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Heteropolyacids Dispersed within a Polymer Matrix as a New Catalytic Systems with Controlled Oxidative-Reductive and Acid-Base Active Centers

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Summary: Polymer support such as polypyrrole was selected as a matrix for heteropolyacid $H_5PMo_{10}V_2O_{40}$ in an attempt to prepare heterogeneous catalysts containing two different active centers: protons and transition metal ions. Exchanging protons from heteropolyanions dispersed in polymer matrix into ferric or ferrous ions cause the modifications of their catalytic properties. It is manifested by decrease of activity of acid-base centers and increase of activity of oxidative–reductive centers. Oxidation state of iron in all samples before and after catalytic reaction is the same (Fe(III)), but their structure is not similar. For catalysts doped with ferric ions the structural order is much more pronounced than for these doped with ferrous ions.

Keywords: catalysts; conducting polymers; heterogeneous catalysis; heteropolyacids; polypyrrole

Introduction

Polypyrrole (PPy), poly(N-methylpyrrole) (P*N*MPy) and polyaniline (PANI) hold a special position among conjugated polymers. This ows to the ease of their preparation and good environmental stability, which make these polymers exceptionally attractive from application point of view. Possible applications of the properly doped PANI and PPy include heterogeneous catalysis. A number of studies in which catalytically active centers have been incorporated into these polymers can be found in the literature [1,2,3]. They have proven to be efficient catalysts of several industrially important reactions such as alcohol conversion, olefins oxidation, to name a few [4,5,6]. Hetereopolyacids such as $H_4SiW_{12}O_{40}$ or $H_5PMo_{10}V_2O_{40}$ are well known for their interesting catalytic properties. They have two separated active sites i.e. acid-base (protons) and

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oxidative-reductive (transition metal ions) [7]. Depositing heteropoliacids in polymer matrix causes molecular dispersion of active species in the whole volume of polymer support and gives new kind of heterogeneous catalysts susceptible for diverse modifications [8]. In our search to diversify the redox properties of these new heterpolyanion – conjugated polymer systems we have recently prepared new catalysts by doping a well known conjugated polymer – polypyrrole – with complex heteropolyanions of the following type: $HFePMo_{10}V_2O_{40}{}^-$. These heteropolyanions contain four redox centers of different type – three associated with three different transition metals and the fourth one being a Brønsted center. In this communication we present the studies of the catalytic behavior our new catalyst using i-propanol conversion as a test reaction. We also present a detailed characterization of the catalysts by EPR, X-ray diffraction, TG, DTA and ^{57}Fe Mössbauer spectroscopy before and after the catalytic test.

Experimental

In an attempt to prepare catalysts with versatile but controllable properties we prepared $H_5PMo_{10}V_2O_{40}$ acid which was then used as an oxidizing-polymerizing agent for pyrrole. Such one-step reaction leads to the doped form of the polymer in which $H_4PMo_{10}V_2O_{40}{}^-$ or $H_3PMo_{10}V_2O_{40}{}^{2-}$ anions serve as dopants. In the next step of the catalyst preparation the remaining protons, present in the dopant, were exchanged for transition metal cations of variable oxidation state, for example Fe(III)/Fe(II). After the synthesis the presence of heteropolyanions as dopants in the prepared polymer was confirmed by C,H,N,Mo elemental and XRD analysis . The calculation of the doping level from analytically determined C/Mo and N/Mo ratios gave, within the experimental error, the same value of $PPy(HPA)_{0.17}$ where PPy denotes polypyrrole mer involving one ring and HPA denotes heteropolyanion dopant ($H_4PMo_{10}V_2O_{40}$). In the next step H^+ ion was exchanged either with Fe^{2+} or Fe^{3+}. To verify the presence and the oxidation state of iron Mössbauer and EPR spectra of resulting $PPy(HPA)_{0.17}/Fe^{2+}$ and $PPy(HPA)_{0.17}/Fe^{3+}$ catalysts were measured.

EPR measurements were performed using an X-band (9.3 GHz) spectrometer with modulation of magnetic field of 100 kHz. The microwave frequency was recorded. EPR spectra were measured with attenuation of 20 dB (~0.7 mW) to avoid microwave saturation of resonance absorption curves. Isopropanol conversion was studied as a test reaction. The conversion reaction was carried out in an oxygen-free atmosphere. The concentration of isopropyl alcohol in nitrogen was 1.79 mol%. Conversion levels ranged from 5 to 20 %.

Mössbauer spectra of the catalysts tested were recorded at 4.2 K. A typical thickness of the absorber was 5 mg/cm^2 of neutral iron. Co-(RH) was used as a Mössbauer source. An α-Fe absorber operating at room temperature was used for the velocity calibration. The spectra were recorded in a constant acceleration mode and analyzed in a least-squares procedure.

Powder X-ray diffractograms were obtained using Cu Kα radiation (λ = 1.54184 Å) on a Simens diffractometer D5005 (AXS-Bruker) in the 2θ range from 3 to 60°.

Results and discussion

X-ray diffractograms of pure $H_5PMo_{10}V_2O_{40}$ heteropolyacid acid as well as PPy+$H_5PMo_{10}V_2O_{40}$ are shown in Fig. 1 and 2, respectively.

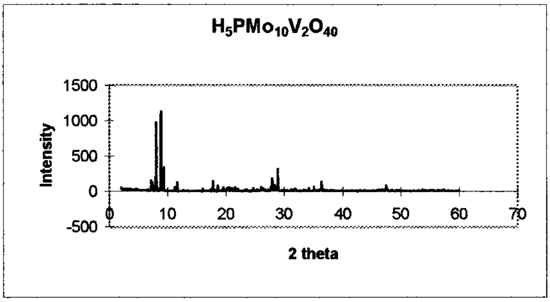


Fig 1. X-ray diffractogram of $H_5PMo_{10}V_2O_{40}$

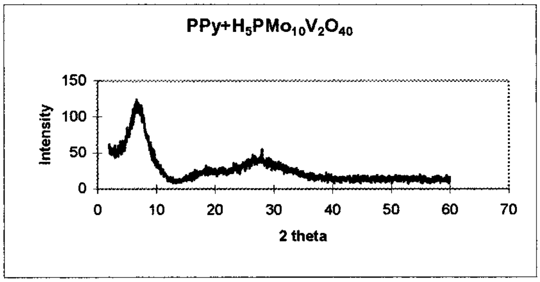
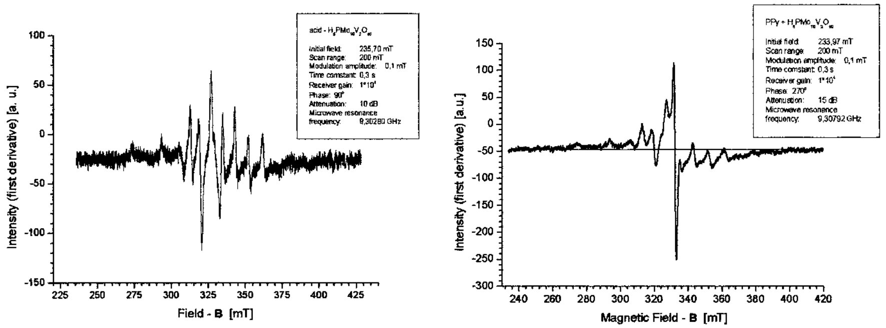


Fig 2. X-ray diffractogram of PPy+$H_5PMo_{10}V_2O_{40}$

The former presents a set of clearly defined Bragg reflections typical of crystalline solids. The diffractogram of the catalyst is different. In this case we notice the total absence of reflections characteristic of the crystalline heteropolyacid. This can be considered as an indication of the molecular dispersion of the dopant within the polymer matrix. The diffractogram of the catalyst is somehow similar to the analogous X-ray patterns reported for other conjugated polymers doped with heteropolyacids [9]. In particular, a strong reflection corresponding to d = 13.1 Å (1) should be noticed which usually is interpreted as originating from polymer chain/dopant/polymer chain stacking. Two broad halos with maxima corresponding to d = 5.3 Å (2) and d = 3.2 Å (3) can also be distinguished. They are usually ascribed to the repeat distances along the polymer chain. Evidently the crystallographic order in this direction is much more poor than the polymer/dopant/polymer stacking order. The exchange of protons for iron ions has minimal effect on the structural order in the doped polymer. The results of this exchange were checked by EPR analysis.



acid - $H_5PMo_{10}V_2O_{40}$

Initial field: 235,70 mT
Scan range: 200 mT
Modulation amplitude: 0,1 mT
Time constant: 0,3 s
Receiver gain: 1*10⁴
Phase: 90°
Attenuation: 10 dB
Microwave resonance
frequency: 9,30280 GHz

PPy + $H_5PMo_{10}V_2O_{40}$

Initial field: 233,97 mT
Scan range: 200 mT
Modulation amplitude: 0,1 mT
Time constant: 0,3 s
Receiver gain: 1*10⁴
Phase: 270°
Attenuation: 15 dB
Microwave resonence
frequency: 9,30792 GHz

Fig 3. EPR spectra of samples a) acid $H_5PMo_{10}V_2O_{40}$ b) PPy + $H_5PMo_{10}V_2O_{40}$

The presented EPR spectra unequivocally show that in the prepared catalysts, the dopants are molecularly dispersed via the formation of dopant-polymer chain association characteristic for doped conjugated polymers (Fig. 3.). The EPR spectrum of $H_5PMo_{10}V_2O_{40}$ acid doped polypyrrole modified by addition of Fe^{3+} ions proves that it is possible to dope transition metal ions into this type of catalysts. Fe^{3+} ions quenched the EPR lines of nonorganic paramagnetic centers (from heteropolyanions) in the studied polymers. Total quenching of the heteropolyacid EPR signal is observed (Fig. 4.).

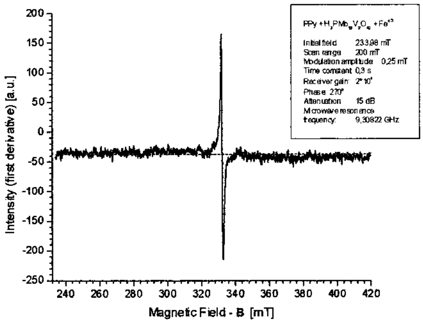


Fig 4. EPR spectrum of PPy + $H_2Fe(III)PMo_{10}V_2O_{40}$

To verify the oxidation state of iron inserted into the polymer matrix as well as to characterize its nearest coordination sphere we have used ^{57}Fe Mössbauer effect measurements. The Mössbauer parameters of the investigated catalysts measured before and after the catalytic tests are collected in Table 1 whereas the representative Mössbauer spectra are presented in Fig. 5, Fig. 6.

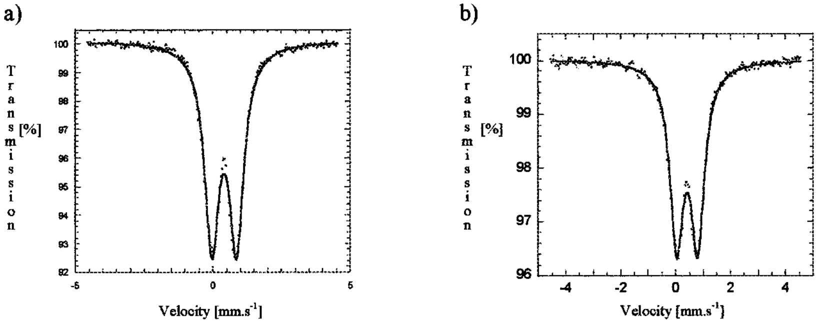


Fig 5. Mössbauer spectra of $PPy+H_2Fe(III)PMo_{10}V_2O_{40}$, a) before reaction, b) after reaction

Interestingly, the Mössbauer parameters of all samples studied are characteristic of high spin Fe(III), independently of the type of iron ion used for the exchange of protons Fe(II) or Fe(III). This means that in the case of $PPy+H_3Fe(II)PMo_{10}V_2O_{40}$, Fe(II) is converted into Fe(III) in the course of the catalysts preparation. Moreover Mössbauer parameters of $PPy+H_3Fe(II)PMo_{10}V_2O_{40}$ and $PPy+H_2Fe(III)PMo_{10}V_2O_{40}$ are very similar.

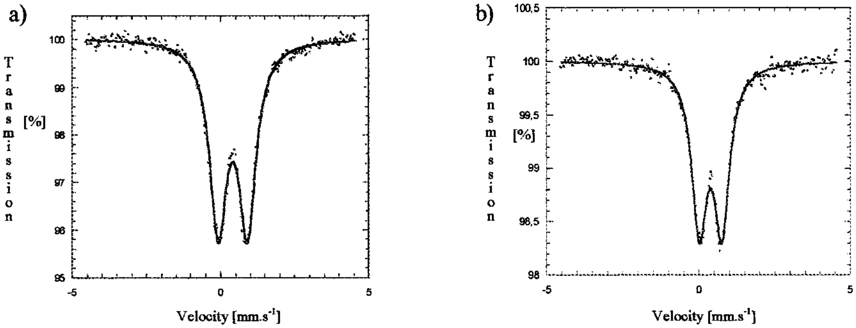


Fig 6. Mössbauer spectra of $PPy+H_3Fe(II)PMo_{10}V_2O_{40}$, a) before reaction, b) after reaction

Table 1. The Mössbauer parameters of $PPy+H_3Fe(II)PMo_{10}V_2O_{40}$ and $PPy+H_2Fe(III)PMo_{10}V_2O_{40}$ measured at 4.2 K

Catalyst	Isomer shift* [mm/s]	Quadrupole splitting [mm/s]	Line width [mm/s]
$PPy+H_3Fe(II)PMo_{10}V_2O_{40}$ before reaction	0.48	0.98	0.68
$PPy+H_3Fe(II)PMo_{10}V_2O_{40}$ after reaction	0.49	0.74	0.58
$PPy+H_2Fe(III)PMo_{10}V_2O_{40}$ before reaction	0.49	0.89	0.62
$PPy+H_2Fe(III)PMo_{10}V_2O_{40}$ after reaction	0.49	0.76	0.57

*With respect to α-Fe at room temperature

The spectra can be fitted with only one doublet which means that only one type of structurally equivalent iron sites are present in the polymer matrix [10]. Despite the fact that both types of catalysts contain iron ions whose spectroscopic features are almost identical, their catalytic behavior is different.

The investigated catalysts are thermally stable in the temperature range of catalytic tests (from 384 to 459 K).

The thermogravimetric measurements show in this temperature range only a small weight decrease of 12 % which can be correlated to a weak endothermic DTA peak with a maximum at 393 K.

In order to verify the influence of proton exchange for iron ions, we have compared the catalytic results of three types of samples: PPy+$H_3Fe(II)PMo_{10}V_2O_{40}$, PPy+$H_2Fe(III)PMo_{10}V_2O_{40}$ and the sample containing no iron PPy+$H_5PMo_{10}V_2O_{40}$.

Catalytic conversion of isopropanol can lead to two reaction products, namely acetone and propene. Acetone being the product of dehydrogenation is formed on redox centers whereas propylene is formed on acid-base centers as the product of dehydration. The results of catalytic tests carried out PPy+$H_3Fe(II)PMo_{10}V_2O_{40}$ and PPy+$H_2Fe(III)PMo_{10}V_2O_{40}$ are shown in Fig. 7a and Fig. 7b, respectively. For comparative reasons the same Arrhenius plots for PPy+$H_5PMo_{10}V_2O_{40}$, i.e. the catalyst in which protons were not exchanged with Fe^{2+} or Fe^{3+}, are shown in Fig. 7c.

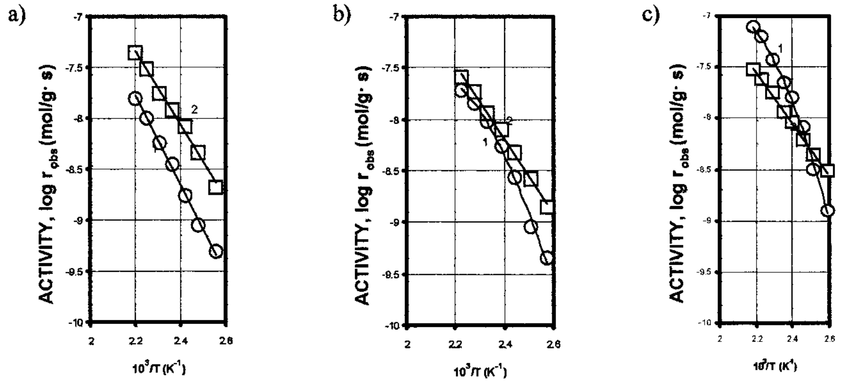


Fig 7. Arrhenius plots of isopropyl alcohol decomposition over a) PPy+$H_3Fe(II)PMo_{10}V_2O_{40}$, b) PPy+$H_2Fe(III)PMo_{10}V_2O_{40}$, **c) PPy+$H_5PMo_{10}V_2O_{40}$**, 1 – Propene, 2 - Acetone

The most striking effect of the exchange of protons with iron ions in the dopant inserted to the polypyrrole matrix is a pronounced change in the catalysts selectivity. The determined selectivities are collected in Table 2 whereas activation energies derived from the Arrhenius plots are listed in

Table 3. Both PPy+$H_3Fe(II)PMo_{10}V_2O_{40}$ and PPy+$H_2Fe(III)PMo_{10}V_2O_{40}$ exhibit much more pronounced redox activity as compared to PPy+$H_5PMo_{10}V_2O_{40}$. This is not unexpected since dehydration of isopropanol involves, in the first step, the protonation of the molecule followed by the abstraction of water molecule with simultaneous creation of a carbocation. Re-arrangement of this carbocation with simultaneous transfer of proton to the catalyst results in the formation of propylene. Since the exchange of H^+ with iron ions efficiently removes active protons from the system the redox activity of the catalyst must increase on the expense of its acid-base activity. One should also note that in PPy+$H_3Fe(II)PMo_{10}V_2O_{40}$ and PPy+$H_2Fe(III)PMo_{10}V_2O_{40}$ the selectivity towards the product formed on redox centers (acetone) is much less temperature dependent than in the case of PPy+$H_5PMo_{10}V_2O_{40}$. The latter shows strongly decreasing redox activity with increasing temperature. The results of Mössbauer spectroscopy studies of both iron containing catalysts after the catalytic tests unequivocally shows that in the course of the test reaction no change in the oxidation state of iron takes place (see Table 1 and Fig.5, 6.

Table 2. The selectivity of isopropyl alcohol conversion

Catalyst	Selectivity [%]					
	393 [K]		418 [K]		443 [K]	
	Propene	Acetone	Propene	Acetone	Propene	Acetone
PPy+$H_5PMo_{10}V_2O_{40}$	40.0	60.0	63.5	36.5	71.5	28.5
PPy+$H_3Fe(II)PMo_{10}V_2O_{40}$	26.6	73.4	41.5	58.5	43.2	56.8
PPy+$H_2Fe(III)PMo_{10}V_2O_{40}$	16.8	83.2	20.8	79.2	24.5	75.5

Table 3. The activation energy of isopropyl alcohol conversion to propene (E_{a1}) and to acetone (E_{a2})

Catalyst	Activation energy, E_a [kJ/mol]	
	E_{a1} (Propene)	E_{a2} (Acetone)
PPy+$H_5PMo_{10}V_2O_{40}$	107.2	49.2
PPy+$H_3Fe(II)PMo_{10}V_2O_{40}$	114.9	72.8
PPy+$H_2Fe(III)PMo_{10}V_2O_{40}$	88.2	67.9

It should be however noted that the value of quadrupole splitting recorded for iron ions in both types of catalysts studied is surprisingly high for high spin Fe(III). This means that some type of distortion occurs upon insertion of heterpolyanions into the polymer matrix which increases the lattice term of the quadrupole splitting. After the catalytic test the quadrupole splitting value decreases (Table 1). Evidently the distortion of the inserted heteropolyanions is partially removed via some relaxation phenomena induced by extended heat treatment. The decrease of the quadrupole splitting value is accompanied by a decrease in the spectral linewidth consistent with better structural order in the samples which underwent thermal treatment.

Conclusions

To summarize, we have demonstrated that using a simple reaction of proton – iron ions exchange it is possible to tune the selectivity of polypyrole supported heteropolyanions catalysts. Since this ion exchange involves the removal of Brønsted centers, the selectivity towards the redox reaction products significantly increases on the expense of the products of the acid-base catalysis.

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