniline initiated by ammonium peroxydisulfate in 1.5 M aqueous HCl solution at 0 °C. In these reactions, PPy doped with chloride ions and PANI hydrochloride were obtained. PPy doped with chloride ions was thoroughly washed with HCl solution (1:10) and dried. PANI hydrochloride was deprotonated in the excess of 0.3 M aqueous ammonia solution; then the resulting PANI base was washed with water, methanol and dried.

Metallic Rh and Pt were introduced into PPy doped with chloride ions matrix, whereas only Pt was incorporated into PANI. The composites were obtained by reduction of Rh^{3+} ions (from $RhCl_3$ solution in water, 0.67×10^{-3} mol/dm^3) or Pt^{4+} ions (from $PtCl_4$ solution in water, 2.3×10^{-3} mol/dm^3) with sodium borohydride carried out in the presence of PPy doped with chloride ions or PANI powders. Molar ratio of $NaBH_4$ to metal ions in all the systems was equal to 2.5. Reactions were performed at room temperature for 2 h. The products were filtered, washed with water and dried. Composites containing 1.75, 2.4, 3.5, 7.0 and 9.4 wt% of Rh or Pt were prepared by using the appropriate volume of $RhCl_3$ or $PtCl_4$ solution for the selected amount of the polymer (usually 1 g). During syntheses, samples of the reaction mixtures were withdrawn and filtered. UV/Vis spectra as well as the results of colorimetric analyses of Pt^{4+} or Rh^{3+} ions contents in the filtrate solutions (Sect. 2.1) confirmed that in the course of the reductions the amounts of metal ions diminished and finally they disappeared from the solutions. This proved that all metals from the initial solutions were incorporated into polymer matrices.

The composites obtained were characterized by X-ray photoelectron spectroscopy (VSW Manchester equipment, Al Kα radiation—1486.6 eV, 200 W; all peak positions referenced to C1 s peak of binding energy equal to 284.6 eV), X-ray diffraction (Philips X'Pert diffractometer, Cu Kα radiation) and scanning electron microscopy (Nova Nanosem 200, FEI Co. microscope equipped with the back-scattered electrons detector and EDS system for microanalysis).

Catalytic isopropyl alcohol conversion was carried out in the way similar to that described in [6]. Thus, the experiments were conducted in the oxygen-free atmosphere, in the temperature range of 355–455 K. Isopropyl alcohol was diluted with gaseous nitrogen, its mole fraction in the mixture was equal to 0.0179. The catalytic process was carried out to low alcohol conversion degrees (below 15%). Products of the reaction were analyzed by gas chromatography (two parallel acid-resistant steel columns, 3 m long, 3 mm internal diameter, packed with 4% Carbowax 20 M on Chromosorb G, AW, DMCS, 80/100 mesh, chromatograph equipped with a FID detector). Based on the results of catalytic experiments, specific rates of the parallel reactions taking place in the systems, their activation energies as well as selectivities of isopropyl alcohol conversion towards the reaction products (acetone and propene) were calculated. Catalytic activity of the composites studied was expressed per 1 g of the metal phase in the catalyst.

3 Results and Discussion

3.1 Characterization of the Composites

As has been already stated, in the present study metallic Rh and Pt particles have been incorporated into PPy doped with chloride ions and PANI in the emeraldine base form. Structures of their molecules are represented by formulas shown in Fig. 1. Besides carbon and hydrogen, these polymers contain nitrogen atoms in their backbones.

Elemental composition of the samples obtained has been investigated by XPS spectroscopy. Typical XPS survey spectra of PPy–Rh, PPy–Pt and PANI–Pt composites are presented in Fig. 2. They contain maxima which can be unambiguously assigned to the atoms occurring in the polymer molecules, i.e., carbon (C1 s binding energy, B.E. equal to ~284 eV), nitrogen (N1 s B.E. equal to ~398 eV) and chlorine (Cl2p B.E. equal to ~198 eV) [21]. The presence of chlorine atoms in PPy-based composites is not surprising since chlorides have been the dopant anions in the starting polymer (Fig. 1). On the other hand, PANI applied as the matrix for incorporation of metallic Pt particles has not contained chlorine atoms (Fig. 1). Therefore, at the first glance, the weak but distinct XPS peak in the Cl2p B.E. region seen in the spectra of PANI–Pt composites (Fig. 2) may seem unexpected. It should be remembered, however, that these composites have been prepared by reduction of Pt^{4+} ions from $PtCl_4$ solution in water using $NaBH_4$ as the reducing agent. Such process must be accompanied by the formation of HCl. It is well known that nitrogen atoms of PANI (especially the imine ones, i.e., –N=) are readily protonated by HCl [22]. Hence, chlorine atoms visible in the XPS spectra of PANI–Pt composites must result from this reaction. It is worth noting that similar effect of polymer protonation has been observed also previously in the case of PANI–Rh composites obtained using $NaBH_4$ [18].

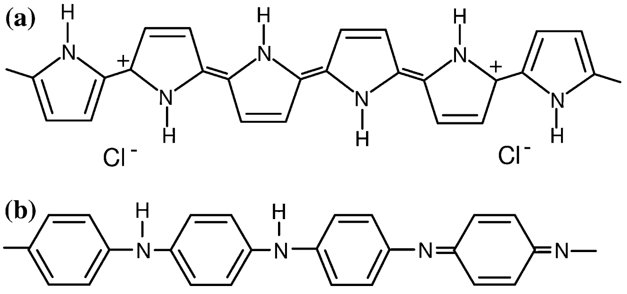

Fig. 1 Structural formulas of: **a** PPy doped with chloride ions; **b** PANI

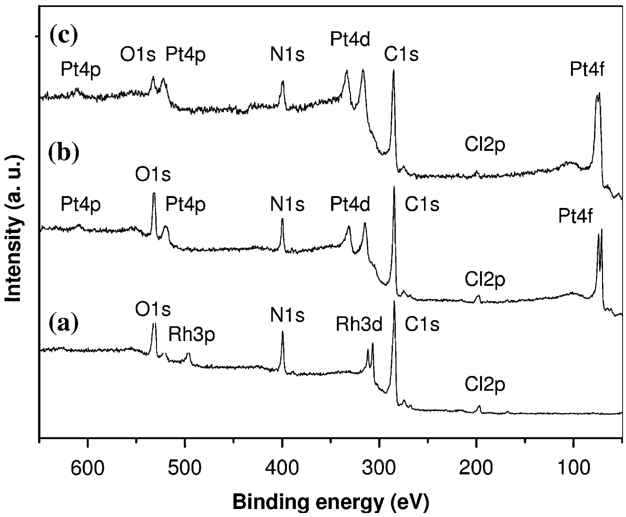

Fig. 2 XPS survey spectra: **a** PPy–Rh (7 wt% of Rh); **b** PPy–Pt (7.0 wt% of Pt); **c** PANI–Pt (9.7 wt% of Pt) composites

Cl2p peaks show very low intensity with respect to the other ones visible in the XPS spectra (Fig. 2). This indicates relatively low amounts of chlorine in the samples. Quantitative evaluations based on XPS are not reliable since only the surface of the sample is analyzed by this technique. In all quantitative considerations, however, it should be taken into account that the contents of chlorine in the composites studied can be influenced by several phenomena occurring during synthesis of these materials. Reduction of $PtCl_4$ or $RhCl_3$ is the undoubtful source of chloride ions which become present in the solutions after this process and can be inserted into the polymer molecules. However, apart from the metal ions, the polymers can be reduced by $NaBH_4$ as well. In the case of PANI this process yields the polymer of lower oxidation state [22], whereas in the case of PPy doped with chloride ions the neutral polymer chain segments and chloride ions are formed [23]. Reduced polymers are unstable in air [22, 23] in which all the experiments have been conducted. Therefore they must have been reoxidized during composite preparations. In principle, this reaction could take place in the solution after the reduction and/or in the composite powders after their recovery from the reaction medium. In the former case, the process can be accompanied by incorporation of chloride ions into polymer molecules. Presence of chlorine atoms in the XPS spectra of PANI–Pt composites suggests that reoxidation of this polymer has occurred in the solution. Similarly, oxidation of PPy can occur in the solution. Then it results in the reinsertion of Cl^- ions into this polymer matrix. Hence, the contents of chlorine in the PPy-based composites are affected by two processes: loss and gain of Cl^- ions during reduction and reoxidation of the polymer, respectively. It should be noted that reoxidation of the polymers in the solution seems probable since in all the experiments the reducing agent ($NaBH_4$) has been used in excess with respect to metal ions but not to the polymers (Sect. 2.2). Therefore it could be quickly consumed during composite preparations. After that, reoxidation of the polymers has been possible without any interference.

Additionally, XPS has confirmed that Rh and Pt have been introduced into the polymer matrices. The peaks characteristic for the metal atoms can be distinguished in the spectra of PPy–Rh and polymer–Pt composites (Fig. 2). They appear in several B.E. regions. The maxima of a well-resolved $Rh3d_{5/2-3/2}$ doublet are located at B.E. values of ~307 eV and ~311 eV, whereas those of a less intensive $Rh3p_{3/2-1/2}$ doublet are seen at B.E. values equal to ~497 eV and ~521 eV. In the case of Pt, three doublets are visible: $Pt4f_{7/2-5/2}$ (B.E. equal to ~71 eV and ~74 eV), $Pt4d_{5/2-3/2}$ (B.E. equal to ~315 eV and ~331 eV) and $Pt4p_{3/2-1/2}$ (B.E. equal to ~520 eV and a weak line at ~600 eV). Positions of these maxima are close to those typical of zerovalent Rh and Pt [21]. Thus, XPS indicates that metallic Rh or Pt have been incorporated into PPy doped with chloride ions and PANI.

In the XPS spectra of PPy–Rh composites, a separate, single peak at B.E. value equal to ~531 eV is seen. This maximum can be ascribed to O1 s signal [21] and suggests that oxygen atoms have been present in the composites. Oxygen has been revealed earlier by XPS in chemically synthesized PPy doped with chloride ions [24]. Hence, it may be a constituent of the polymer matrix. Additionally, oxygen atoms occurring in the PPy–Rh composites studied in this work may result from partial surface oxidation of rhodium particles taking place in air and yielding metal oxide. Such phenomenon has been observed for noble metals [25]. In the spectra of Pt-containing composites the O1 s line, located close to the $Pt4p_{3/2}$ signal, is also seen. This shows that surface oxidation of metallic Pt in the composites takes place as well.

In order to check if metallic particles occurring in the synthesized composites are partially oxidized on their surfaces, the XPS spectra in the regions of Rh3d and Pt4f binding energies have been measured separately. This has allowed us to obtain the spectra with higher accuracy. They have been deconvoluted into component peaks. Results of decompositions for selected samples are collected in Table 1. In all the cases, the best fits have been obtained when two $Rh3d_{5/2-3/2}$ or $Pt4f_{7/2-5/2}$ doublets have been considered. The first, major one, can be ascribed to metallic Rh or Pt, whereas the second one—to Rh^{3+} or Pt^{2+} ions. Positions of the latter doublets correspond to those recorded for Rh_2O_3 and PtO, respectively [21]. Hence, XPS spectroscopy has confirmed that surface oxidation of metal particles formed during reduction of Rh^{3+} or Pt^{4+} ions carried out in the presence of PPy doped with chloride ions or PANI takes place.

Table 1 Shares of peak components in Rh 3d or Pt 4f XPS spectra of selected composites studied in the work

Composite	Peak shares (%)			
	$Pt4f_{7/2}$ (Binding energy [eV])[a]		$Rh3d_{5/2}$ (Binding energy [eV])[b]	
	Pt^0 (71.0)	Pt^{2+} (72.3)	Rh^0 (307.1)	Rh^{3+} (308.6)
PPy–Rh (1.75 wt% Rh)	–	–	70	30
PPy–Pt (7 wt% Pt)	64	36	–	–
PANI–Pt (9.7% Pt)	80	20	–	–

[a] During spectra deconvolution, doublet splitting has been fixed at 3.3 eV

[b] During spectra deconvolution, doublet splitting has been fixed at 4.7 eV

Reflections originating from metallic Rh and Pt crystallites are visible in the X-ray diffraction patterns of the prepared composites. Representative X-ray diffractograms are shown in Fig. 3. The patterns of PPy–Rh composites contain reflections at 2θ angle values equal to 40.9° and 47.1° due to Rh(111) and Rh(200) planes, respectively [26]. Pt-containing composites show sharp, "crystalline" reflections at $2\theta = 39.8°$ and 46.2° ascribed to Pt(100) and Pt(200) planes, respectively [26]. Additionally, the reflections corresponding to polymer phases are seen in all the

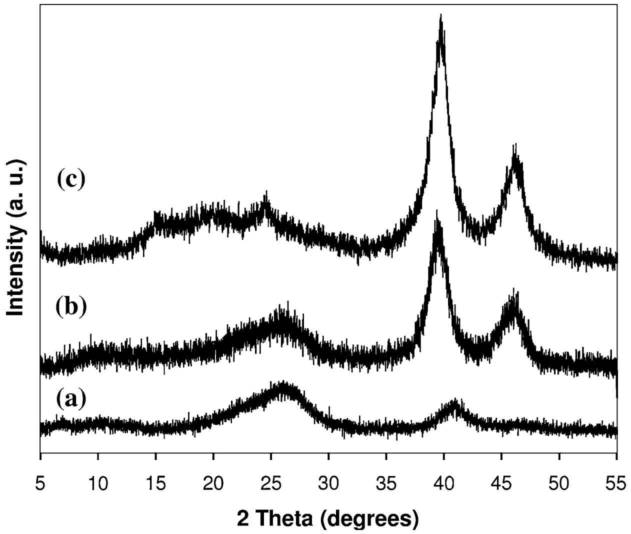

Fig. 3 XRD patterns of: **a** PPy–Rh (1.75 wt% of Rh); **b** PPy–Pt (7.0 wt% of Pt); **c** PANI–Pt (9.7 wt% of Pt) composites

diffractograms. Those due to PANI are located in the 2θ range of 10°–33°, whereas PPy doped with chloride ions gives a broad reflection centred at 2θ angle value of $\sim 27^{\circ}$. This is consistent with the literature data [15, 27]. It is interesting to note that as the content of Rh or Pt in the composite increases, the reflections due to metal phases grow at the expense of those related to the polymers. This is seen in Fig. 3: in the diffractogram of PPy–Rh sample containing 1.75 wt% of Rh the reflections corresponding to the metal phase show lower intensity than that due to PPy doped with chloride ions. In contrast, the XRD patterns of the composites containing 7 and 9.4 wt% of Pt in polymer matrices are dominated by the reflections originating from crystalline metal particles.

Based on the X-ray diffraction patterns, the mean sizes of Rh and Pt crystallites present in the composites have been calculated using Scherrer's equation. They have been comparable for all the samples: 4–9 nm in the case of Rh dispersed in PPy doped with chloride ions matrix, 5–7 nm for Pt dispersed in PPy doped with chloride ions and PANI matrices. Hence, based on XRD it can be concluded that metal nanoparticles have been formed in all the systems. SEM microscopic studies have revealed, however, that the particles may be agglomerated. As has been established by EDS, the white spots visible in the BSE images of the composites (Fig. 4) contain mainly metal atoms and therefore it can be assumed that they correspond to Rh or Pt particles existing in polymer matrices. Their sizes have been in the range of 40 nm–0.2 μm for the PPy–Rh composites and 60 nm–1.1 μm for the Pt-containing composites, i.e., significantly larger than found by XRD.

3.2 Catalytic Properties of the Composites

For the catalytic studies, isopropyl alcohol conversion has been selected since it is a very sensitive test to determine redox and acid–base properties of various catalysts [6, 28]. During this process, three parallel reactions can take place:

1. Dehydration of the alcohol on the acidic centers of the catalyst leading to propene in accordance with the equation:
   $(CH_3)_2CHOH \rightarrow CH_3{-}CH = CH_2 + H_2O$;
2. Dehydrogenation of the alcohol on the redox centers of the catalyst yielding acetone as described by the equation: $(CH_3)_2CHOH \rightarrow CH_3C(O)CH_3 + H_2$.
3. Intermolecular dehydration of two isopropyl alcohol molecules resulting in diethyl ether according to the equation: $2(CH_3)_2CHOH \rightarrow (CH_3)_2CH{-}O{-}CH(CH_3)_2 + H_2O$.

This reaction has been found to proceed on acidic centers (particularly Lewis-type) of some catalysts.

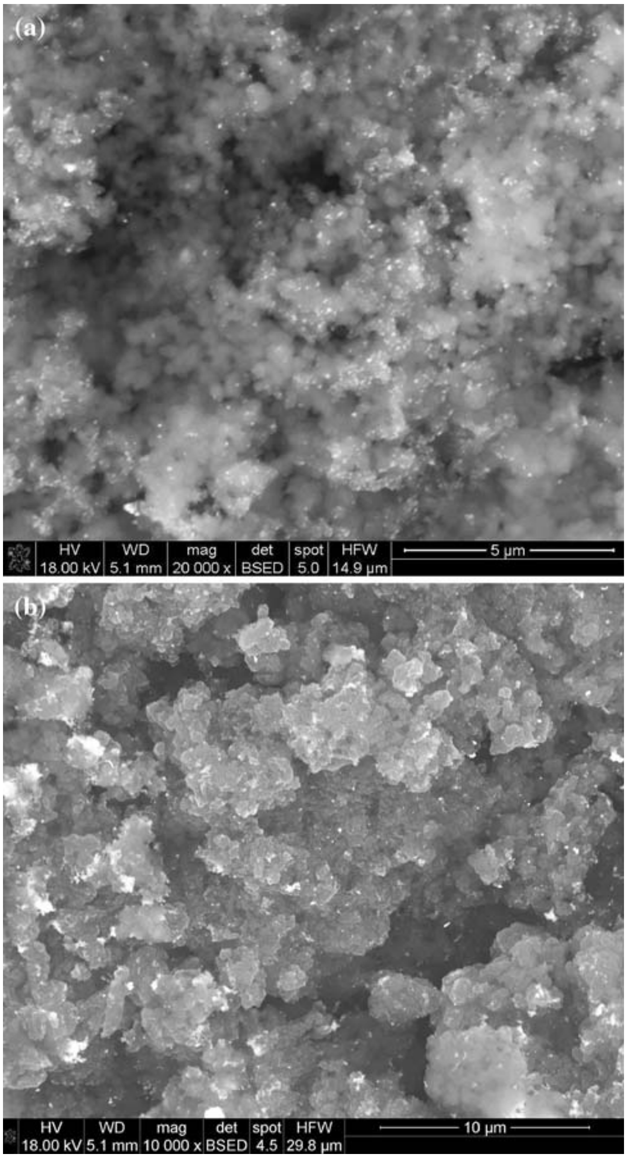

Fig. 4 BSE image of: **a** PPy + 1.75 wt% Rh composite (magnification: 20,000) and **b** PANI + 9.7 wt% Pt composite (magnification: 10,000)

Only acetone and propene are formed when PPy–Rh, PANI–Pt and PPy–Pt composites are applied as catalysts in isopropyl alcohol conversion. Arrhenius plots showing their catalytic activity in this process are presented in Fig. 5. Selectivity and activation energy values calculated based on the results of catalytic experiments are collected in Tables 2 and 3, respectively.

When two parallel reactions taking place during isopropyl alcohol conversion are considered, it is seen that all the investigated catalysts show high activity in alcohol dehydrogenation, i.e., the redox process (Fig. 5a). Their redox activity is usually about ten times higher than that exhibited in alcohol dehydration, i.e., the acid–base

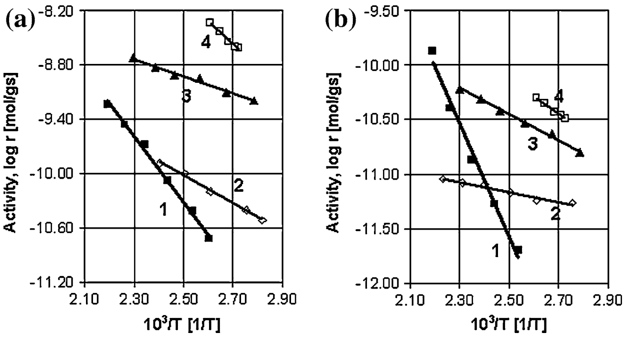

Fig. 5 Arrhenius plots of catalytic isopropyl alcohol conversion to: **a** acetone, **b** propene over the catalysts studied. 1—PPy + 1.75 wt% Rh, 2—PANI + 2.4 wt% Pt, 3—PANI + 9.70 wt% Pt, 4—PPy + 7.0 wt% Pt. Results are expressed per 1 g of the metal (Rh or Pt) in the catalyst

Table 3 Activation energy values of catalytic isopropyl alcohol conversion performed over the composites studied in the work

Catalyst	$E_{a(1)}$ (kJ/mol)	$E_{a(2)}$ (kJ/mol)
PPy + 1.75% Rh	99.51	68.87
PANI + 2.40% Pt	8.72	29.57
PANI + 9.70% Pt	22.69	18.28
PPy + 7.00% Pt	30.79	48.69

$E_{a(1)}$ denotes activation energy of alcohol dehydration reaction, whereas $E_{a(2)}$ refers to activation energy of alcohol dehydrogenation reaction

reaction (Fig. 5b). High redox activity of PPy- and PANI-based catalysts can be explained by the electronic structure of the polymer molecules which facilitates electron transfer during the catalytic reaction. Participation of the polymers in the catalytic reduction of nitrite by hydrogen (i.e., the redox process as well) has been also postulated [15]. In all the cases, selectivity towards acetone is also significantly higher than that to propene (Table 2). This proves that PPy–Rh, PPy–Pt and PANI–Pt composites are very selective catalyst. It is worth noting that the selectivity of the composites in isopropyl alcohol oxidation exceeds 90% in most cases (Table 2) which is more than that found in ,e.g., hydrogenation of citral carbonyl groups over PANI–Pt (75% or 78% depending on the metal load in the catalyst) [17].

Additionally, most calculated activation energy values (Table 3) are sufficiently high to conclude that the reactions have proceeded in the kinetic range. Only dehydration of isopropyl alcohol in the presence of the catalyst containing 2.4 wt% of Pt in PANI has occurred in the diffusion range which is manifested by the lowest value of activation energy found for this reaction (Table 3).

Results of the catalytic measurements have made it possible to examine the influence of both, the active component (Rh or Pt) and the polymer matrix on catalytic properties of the PPy- or PANI-based composites obtained. The influence of the active component can be evaluated by comparing activity of Rh and Pt particles dispersed in the same polymer matrix, i.e., PPy doped with chloride ions (curves 1 and 4, Fig. 5). As can be seen, Pt exhibits significantly higher catalytic activity than Rh. Additionally, Pt dispersed in the polymer matrices studied in this work shows higher redox activity than Rh. This is seen when the catalysts containing similar amounts of Rh in PPy and Pt in PANI are compared (curves 1 and 2, Fig. 5a) and is confirmed by lower activation energy value of the dehydrogenation reaction taking place on Pt catalyst in PANI than that of Rh in PPy (Table 3).

The influence of the polymer matrix on the catalytic properties of the composites can be compared when the results of isopropyl alcohol conversion carried out over Pt particles dispersed in PPy and PANI are analyzed (curves 3 and 4 in Fig. 5). The activity of PPy-based composite is higher than that exhibited by the PANI-based one. This suggests that PPy doped with chloride ions as the support for Pt catalysts has a promoting effect on isopropyl alcohol conversion. In the case of Rh catalyst, PPy doped with chloride ions seems to influence the acid–base activity. This is suggested by differences in selectivity of alcohol dehydration reaction proceeding in the presence of PPy–Rh and PPy–Pt composites containing various amounts of the active component (1.75 wt% of Rh or 7 wt% of Pt). As the temperature increases, selectivity of isopropyl alcohol conversion towards propene grows in the presence of the PPy–Rh composite and decreases over the PANI–Pt composite (Table 2). Since the Rh catalyst has contained lower amount of the active component and has been less active than the Pt one (curves 1 and 4, Fig. 5, activation energy values in Table 3), these differences in selectivity must be

Table 2 Selectivity values of catalytic isopropyl alcohol conversion performed over the composites studied in the work

Catalyst	Selectivity (%)					
	$T = 370$ K		$T = 400$ K		$T = 430$ K	
	Propene	Acetone	Propene	Acetone	Propene	Acetone
PPy + 1.75% Rh	2.51	97.49	5.15	94.85	9.36	90.64
PANI + 2.40% Pt	10.64	89.36	6.69	93.31	4.42	95.58
PANI + 9.70% Pt	2.62	97.38	2.90	97.10	3.18	96.82
PPy + 7.00% Pt	1.31	98.67	0.85	99.15	0.59	99.41

related to the effect of PPy doped with chloride ions on the catalytic properties of the Rh catalyst.

The effect of PANI on isopropyl alcohol dehydration should be also noted. The results of catalytic experiments conducted over PANI–Pt composites containing 2.4 and 9.7 wt% of Pt show that the acid–base process may be catalyzed by the polymer matrix. This hypothesis is supported by selectivity and activation energy values of this reaction for these catalysts (Tables 2, 3). Thus, alcohol dehydration shows markedly higher selectivity over the catalyst containing lower amount of Pt in PANI (2.4 wt%) than that over the catalyst with higher Pt content, particularly at lower temperatures (Table 2). Very low value of activation energy of the dehydration reaction proceeding in the presence of the catalyst with lower Pt content ($E_a = 8.30$ kJ/mol, Table 3) shows—as has been already mentioned—that the reaction proceeds in the diffusion range. This suggests that it takes place in the bulk of the polymer phase. In the case of the composite containing higher amount of Pt (9.7 wt%) such phenomenon can also occur. However, it may be not reflected in the results of catalytic experiments due to its insignificance with respect to the strongly predominating redox process.

As has been already stated, dehydration of isopropyl alcohol proceeds on the acidic centers of a catalyst. It has been found that both, Lewis and Brønsted acids can catalyze this reaction [28]. However, for dehydration of isopropyl alcohol over Lewis acids higher temperatures are required (starting from 450 K) [28]. Therefore in the present study (temperatures of the catalytic process between 355 and 455 K) Brønsted acidic centers should be involved. Hence, the observed influence of PPy doped with chloride ions and PANI on isopropyl alcohol dehydration over Rh and Pt catalysts must be related to the presence of Brønsted acidic centers in the polymers. In the case of PANI, such centers are formed upon protonation which occurs during composite preparation process (Sect. 3.1). They can be catalytically active since it has been established earlier that esterification, i.e., a typical reaction catalyzed by acids, takes place over PANI protonated with HCl [29]. PPy, which is a weaker base than PANI, has been found to exhibit some acid–base properties as well [30]. Hence, the influence of this polymer on isopropyl alcohol dehydration carried out in the presence of PPy-based composites implies that PPy with protonated molecular segments has existed in these catalysts.

4 Conclusions

Metallic Rh and Pt particles can be incorporated into conjugated polymer matrices, namely: polypyrrole (PPy) doped with chloride ions and polyaniline (PANI) in the emeraldine base form by a simple chemical reduction of metal ions conducted in the presence of the polymers.

PPy–Rh, PANI–Pt and PPy–Pt composites thus obtained show mainly redox activity in catalytic isopropyl alcohol conversion carried out in their presence. Catalytic properties of the composites depend on the type of the active component and on the kind of the polymer matrix. Pt-containing catalysts are more active than the Rh ones. Promoting effect of PPy doped with chloride ions on catalytic activity of Pt catalysts has been found. The polymers seem to participate in the catalytic process, especially at low metal contents in the composite.

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