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CATALYTICALLY ACTIVE COBALT AND COPPER COMPLEXES IN POLYELECTROLYTE MULTILAYER FILMS

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Abstract

In this work an approach to obtain effective and easy reusable heterogeneous catalyst, LbL deposition of polyelectrolytes followed by covalently binding with cobalt (II) and copper (II) ions were described. Immobilization of metal complexes via covalent attachment to insoluble template is an attractive method to facilitate catalyst recovery, recycling. The reaction in the heterogeneous catalysis goes in the interface of catalyst and reaction solution and it is important to create a catalyst with large surface area. We have used polycations as polyethyleneimine (BPEI), quaternized poly(4-vynilpyridine) (QPVP) and polyanions as poly(acrylic acid) (PAA), poly(styrene sulphonate) sodium salt (PSS) and the electrostatic layer-by-layer assembly technique to make uniform thin film coating on SiO_2 nanoparticles and glass slides with controllable thickness, roughness and mechanically durability. The stability of metals within multilayers in reaction condition were tested. We compared the amount of metal in PEMs of different polyelectrolytes. The stability constants of complexforming processes of the polymer-metal complexes in water and in alcohol were calculated by modified method of Bjerrum. Catalytic activity of immobilized catalysts was investigated for oxidation of toluene by molecular oxygen. Catalysts were separated from reaction mixture easily and had been used for this reaction five times without significant loss of activity.

Key words: *catalysis, layer-by-layer (LbL), polymer-metal complexes, oxidation, cobalt and copper immobilization*

1. INTRODUCTION

Polyelectrolyte multilayer (PEM) coatings created by alternate LbL adsorption of oppositely charged poly-ion molecules were first introduced by Decher (1996). The LbL deposition of polycations and polyanions on solid substrate is an attractive method for preparation of organized uniform surface film with controlled thickness. Metal-containing polyelectrolyte multilayers PEMs were wildly investigated and have found applications in various fields. One of the interesting and attractive areas of using of LbL technique is preparation of PEMs films with catalytic activity. Process of oxidation of aromatic hydrocarbons did not lose actuality and still needs a suitable catalyst. Homogeneous catalysts have enormous relevance in various organic reactions. However, homogeneous catalysts have some disadvantages in that they can decompose during the course of the reaction and are not easily recovered after the reaction for reuse. This leads to the loss of metal and ligands and incorporation of impurities in the products. Immobilization of metal complexes via covalent attachment to the functionalized polymers is an attractive method to facilitate catalyst recovery, recycling and also helps to avoid purification study of products from metal cation trace due to strong metal-polymer interaction. The main benefits are due to the ease of physical separation of the polymer and its bound component from the reaction mixture, the ease of recycling. Another advantage is due to the unique microenvironment created for the reactants within the polymer support. Improved

catalyst stability within the polymer matrix and increased selectivity for intramolecular reactions have all been reported – see for example Fraile et al. (1996), Trost et al. (1982). The properties of heteropoly compounds, their stability and resistance in oxidation conditions make them useful catalysts.
The potencial of PEMs in heterogeneous catalyst has been previously explored with focus on zero-charge catalytic nanoparticles within PEMs. In the most of cases they were used to obtain and stabilize the nanozise-particles of noble metals such as Pt, Pd, Au in order to produce large surface area of heterogeneous catalyst. LbL method proved to have many advantages in immobilization and surface modification of noble metal nanoparticles such as diversity of film composition and controllability of the thickness. One interesting approach has been proposed by Wang and Lee (2007), who fabricated nano-size Pd catalyst attached to the core magnetic nanoparticles by LbL self-assembled multilayer films and could easily and efficiently isolate and reuse. Macanas et al. (2010) created reactors by modification of hollow fiber microfiltration membranes through LbL adsorbtion of polyelectrolytes and citrate-stabilized metal. Characterization of the catalytic effect of the fibers was performed using a reaction model widely used in the evaluation of new catalysts for reactions in aqueous phase, the reduction of p-nitrophenol in presence of sodium borohydride. Hollow fiber modules with Pd MNPs have been tested in dead-end and cross-flow filtration. Complete nitrophenol degradation was possible depending on operation parameters such as applied pressure and permeate flux.

Good performance for the total oxidation and oxidation of toluene to benzaldehyde, benzyl alcohol, and benzoic acid in good yield was observed (see for example Bautista et al., 2001, Bejer et al., 2010) but necessity to use noble metals and additives restrict their widely application. Polymer supported transition metal complexes, especially Co(II), Cu(II) and Fe(III) based systems were found to be efficient homogeneous and heterogeneous catalysts for the oxidation of various aliphatic and aromatic hydrocarbons under mild and friendly condition. Usually, they are supported on inorganic carriers as zeolite, porphyrins, mesoporous molecular sieves, polysterene resin and also immobilized by covalently grafting on insoluble in reaction medium polymers. A.J. Pardey et al. (2005) studied the use of the poly(4-vinylpyridine)/divinylbenzene (2%) polymeric matrix as a ligand coordinated to $CuCl_2$ salt. The material catalyzed the water gas shift reaction as well as the reduction of nitrobenzene to aniline and azobenzene. The study suggests that the nitrogen lone pair of the vinylpyridine of the P(4-VP) coordinates to the copper metal center. Chen et al. (2006) reported the synthesis of temperature sensitive soluble polymer with a lower critical solution temperature an preparation of poly(N-isopropylacrylamide) supported cobalt phthalocyanine asa homogeneous catalyst for the oxidation of thiols below 31.0 °C.

In this paper an alternative approach to obtain easy reusable, with reduced waste and effective heterogeneous catalyst, LbL deposition of polyelectrolytes followed by covalently binding with cobalt and copper ions were described. During our research polycations as poly(ethyleneimine), propyl bromide-quaternized poly(4-vynilpyridine) with different quaterization degree and polyanions poly(acrylic acid), poly(sterуne sulphonate) sodium salt were deposited on silica oxide nanoparticles. Role of different polyanions on binding of metals within PEMs and leachability of metal cations from multilayer films were studied. The stability constants of polymer-metal complexes in water and alcohol solutions were calculated by modified Bjerrum method. Catalytic activity of different systems was investigated for oxidation of toluene with molecular oxygen. The catalysts were separated from reaction mixture and were recovered. Reusability of catalysts in several cycles of this reaction was tested.

2. MATERIALS AND METHODS

2.1. Materials

Poly(ethyleneimine) (PEI; M_w 65 kDa), poly(4-vinylpyridine) (PVP; M_w 160 kDa), propyl bromide, acetonitrile, toluene, trizma hydrochloride, hydrochloric acid, sodium hydroxide, nitric acid, sulfuric acid, cobalt (II) chloride, copper (II) chloride were purchased from Sigma Aldrich. Acetic acid was from Fluka. Poly(acrylic acid) (PAA; M_w 450 kDa), polysterene sulfonate sodium salt (PSS; M_w 500 kDa) were purchased from Scientific Polymer Product, Inc. Quaternized poly(4-vinylpyridine) was synthesized by the reaction of poly(4-vinylpyridine) with propane bromide in dimethylformamide solution. Monodisperse silica oxide particles with diameter of 4.0 ± 0.2 μm were purchased from Polysciences Inc. as 10 % dispersions in water. Microscope glass slides Precleaned slides with a size of 3" x 1" and a .039 -.047" thickness (76.2 x 25.4mm and a 1mm thickness) were bought from Logitech LTD and cut with Fletcher steel wheel glass cutter. All chemicals were used without any further purification. Millipore (Milli-Q system) filtered water with a resistivity 18.2 MΩ was used in all experiments.

2.2. Preparation of catalysts

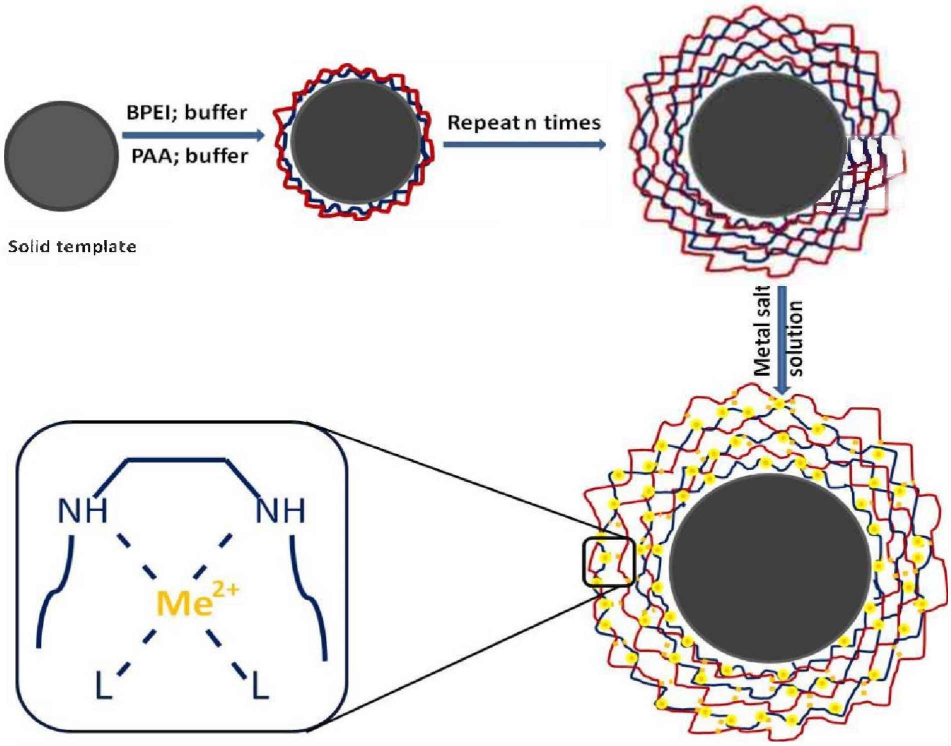
Glass slides were pre-cleaned under a quartz UV lamp for at least 2 hours, soaked in concentrated sulfuric acid for 1 hour, and then carefully rinsed with Milli-Q water. Then, the silicon wafers and glass slides were immersed in 0.25 M NaOH solution for 10 min, rinsed with water, and dried under a flow of nitrogen. Preparation of multilayers at the surface of substrates was performed using 0.3 mg/mL of polyelectrolyte solutions at pH 8.5 buffer. Polycations and polyanions were allowed to sequentially adsorb 10 minutes at the surface. Each deposition step was followed by rinsing with buffer solution at the same pH value. The BPEI/PAA film was then stabilized by thermal crosslinking in an oven at 125 °C for 1 h. Desired number of layers was deposited. To load a metal cation, multilayers films were exposed to $CoCl_2$ or $CuCl_2$ solutions (0.05 mole/L in water at pH 5.0 for 12 h) to achieve complete absorption within the films. Loading was followed by rinsing with water. Preparation of catalyst (PEI/PAA)-Me and coordination of metal cations in the multilayer are schematically illustrated in scheme 1.

2.3. Methods

Scanning electron microscope (SEM) images were obtained using Scanning Electron Microscope Auriga. Silicon wafers were glued to the SEM stage by conductive tape. Au-Pt alloy was sputtered onto the sample surfaces with RF-plasma chamber for 10 seconds. The applied voltage was varied from 1 to 3 kV. UV-visible analysis was performed on a Perkin Elmer Lambda 40 spectrometer. Atomic Force Microscopy (AFM) measurements were performed in air at room temperature using a NSCRIPTOR™ dip pen nanolithography system (Nanoink, USA) operating in AC (tapping) mode. Ellipsometry measurements were performed using a home-built, single-wavelength, phase-modulated ellipsometer at 65° of incidence. Optical properties of the substrates and oxide layer thickness were determined (2nm) prior to film deposition. In measurements of dry film thickness, the refractive index was fixed at a value of 1.5.

2.4. Catalytic activity and leaching test

Oxidation reaction of toluene was carried out during 1 h at 348 K under atmospheric pressure of O_2 in a fixed-bed U-shaped reactor charged with 10 ml of reaction mixture. The volume of the reactor is 350 ml. The reaction mixture contains toluene (0.95 mole/L) and acetonitrile (17.2 mole/L) as solvent. Kinetic regime was kept by shaking 400 times per minute. Prior to the admission of the catalyst in the reaction mixture the reactor was purged with oxygen in order to remove the air from the system. The oxygen burette and the reactor were thermostated and the temperature of the system could be regulated by controlling the temperature of the water jacket. Reaction rates were monitored by determining the oxygen consumption in the reaction mixture with a gas burette. The turn-over-frequency (TOF) was calculated as the converted number of toluene molecules per a metal atom per a second. To study the stability of catalyst the metal loaded films were shaken for 2 hours in the acetonitrile and solutions were evaporated and the residue was dissolved in the 5% nitric acid solution. The solutions were analyzed for Co(II) and Cu(II) contain, using a Varian Vista MPX inductively coupled plasma spectrophotometer (ICP-OES).



Scheme 1. Preparation of BPEI/PAA multilayers coating on solid template and metal ion`s coordination in the film

3. RESULTS AND DISCUSSION

3.1. Growth of PEMs

In order to create multilayer thin films with large amount of ligands and capable to absorb catalytic active transition metal cations such as Cu^{2+} and Co^{2+}, we explored the use of strong and weak polyelectrolytes such as poly(ethyleneimine) (PEI), quaternised poly(4-vinylpyridine) (QPVP or QX, x-quaternisation degree), poly(acrylic acid) (PAA) and polysterene sulfonate sodium salt (PSS). The polymers were chosen with the idea that they have functional groups capable to form strong complexes with metal cations. Because of ionization of weak polyelectrolytes PAA and PEI is very sensitive to local pH and the linear charge density of polymers depends on it, the layer thickness, molecular organization and amount of an adsorbed polymer chain can be controlled by simple adjustment of the pH of the dipping solution of weak polyelectrolytes. At neutral pH both of polyelectrolytes totally ionized and form highly ionically crosslinked film, with the smallest thickness. In acidic medium PAA (pKa 5.0) is partly protonated and because of low charge density forms more “loopy” conformation, in contrast when pH goes up PAA is totally charged and PEI (pKa~8.5) gradually loses charge forming thicker layer with free ammonium groups.

Poly(4-vinyl pyridine) was quaternised by propane bromide to make it soluble at alkali pH 8.5 where pyridine groups (pKa 3.5) are deprotonated and available for complexforming with metal cations. Charge density of quaternised poly(4-vinylpyridine) easily can be controlled by variation of quaternisation degree. In order to form the thickest film with large amount of free pyridine groups, 17% quaternised poly(4-vinylpyridine) was chosen, thickness of film with Q17 is almost 1.5 times more than film with Q65. The polymer with less than 15% QD is not soluble at pH 8.5 because of too small charge density on polymer molecules. PEI/PAA, PEI/PSS, Q17/PAA and Q17/PSS films were deposited at pH 8.5 in order to have large amount of free ammonium groups capable to coordinate metal cations. Figure 1 shows the dependence of dry PEMs film thickness on number of bilayers. The thickness growth shows a linear profile in all systems. The data of film thickness measured by different methods ellipsometry and AFM are in good agreement. Both polyanions PAA and PSS are fully charged at pH 8.5 and should have approximately same charge density on polymer molecules; however thickness of films with PAA is significantly higher than the one with PSS. Thickness and comformation of polyelectrolytes depend not only on charge density they also depend on the nature of polymers. Earlier it was shown by Sukhishvili et al. (2006) that polycations bind stronger with SO_3^- and SO_4^--containing polyanions than polymers with carboxilate groups.

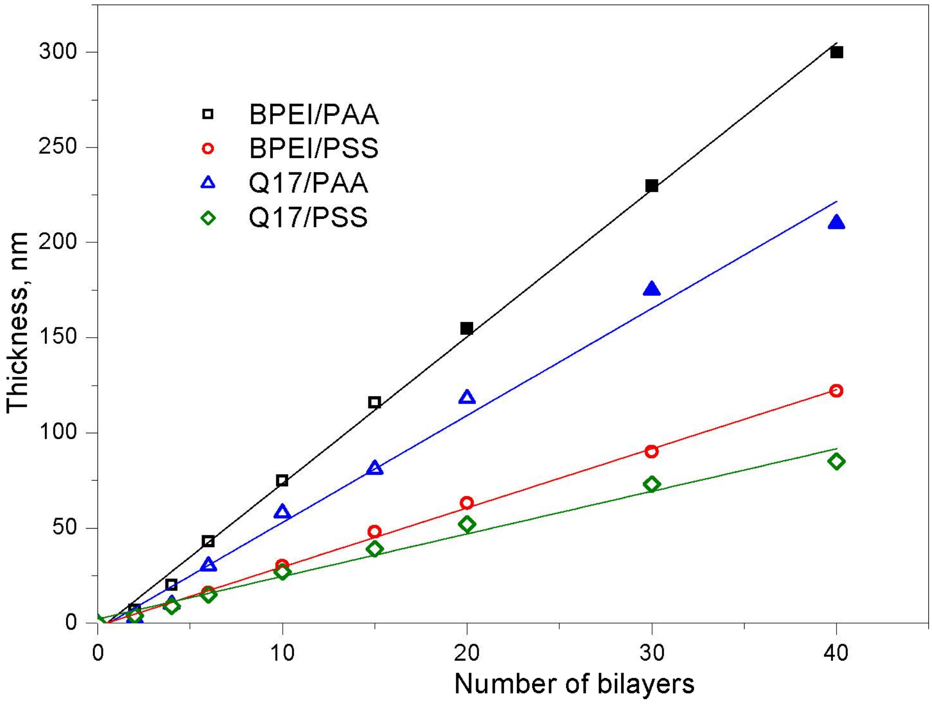


Fig. 1. Thickness of dry LbL films of BPEI/PAA (squares), BPEI/PSS (circles), Q17/PAA (triangles), Q17/PSS (diamonds) as an increase of bilayers number. Thickness measured by elipsometry (open symbols) and AFM (filled symbols). In the all systems layers deposited from 0.01M trizma buffer solutions at pH 8.5

3.2. Binding Me^{2+} with PEMs films

The metal cations were absorbed from water solution of diclorocopper and diclorocobalt at pH 5.0 for 10 hours by PEMs. Positively charged metal cations could be electrostatically bound within carboxylic or sulphate groups and/or covalently attached into aminocomplexes. In the case of QPVP/PAA and QPVP/PSS films Co^{2+} and Cu^{2+} were loaded from alcohol solution of salt since very small amount of metal ions was absorbed from water solution. Figure 2 presents the ACM images and photography of bare and $(BPEI/PAA)_8$, $(Q17/PAA)_8$, $(BPEI/PSS)_8$ deposited SiO_2 particles with size 4±0.2 microns. One can see that particles were covered uniform and smooth by BPEI/PAA and Q17/PAA multilayers, while BPEI/PSS coated SiO_2 particles are stacked together and not uniform.

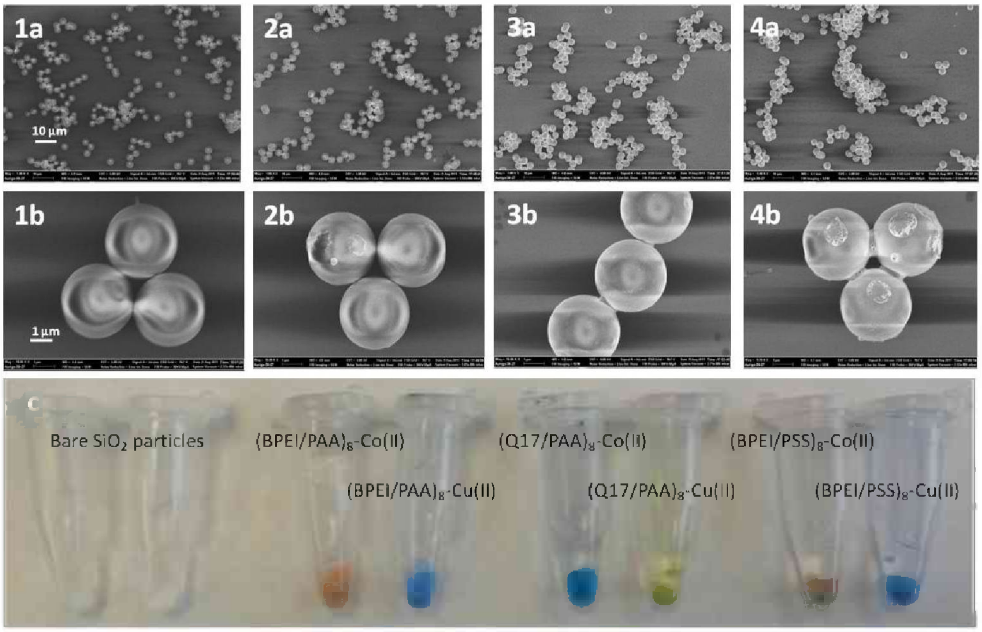


Fig. 2. SEM images (a, b) and picture (c) of bare (1a,b) and $(BPEI/PAA)_8$ (2a,b), $(Q17/PAA)_8$ (3a,b), $(BPEI/PSS)_8$ (4a,b) deposited SiO_2 particles with size 4±0.2 microns

Metal loaded BPEI/PAA films deposited at pH 8.5 on glass slides are transparent and have colors of water-soluble blue BPEI-Cu^{2+} (710nm) and brown BPEI-Co^{2+} (523nm) complexes and same UV-vis. absorption maximum (Figure 3). It means that multilayers deposited at alkali medium contains mostly BPEI-Me binds. QPVP/PAA-Me multilayers are also transparent and can be examined by UV-vis. spectroscopy. QPVP/PAA-Co^{2+} and QPVP/PAA-Cu^{2+} films have an absorption maximum at 695nm and 945nm respectively, which also belong to solution of $CoCl_2$ and $CuCl_2$ in alcohol.

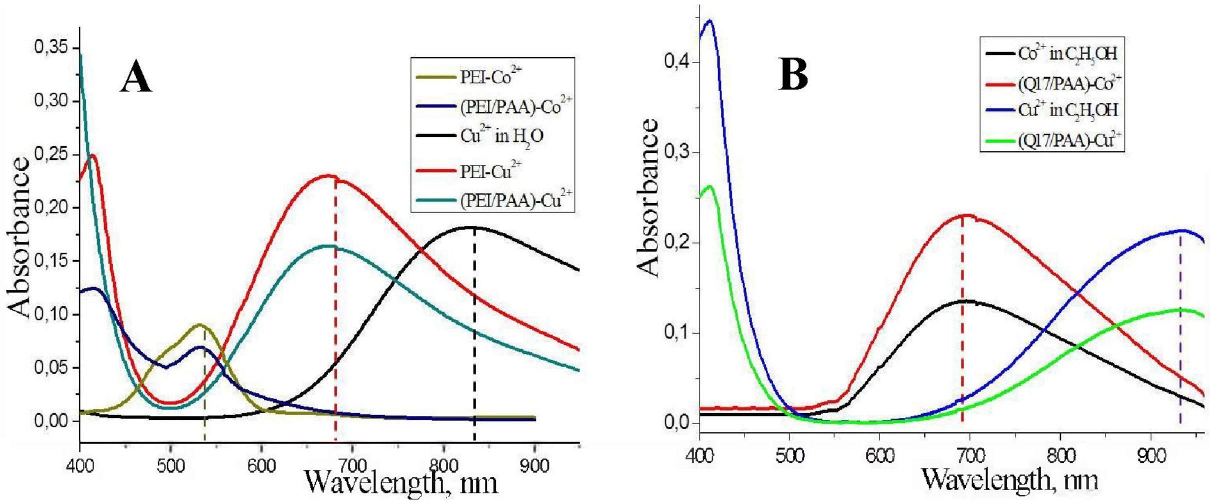


Fig. 3. UV-vis. absorption of metal salt solutions and metal loaded BPEI/PAA (A) and Q17/PAA (B) multilayers. Films are deposited at pH 8.5.

λ_{max}(BPEI/PAA-Co^{2+}) = 523nm; λ_{max}(BPEI/PAA-Cu^{2+}) = 690nm; λ_{max}(Q17/PAA-Co^{2+}) = 695nm; λ_{max}(Q17/PAA-Cu^{2+}) = 930nm

Figure 4 demonstrates the difference of contents of coordinated copper and cobalt ions in the multilayer films formed from same polycations and different polyanions as PAA or PSS. All of PEMs were deposited at pH 8.5 and metal cations were loaded at pH 5.0 to BPEI/PA films from salt solution in water and to QPVP/PA films from salt solution in alcohol. We compared the films with same amounts of bilayers. In order to all of films deposited at same pH, in the case of different polyanions the amount of absorbed BPEI or Q17 should be approximately similar. One can see the coordination of metal cations in the PEMs also depends on the nature of polyanions. We suggested before that at pH 8.5 PAA is highly charged and layers of PAA and strong polyacid PSS are relatively thin. However the amount absorbed metals in the films with PAA larger than in the one with PSS. It might be explained that the linear charge of PSS molecules is high and layers are thin and there is not much free sulphate groups for binding metal cations. In the systems Q17/PAA and Q17/PSS where metal cations were loaded from alcohol solutions of salt, the difference is greater. It might be because of insolability of PSS in ethanol and difficulty of metal binding. According to these data we can make a conclusion, that even PEMs deposited at basic pH contain more polycations than polyanions, polyanions are also take part in the metal coordination and carbocylic groups are more likely than sulphate groups. The PEMs Q17/PSS have very small amount of metal cations and we did not use this system for further studies.

3.4. Stability of catalyst and stability constants of polymer-metal complexes

The stability of immobilized catalyst is also important factor in heterogeneous catalysis. The Figure 5 shows the degree of leachability of metal cations in the BPEI/PAA, Q17/PAA and BPEI/PSS PEMs films in three cycles of shaking in reaction condition. The solutions after each cycle of catalytic reaction were tested by ISP OES method and leachability was calculated as percentage of leached metal to the total amount of metal in the PEMs. In all of the systems during cycle of reaction degree of leaching was less than 10%, less than 2% in second cycle and metal cations stood stable in PEMs within further cycles of reaction. The system Q17/PAA-Me has the lowest stability. 9% of copper and 7% cobalt ions were leached during first cycle of reaction. According to the stability constants of polycation-Me complexes given in the Table 1 the stability of Q17-Me complexes are lower than BPEI-Me complexes.

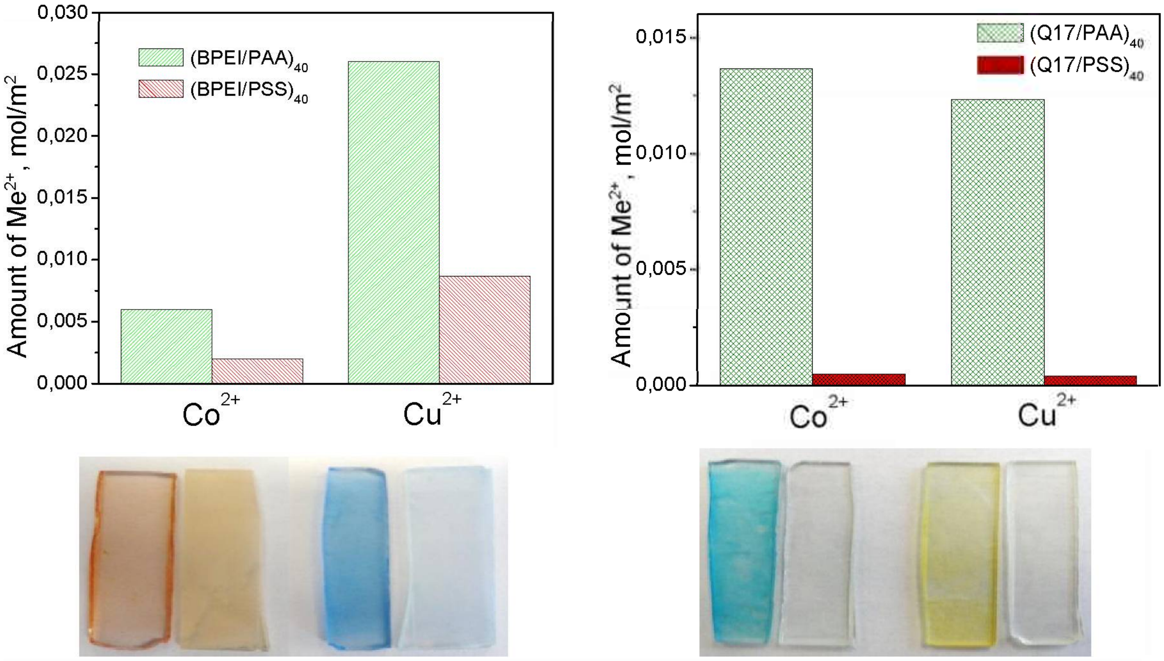


Fig. 4. Role of the type of polyanions on the amount of absorbed metal cations in the PEMs films. In the all systems PEMs deposited from polymer solutions at pH 8.5. Metal concentration was calculated by UV-vis. absorption. Snapshot of corresponding metal loaded films deposited on glass slides.

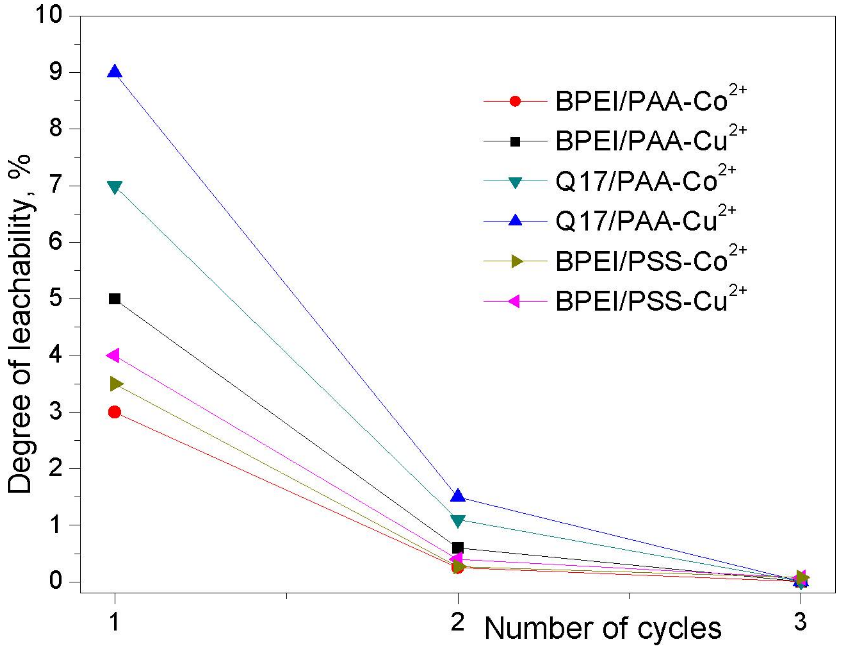


Fig. 5. Leachability of Co^{2+} and Cu^{2+} during several cycles of reaction

Table 1. Thermodynamic characteristics of complex forming processes in polymer - Me^{2+} systems in water and alcohol

Polymer-metal complexes	Stability constant of polymer-metal complexes	
	In water	In alcohol
BPEI-Co^{2+}	$2.82 \cdot 10^{25}$	$1.86 \cdot 10^{28}$
BPEI-Cu^{2+}	$2.10 \cdot 10^{17}$	$5.89 \cdot 10^{18}$
Q17 -Co^{2+}	$5.69 \cdot 10^{18}$	$7.94 \cdot 10^{23}$
Q17-Cu^{2+}	$9.01 \cdot 10^{12}$	$3.09 \cdot 10^{15}$

3.5. Examination of the catalytic activity

The oxidation of hydrocarbons with molecular oxygen catalyzed by transition metal complexes is more attractive and challenging; due to oxygen is clean, cheep and readily available oxidant. The use of molecular oxygen in place of other oxidants is highly desirable on economical and environmental points of view. However, oxygen is a weak, non-selective oxidant and suitable catalyst is required to activate oxygen. Here characterization of catalytic effect of immobilized copper and cobalt complexes in PEMs as $(PEI/PAA)_{30}$, $(Q17/PAA)_{30}$ and $(PEI/PSS)_{30}$ was performed using a reaction of toluene oxidation by molecular oxygen in atmospheric pressure and relatively low temperature 75^0C. On the base of FTIR and gas chromatography analysis it was found that the main product of oxidation reaction of toluene with oxygen is benzaldehyde. The result of oxidation experiments is summarized in table 2. It is interesting to note that the systems $(PEI/PAA)_{30}$–Me and $(Q17/PAA)_{30}$–Me have better kinetic characterizations for this reaction than $(PEI/PSS)_{30}$–Me, which could be explained as influence of polyanion since PSS deactivates the metal complexes as catalyst. Catalysts on the base of cobalt are almost twice more active than the one with copper.

Table 2. Maximum rate (Wo_2), yield and TOF of toluene oxidation reaction during 1 h catalyzed by different systems

Systems	$Wo_2 \cdot 10^{-5}$, mole/(L·sec)	Yield (1h, %)	TOF
$(PEI/PAA)_{30} – Co^{2+}$	2.54	3.5	527
$(PEI/PAA)_{30} – Cu^{2+}$	2.20	3.3	315
$(PEI/PSS)_{30} – Co^{2+}$	1.25	1.3	48
$(PEI/PSS)_{30} – Cu^{2+}$	0.72	1.5	27
$(Q17/PAA)_{30} – Co^{2+}$	1.48	2.6	298
$(Q17/PAA)_{30} – Cu^{2+}$	1.65	1.7	196

This indicates that the oxidation reaction seems to be catalyzed only by metal complexes in the outermost layers. After completion of the reaction, the catalysts were separated by filtration, washed with acetonitrile, dried and then reused for another cycle with the fresh reaction mixture. The system $(PEI/PAA)_{30}$–Co^{2+} shows a good recoverable properties and the TOF decreased to 490, 475, 462 and 447 within second, third, fourth and fifth cycles of reactions respectively. $(Q17/PAA)_{30}$–Me systems demonstrate high kinetic properties for oxidation of toluene but their activity decreased dramatically after first reaction, TOF=18 for $(Q17/PAA)_{30}$–Co^{2+} in second cycle, may be in order to weak stability of QPVP-Me complexes and rearrangement during the reaction.

4. CONCLUSIONS

The above presented results lead to the conclusion that the alternative LbL deposition of polyelectrolytes on solid template followed by covalently biding with transition metal ions provides a new method for creating a recyclable catalyst with large surface area. It was found that the amount of impregnated metal ions, their stability within PEMs and catalytic activity depend on the nature of both metal and polyelectrolytes. The highest catalytic activity and effective reusability were performed by using PEI/PAA-Co^{2+} system. The differences of activity between the immobilized cobalt and copper complexes in various PEMs may be a consequence of the different susceptibility for oxidation-reduction of the central transition metal ion. On the other hand, the different interactions of metal cations with the supporting polymer may influence in some cases the distribution of the bases sites. The facile synthesis of catalysts, the simplified reaction and the ease of recycling and isolation procedure make them an attractive alternative to current methodologies.

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