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Electrostatic Self-assembly of Polyoxometalates on Chitosan as Catalysts of Oxidation of Cyclic Hydrocarbons

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Abstract The Keggin type heteropolyacids of tungsten and molybdenum (HPW and HPMo) and heteropolyacid salts of cobalt with changing stoichiometry $H_{3-2x}Co_x PM_{12}O_{40}$ where M = Mo or W, x = ½, 1, 1½ were synthesized and immobilized on chitosan. The complexes were characterized by X-ray diffraction and for first time by zeta potential measurements. These complexes were employed as catalysts in the cyclooctane oxidation with molecular oxygen. The introduction of cobalt into HPW structure shows a substantial influence on the catalytic activity of heteropolyacid salts in the oxidation of cyclooctane while the incorporation of cobalt atoms into HPMo only to some extent improves its catalytic properties. The cobalt molybdophosphates supported on chitosan show a similar catalytic activity as unsupported catalysts while the catalytic activity of cobalt tungstophosphate upon immobilization decreases.

Keywords Polyoxometalates · Cobalt dodecatungstophosphate · Cobalt dodecamolybdophosphate · Chitosan · Zeta potential · Oxidation of cyclooctane

1 Introduction

Heteropolyacids and their salts are promising "green catalysts" and possess structures that are well characterized at the molecular level [1], and acidity and redox properties that can easily be controlled. The oxidation of saturated organic substrates like light paraffins [2] is an example of catalytic reaction which requires both functions. The introduction of transition metal cations into heteropolyacid structure influences its oxidation properties by activating reducing agents and molecular oxygen and possibly providing reservoirs of electrons. Such heteropoly compounds are catalytically active both at the second and third oxidation state. They are subjected to the reduction and oxidation while the initial structure is preserved.

The oxidation of hydrocarbons with molecular oxygen catalyzed by transition metal polyoxometalates is potentially a method for obtaining industrially important products from comparatively cheap starting materials [2]. The oxidation of cycloalkanes is still a challenge in catalysis [3–5]. Because of low efficiency of this reaction a lot of effort has been made to design a better catalytic system. The properties of heteropoly compounds, their stability and resistance in oxidation conditions make them useful catalysts of oxidation of cycloalkanes. [6, 7]. An extensive study has been carried out on the application of transition metal substituted lacunary polyoxometalates [8, 9] in the oxidation of hydrocarbons. However, there are hardly any papers describing the catalytic activity of transition metal cations compensating the negative charge of Keggin anions in the oxidation of hydrocarbons.

Recently, a lot of research has been focused on the deposition of polyoxometalates on different supports [10, 11]. Polysaccharide can provide a suitable microenvironment for the accommodation of the Keggin anion catalytic center [12]. The properties of immobilized metallocomplexes are governed by the properties of both the metallocomplex and the support. Therefore, it is of interest to find a universal carrier that possesses mechanical stability, regenerability, reactive functional groups for direct reactions with metallocomplexes, is easy to prepare and inexpensive.

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Furthermore, there is a growing interest in the use of biodegradable materials. Chitosan is the kind of carrier that offers most of the above properties. It is natural polysaccharide and the presence of amino groups makes chitosan a cationic polyelectrolyte, one of few found in nature. Physicochemical studies resulted in the formulation of the experimental conditions in which the formation of a series of polyoxometalates immobilized on a multilayer film occurs.

In this study we focus on cobalt cations compensating the negative charge of Keggin anions. We have prepared a series of cobalt 12-tungstophosphoric (HPW) and 12-molybdophosphoric (HPMo) salts: $H_2Co_{0.5}PM_{12}O_{40}$, $HCoPM_{12}O_{40}$ and $Co_3(PM_{12}O_{40})_2$, where M = Mo or W, immobilized these salts on chitosan and applied them as catalysts in the oxidation of cyclooctane with molecular oxygen. The oxidation of cyclooctane is a test reaction for the redox properties of the catalysts.

2 Experimental

2.1 Catalysts Preparation

Cobalt dodecatungstophosphate or dodecamolybdophosphate was obtained as precipitate by mixing an aqueous solution of an appropriate amount of cobalt (II) carbonate hydrate (Aldrich) with an aqueous solution of appropriate heteropolyacid. The resultant salts were dried in the oven at 363 K.

Figure 1 shows the structural formula of the polyelectrolytes: chitosan (CHIT) and alginate (ALG), used in our studies. The chitosan (polycation) of average molecular weight 390 kDa was purchased from Marine Chemicals, polyalginic acid sodium salt (polyanion) of molecular weight between 75 and 100 kDa was purchased from Aldrich. Chitosan and alginate are both weak polyelectrolytes, so their degree of dissociation depends on pH of the solution.

Doubly distilled water was used for the preparation of all solutions. Sodium chloride, HCl and NaOH were commercial products of Sigma-Aldrich. NaCl was used as a background electrolyte. All electrolyte solutions were filtered using a 0.22 μm Millipore filter. The temperature of experiments was kept constant at 293 ± 0.1 K.

Solutions of metallocomplexes were prepared by dissolving in deionized water at pH = 2. The pH was adjusted with standard analytical grade HCl solution. The chitosan powder was dispersed in distilled water with ionic strength 1×10^{-3} M at pH adjusted by the standard solution of 0.1 M HCl. The suspension was treated in an ultrasonic bath for 30 min in order to break up aggregates in the suspension. After addition of the chitosan suspension to the metallocomplex solution under vigorous stirring the mixture was centrifuged at 10,000 rpm for 20 min. This was sufficient for a complete sedimentation of the particles. The amount of metallocomplexes adsorbed on chitosan was determined by the depletion method. The supernatant was decanted and the concentration of not adsorbed metallocomplexes was determined by the UV spectroscopy. The amount of heteropolyacid salts supported on 1 g chitosan are presented in Table 1.

Further confirmation of the strong binding and its induced supramolecular assembly is clearly visible as depicted by the pictures shown in Fig. 2, which demonstrates the behavior of chitosan in the presence of HPW at 7 min, 20 min and 24 min after interaction.

2.2 Catalysts Characterization

2.2.1 X-ray Diffraction

X-ray diffraction patterns were obtained with a Siemens D5005 automatic diffractometer equipped with a graphite monochromator of the diffracted beam using Cu K alpha

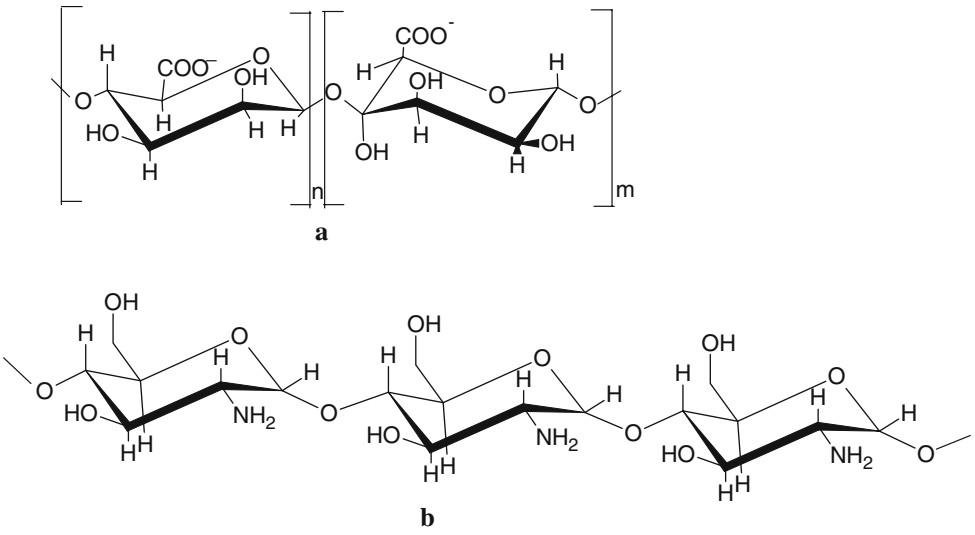

Fig. 1 Structural formula of alginate (left) and chitosan (right)

Table 1 Contents of polyoxometalate on support

Heteropolyacid	Support	[HPA/support][a] mmol/g
HPW	Chitosan	0.8346
$H_2Co_{0.5}PW$	Chitosan	0.7152
HCoPW	Chitosan	0.4715
$Co_3(PW)_2$	Chitosan	0.3243
HPMo	Chitosan	0.9909
$H_2Co_{0.5}PMo$	Chitosan	0.6990
HCoPMo	Chitosan	0.4660
$Co_3(PMo)_2$	Chitosan	0.2411

[a] Conditions of immobilization are given in experimental part

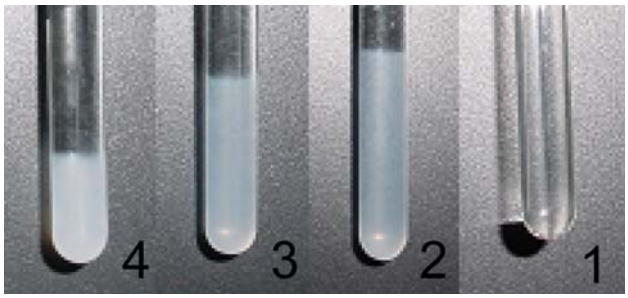

Fig. 2 Pictures depicting: 1—chitosan solution, 2–4 HPW solutions mixed with chitosan solution after 7 min, 20 min and 24 h, respectively

radiation ($U = 55$ kV, $I = 30$ mA). The samples were measured at ambient temperature.

2.2.2 Zeta Potential Measurements

Zeta potential in Zetasizer nano ZS was measured using the Laser Doppler Velocimetry (LDV) technique, measurement range of 3 nm to 10 μm. In this technique, a voltage was applied across a pair electrode placed at both ends of a cell containing the particle dispersion. Charged particles were attracted to the oppositely charged electrode and their velocity was measured and expressed per unit field strength as the electrophoretic mobility μ_e. Then, the zeta potential was calculated using Henry's equation

$$\zeta = \frac{3\eta}{2\varepsilon F(\kappa a)}\mu_e \quad (1)$$

where ζ is the zeta potential of polyelectrolyte, μ_e is the electrophoretic mobility, ε is the dielectric constant of water and $F(\kappa a)$ the function of the dimensionless parameter κa, $\kappa^{-1} = (\varepsilon kT/e^2 I)^{1/2}$ is the double-layer thickness, e the elementary charge, k the Boltzmann constant, T the absolute temperature, $I = \left(\sum_i c_i z_i^2\right)/2$ is the ionic strength, c_i the ion concentrations, a is the characteristic dimension of the polyelectrolyte. Electrophoretic mobility was determined for fixed ionic strength, regulated by addition of NaCl of $I = 10^{-3}$ M, 5×10^{-3} M, 10^{-2} M and 0.15 M, and pH range 2.5–10.5.

2.2.3 DSC-TG Measurements

The simultaneous differential thermal analysis and thermogravimetry measurements were performed using NETZSCH STA 409 PC apparatus. The parameters of measurements were as follows: temperature range from ambient to 923 K, heating rate 25 K/min, measurements were performed in dynamic air atmosphere with the flow rate 30 mL/min. For each measurement a sample of about 8–10 mg was used.

2.3 Catalytic Activity Measurements

The liquid-phase oxidation of cyclooctane was performed in a stainless-steel batch reactor system at the optimum temperature of 393 K and under the pressure of 10 atm., with the reagents molar ratio C_8H_{16}:O_2 = 13:2. The teflon lined reactor of 1 L volume equipped with magnetic stirrer was used. In a typical experiment, the following catalysts having the concentration of 3.3×10^{-4} M were used: the selected heteropoly compound and the equivalent of the supported polyoxometalete. The catalyst together with the substrate were closed in the air-free autoclave and were heated together with the whole system until temperature of 393 K was reached. In due time air was added to the hot reaction mixture in such amount that final pressure of 10 atm. was obtained and the reaction started. After 6 h of reaction time the oxidation was stopped by immersing the hot reactor in a cold water bath. The products were analyzed by means of Agilent Technologies 6890 N gas chromatograph equipped with Innowax (30 m) column.

3 Results and Discussion

3.1 Cobalt Dodecatungstophosphates

The structures of the series of cobalt salts with changing stoichiometry $H_{3-2x}Co_xPM_{12}O_{40}$, where M = W or Mo, x = ½, 1, 1½ were studied by means of DSC-TG and XRD analysis. The diffraction patterns of tungstophosphoric acid and its cobalt salts show that only two of them, HPW and the neutral $Co_3(PW)_2$ salt, form pure phases. The reflexes observed for neutral salt in Fig. 3 are similar to those present in the HPW pattern. They are slightly shifted from those originating from heteropolyacid, indicating the decrease of lattice parameter from 12.15 Å to about 11.9 Å. The synthesis of acidic salts results in biphasic mixture of the neutral $Co_3(PW)_2$ salt and unreacted heteropolyacid. As the content of cobalt atoms, grows the

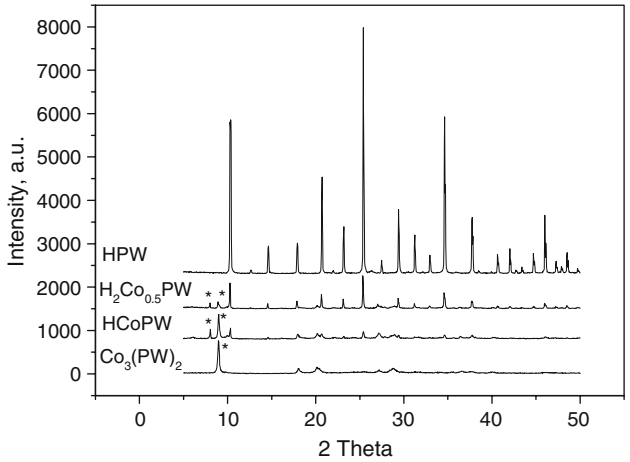

Fig. 3 X-ray diffraction patterns of series of cobalt dodecatungstophosphates

intensities of heteropolyacid reflexes decrease while the intensities of reflexes originating from cobalt salts increase. In the diffraction patterns of the $H_2Co_{0.5}PW$, HCoPW and $Co_3(PW)_2$ salts additional reflexes (marked with the asterisks) are visible which are not present in the case of parent heteropolyacid HPW. This could possibly indicate the existence of a small content of heteropolyacid or its salt, having different degree of hydration.

The results of thermal analysis fully confirms the findings obtained with XRD. Figure 4 demonstrates DSC profiles of cobalt dodecatungstophosphates compared with the parent heteropolyacid. Endothermic effects observed up to 523 K are connected with the loss of water. The intensity of those effects is strictly connected with the number of cobalt cations introduced into heteropoly salts. The exothermic effect, observed for the cobalt salts at about 859–864 K, corresponds to the sample decomposition. This effect is the largest for the neutral salt and reduces as the number of cobalt atoms decreases.

3.2 Cobalt Dodecamolybdophosphates

The introduction of the cobalt atoms into the structure of 12-molybdophosphoric acid leads to the formation of the series of heteropoly salts having properties different from those observed for cobalt salts of 12-tungstophosphoric acid. Their diffraction patterns, presented in Fig. 5 suggest the existence of one crystalline phase only. This indicates the formation of either solid solution or epitaxially dispersed heteropolyacid on the particles of its neutral salt. The diffraction pattern of the $Co_3(PMo)_2$ is similar to that of the $Co_3(PW)_2$ salt, although the latter has higher crystallinity. A larger hydrogen content results in a further increase of crystallinity without changing the structure or lattice parameter. However, the diffraction patterns of cobalt dodecamolybdophosphates are different in comparison to HPMo suggesting a large influence of cobalt on the structure formation.

Contrary to the XRD results, the thermal analysis of the cobalt dodecamolybdophosphates (Fig. 6) suggests the existence of a two-phase mixture. At ambient conditions in which XRD patterns were collected, cobalt salts are one-phase compounds. On heating, during DSC measurement, one-phase salt transforms into two-phase mixture consisting of the neutral $Co_3(PMo)_2$ salt and heteropolyacid. The exothermic effects, observed at about 741–745 K prove their decomposition. The effect is more pronounced the larger number of cobalt atoms is incorporated. The thermal stability of the $Co_3(PMo)_2$ salt is higher than of the corresponding heteropolyacid because its decomposition temperature is lower from its neutral salt.

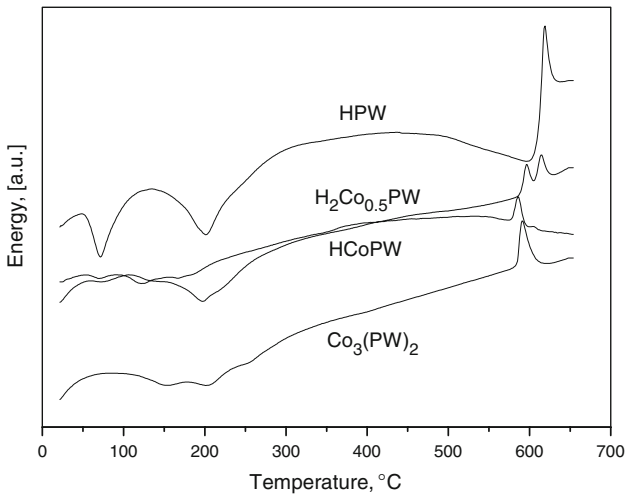

Fig. 4 DSC profiles of cobalt salts of tungstophosphoric acid

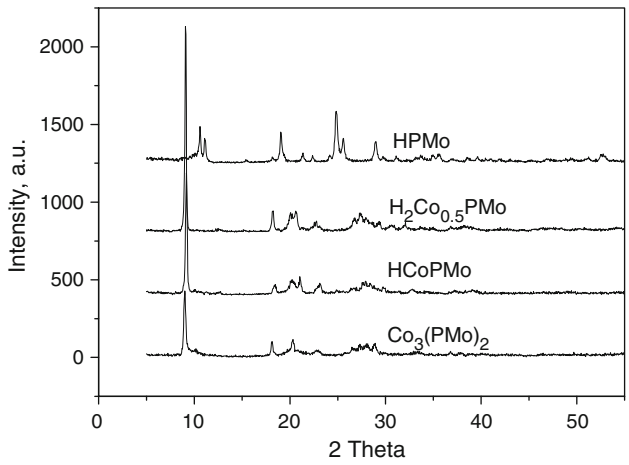

Fig. 5 X-ray diffraction patterns of series of cobalt dodecamolybdophosphates

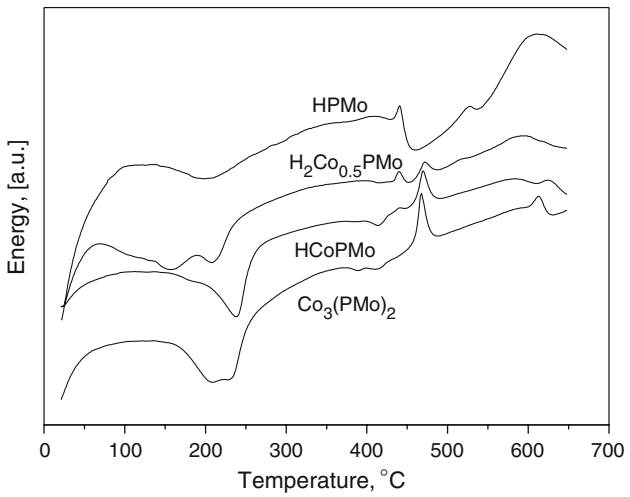

Fig. 6 DSC profiles of cobalt salts of molybdophosphoric acid

3.3 Cobalt Salts on Chitosan—Physicochemical Characterization of Polyelectrolyte

To establish optimum conditions for the formation of polyelectrolyte–polyoxometalate system, the measurements of zeta potential of polyelectrolytes were plotted as a function of pH and ionic strength. Figures 7 and 8 illustrates the dependence of zeta potential of chitosan and alginate on pH of the solutions. The effect of ionization degree of the polyelectrolyte, regulated by the change in the pH of the solution, was studied for three ionic strengths. As can be seen in Fig. 7 the zeta potential of CHIT decreased from 80 mV at pH 3 to −8 mV at pH = 9 for $I = 1 \times 10^{-3}$ M. For a higher ionic strength $I = 0.1$ M, the zeta potential was 38 mV at pH = 3 and 0 at pH = 8. Independently of the ionic strength a zero value of the zeta

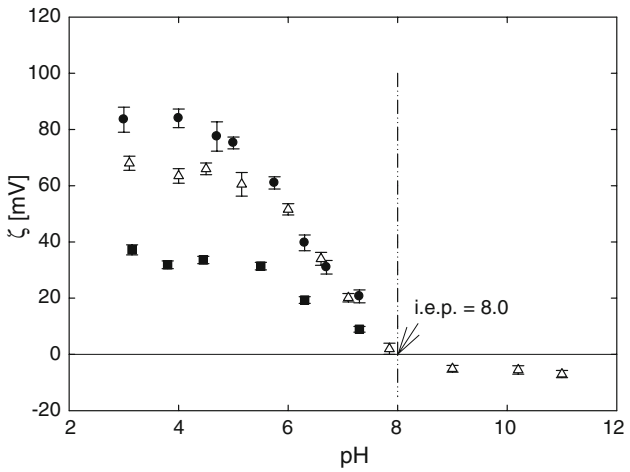

Fig. 7 Zeta potential of chitosan as function of pH at $T = 298$ K. Respective marks denote experimental values determined for different ionic strength ●, $I = 1 \times 10^{-3}$ M; ▲, $I = 1 \times 10^{-2}$ M; ■, 1×10^{-1} M

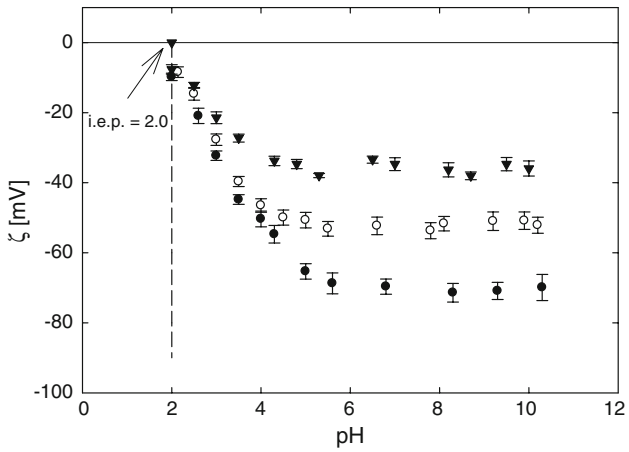

Fig. 8 Zeta potential of alginate as a function of pH at $T = 298$ K. Respective marks denote experimental values determined for different ionic strength ●, $I = 1 \times 10^{-3}$ M; ○, $I = 1 \times 10^{-2}$ M; ▼, $I = 1 \times 10^{-1}$ M

potential was attained for pH = 8, which is usually referred to as the isoelectric point (i.e.p.). The results obtained confirmed that an increase in the ionic strength caused a decrease in the zeta potential. The observation of decrease of positive charge of chitosan at low pH is due to deprotonation of amino groups NH^{3+}-NH_2. The same result was described by S. Yu et al. in [13]. The zeta potential of alginate is shown in Fig. 8. For the ionic strength 1×10^{-3} M, the zeta potential decreased from 0 mV at pH = 2 to −70 mV at pH = 10. The point of zero charge for alginate occurs at pH = 2. The observed decrease of negative charge is due to protonation of carboxylic groups. The dependence of zeta potential of both polyelectrolytes on the pH of the solution exhibits the behavior which is typical for weak polyelectrolytes.

The most convenient method for controlling effective immobilization of metallocomplexes in polymer matrices

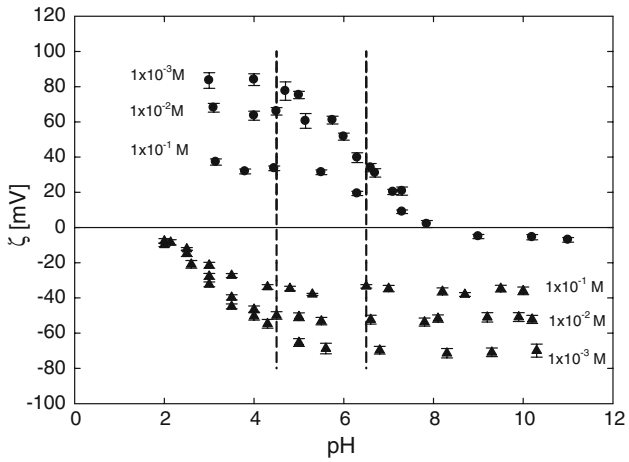

Fig. 9 Zeta potential of chitosan—● and alginate—▲ as a function of pH at $T = 298$ K

Table 2 Multilayer thickness, density and roughness obtained using small angle X-ray scattering method

Layer	$(Chit/Alg)_5$	$(Chit/Alg)_5HPW$
Thickness (nm)	3.7	2.8
Density	1.7	1.9
Roughness (nm)	1.4	1.7

is the formation of polyelectrolyte multilayers (PEMs) obtained via sequential adsorption of oppositely charged polyions from a solution. From zeta potential measurements in Fig. 9 it can be seen that there exists a limit pH range from 3 to 7, in which the multilayer film can be formed from the CHIT/ALG polyelectrolyte pair when both polyelectrolyte are sufficiently charged. The formation of polyelectrolyte films can be conveniently followed by Elipsometry or Small Angle X-ray Scattering method. To observe the deposition process on silica wafer we used Small Angle X-ray Scattering method (X'Pert). In Table 2 the results of our measurements of CHIT/ALG films deposited on Si/SiO_2 wafer surface are collected.

3.4 Catalytic Activity

The activity of all synthesized catalysts was studied in the oxidation of cyclooctane with molecular oxygen. The catalytic properties of four series of compounds were investigated: Keggin type heteropolyacids of tungsten and molybdenum (HPW and HPMo), heteropolyacid salts of cobalt with changing stoichiometry ($H_2Co_{0.5}PM_{12}O_{40}$, $HCoPM_{12}O_{40}$ and $Co_3(PM_{12}O_{40})_2$ where M = Mo or W) and the above two groups of catalysts electrostatically attached to chitosan. The immobilization of heteropolyacids and their salts on supports like polysaccharides results in the formation of self-assembly systems. The results of the catalytic studies are presented in Table 3. They indicate that all synthesized unsupported catalysts were active in the investigated process. The oxidation of cyclooctane in the presence of cobalt catalysts produced cyclooctanone as the main product and cyclooctanol in a small yield. No reaction was observed in the blank experiment. The parent

Table 4 Zeta potentials of metallocomplexes at pH = 2.7 and ionic strength $I = 1 \times 10^{-3}$ M

Catalyst	ζ [mV]			
	HPM	$Co_{0.5}H_2PM$	CoHPM	Co_3PM_2
M = W	−65.5	−59.3	−48.3	−37.5
M = Mo	−47.4	−41.0	−31.1	−26.0

HPW which is known to be strong acid, shows the lowest catalytic activity among the tested unsupported catalysts. The incorporation of cobalt atoms in the HPW structure has a major influence on their catalytic activity. The activity of neutral $Co_3(PW)_2$ salt is almost three times higher in comparison with 12-tungstophosphoric acid. The following order of activity is obtained: $Co_3(PW)_2 > CoHPW > Co_{0.5}H_2PW > HPW$. Moreover, the increase of the number of cobalt atoms results in a higher selectivity to ketone. The highest selectivity to cyclooctanone is observed for $Co_3(PW)_2$ salt. A different situation is observed for dodecamolybdophosphoric acid, which is known to possess redox properties. It demonstrates high catalytic activity in the studied reaction (Table 3). The incorporation of cobalt atoms into the HPMo structure improves its catalytic activity only to some extent and decreases the selectivity to ketone. Neutral salt $Co_3(PMo)_2$ is the most active catalyst in the series of phosphomolybdic catalysts. It also is the most active of all the investigated catalysts. The increase of the number of cobalt atoms in the catalyst structure results in rather very small changes in their catalytic activity.

It is clearly visible, that cobalt atoms have a significant influence on the catalytic activity only when they are incorporated into tungstophosphoric acid. In the case of heteropolyacid with strong redox properties, like HPMo, the presence of cobalt atoms does not improve its oxidation properties considerably.

Table 4 presents the changes of zeta potentials measured for the series of cobalt dodecatungstophosphate and dodecamolybdophosphate which are consistent with the variation in their catalytic properties. The highest zeta potential is observed for the most acidic catalyst in this

Table 3 Oxidation of cyclooctane with molecular oxygen catalyzed by heteropolyacids and their cobalt salts

Catalyst	Yield of cyclooctanone %[a]	Yield of cyclooctanol %[a]	Cyclooctanone + Cyclooctanol %	Cyclooctanone/ Cyclooctanol
HPW	3.4	0.9	4.3	3.8
$Co_{0.5}H_2PW$	5.4	1.1	6.5	4.9
CoHPW	8.6	1.4	10.0	6.1
$Co_3(PW)_2$	9.2	1.4	10.6	6.6
HPMo	9.2	1.6	10.8	5.8
$Co_{0.5}H_2PMo$	9.7	1.7	11.1	5.7
CoHPMo	10.2	2.0	12.2	5.1
$Co_3(PMo)_2$	10.2	2.1	12.3	4.9

[a] Conditions are given in experimental part

Table 5 Oxidation of cyclooctane with molecular oxygen catalyzed by heteropolyacids and their cobalt salts on chitosan

Catalyst	Yield of cyclooctanone %[a]	Yield of cyclooctanol %	Cyclooctanone + Cyclooctanol %	Cyclooctanone/ Cyclooctanol
HPW/chitosan	3.0	0.7	3.7	4.9
$Co_{0.5}H_2PW$/chitosan	4.1	0.9	5.0	4.6
CoHPW/chitosan	4.4	1.3	5.7	3.4
$Co_3(PW)_2$/chitosan	1.1	0.3	1.4	3.7
HPMo/chitosan	9.2	1.5	10.7	6.1
$Co_{0.5}H_2PMo$/ chitosan	8.4	1.4	9.8	6.0
CoHPMo/chitosan	8.3	1.4	9.7	5.9
$Co_3(PMo)_2$/chitosan	8.3	1.4	9.7	5.9

[a] Conditions are given in experimental part

series, i.e. HPW. With the increase of number of cobalt cations the acidic properties gradually weaken while the redox properties increase. HPMo which is weaker acid than HPW demonstrates significantly lower zeta potential than the latter. Furthermore, the zeta potential measurements prove that the incorporation of cobalt cations into molybdophosphoric acid reduces the acidic properties of the synthesized cobalt salts.

The catalytic results of heteropolyacids and their cobalt salts supported on chitosan are gathered in Table 5. All catalysts supported on chitosan show catalytic activity in investigated reaction and form stable hybrids with support. Moreover, in the presence of chitosan alone the reaction does not occur. The catalytic activity of the tungstophosphoric acid upon deposition on chitosan is the same as for unsupported heteropolyacid, however, the catalytic activity of the cobalt salts of tungstophosphoric acid decreases upon immobilization on the chitosan carrier. Immobilization on chitosan has a particularly strong influence on catalytic activity of $Co_3(PW)_2$/chitosan. This catalyst shows the lowest activity among all the tested samples. In the case of $H_3PMo_{12}O_{40}$/chitosan the catalytic activity practically does not change in comparison with unsupported heteropolyacid. On the contrary, the catalytic activity of cobalt dodecatungstomolybdates decreases after immobilization only to some extent.

Chitosan have been widely used as support for immobilization of the different macrocyclic catalysts [14–20]. It forms microenvironment around metallocomplex, which induces the changes of its catalytic properties. In our catalytic system lower catalytic activity of immobilized polyoxometalates could be explained by interaction of metal center with amino or hydroxyl groups.

4 Conclusions

The introduction of cobalt into HPW structure shows substantial influence on the catalytic activity of heteropolyacid salts in the oxidation of cyclooctane. The exchange of protons for cobalt cations in the heteropolyacid structure results in a decrease of acidity and improves the redox properties of the catalysts. The incorporation of cobalt atoms into HPMo only to some extent improves its catalytic properties. Cobalt molybdophosphates supported on chitosan show a similar catalytic activity as unsupported catalysts while the catalytic activity of cobalt tungstophosphate decreases upon immobilization. Our paper shows, for the first time, the application of heteropolyacid salts of cobalt with changing stoichiometry and of the same salts on chitosan as catalysts of the oxidation reaction.

Acknowledgments The authors thank the Ministry of Science and Higher Education for financial support within Grant N204 122 32/3142 and Grant 3T09A 092 29.

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