Semi-Interpenetrating Hydrogels of Polyelectrolytes, Polymer-Metal Complexes and Polymer-Protected Palladium Nanoparticles

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Summary: Semi-interpenetrating hydrogels (SIHs) of polyelectrolytes consisting of poly(acrylamide) hydrogel (PAAH) as matrix and sodium poly(styrenesulfonate) (NaPSS), poly(N,N′-dimethyl-N,N′-diallylammonium chloride) (PDMDAAC), stoichiometric interpolyelectrolyte complex of NaPSS-PDMDAAC, and linear polyethyleneimine-metal complexes (PMC) as well as polymer-protected palladium nanoparticles were prepared by *in situ* polymerization, e.g. crosslinked acrylamide chains were formed in aqueous solutions of NaPSS, PDMDAAC, NaPSS-PDMDAAC (1:1 mol/mol), PMC and palladium nanoparticles protected by poly(N-vinylpyrrolidone) (PVP), poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), and linear poly(ethyleneimine) (LPEI) respectively in the presence of N,N′-methylenebisacrylamide. For each system the equilibrium swelling degree α and the parameters n and k describing the mechanism of water transport into SIHs volume was determined. Catalytic properties of SIHs were studied in allyl alcohol hydrogenation and cyclohexane oxidation reactions.

Keywords: hydrogenation of allyl alcohol; immobilization; oxidation of cyclohexane; polyelectrolytes; polymer-metal complexes; polymer-protected metal nanoparticles; semi-interpenetrating hydrogels

Introduction

Semi-interpenetrating hydrogels (SIHs) are systems consisting of hydrogels within the volume of which linear water-soluble polymers, polymer-metal complexes and polymer-protected metal nanoparticles are embedded.[1–3] Authors[4] synthesized pH switching "on-off" SIHs of crosslinked poly(acrylamide-*co*-acrylic acid) and linear polyallylammonium chloride. A series of SIHs composed of poly[(acrylamide)-*co*-(sodium acrylate)] and poly[(vinylsulfonic acid), sodium salt],[5] chitosan and poly(diallyldimethylammonium chloride)[6] were studied. Some examples of amphoteric SIHs preparation were reported by authors.[7–9] The SIHs can also be obtained by interpolymer reactions, e.g. by interaction of ionic or nonionic polymer gels with linear macromolecules at the gel-solution interface.[10] Immobilization of polymer-metal complexes and metal nanoparticles stabilized by water-soluble polymers into hydrogel volume is perspective to design the catalytic systems that enhance the reactions of decomposition, hydrogenation, oxidation, isomerization etc.[11–13] SIHs are able to change the size, form and morphology continuously or discontinuously in dependence of such environmental factors, as temperature, pH medium, ionic strength and mixture of water-organic solvents.[14–16] This in its turn allows to tune the structure and properties of immobilized into the

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hydrogel matrix polymer-metal complexes and nanoparticles and consequently to regulate and control their architecture as well as catalytic behavior. The present paper is devoted to preparation, characterization and catalytic properties of semi-interpenetrating hydrogels based on crosslinked acrylamide and some linear polyelectrolytes, linear polyethyleneimine-metal complexes and palladium nanoparticles protected by hydrophilic polymers.

Experimental Part

Materials and Methods

Acrylamide (AAm), N,N-methylenebisacrylamide (MBAAm), and ammonium persulfate (APS), linear poly(ethyleneimine) (LPEI) with $M_n = 25 \cdot 10^3$, sodium poly(styrenesulfonate) (NaPSS) with $M_w = 500 \cdot 10^3$, poly(N,N′-dimethyl-N,N′-diallylammonium chloride) (PDMDAAC), $M_w = 219 \cdot 10^3$, poly(N-vinylpyrrolidone) (PVP) with $M_w = 40 \cdot 10^3$, poly(vinyl alcohol) (PVA) with $M_w = 100 \cdot 10^3$ and poly(acrylic acid) (PAA) with $M_w = 450 \cdot 10^3$ are the products of Aldrige were used without additional purification. Reagent-grade metal salts $Ni(NO_3) \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $FeCl_3 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$, $MnCl_2$ and $PdCl_2$ were used. Allyl alcohol, ethanol, acetone, cyclohexane and acetonitrile were purified by distillation. Identification of cyclohexane and its oxidative products was provided with the help of gas chromatograph "Crystal 2000-M" (Russia). Product quantification was carried out using calibration curves obtained with standard solutions of cyclohexane, cyclohexanone, and cyclohexanol. SEM pictures of hydrogel samples preliminary covered by gold-platinum mixture on the "SCD 050" were obtained with the help of electron microscope "Hitachi S-4800" (Japan).

Preparation of SIHs Based on PAAH and Linear Polyelectrolytes

Reaction mixture consisting of AAm (500 mg), 5 mL aqueous solution of NaPSS (100 mg), MBAA (10 mg), and APS (5 mg) was thoroughly stirred to obtain homogeneous solution, bubbled by nitrogen gas during 10 min to remove the dissolved oxygen. The reaction mixture was placed into plastic syringe with closed outlet at the bottom and thermostated at 60 °C during 30 min. In other series of experiments instead of NaPSS, 5 mL aqueous solution of PDMDAAC (100 mg) or preliminary dissolved in aqueous solution of NaBr stoichiometric interpolyelectrolyte complex of NaPSS-PDMDAAC (100 mg) was used. All prepared samples were washed out periodically by distilled water during 1 week and dried in vacuum to constant mass at room temperature.

Preparation of Polymer-Protected Palladium Nanoparticles

Palladium nanoparticles protected by hydrophilic polymers were prepared by procedure described in.[17,18] For this 1.35 mmol of PVP (PVA, LPEI, PAA) and 0.033 mmol of $PdCl_2$ powder were dissolved in the mixture of water (25 mL) and ethanol (25 mL) and boiled at 333 K during 4 h till the formation of brown solution.

Immobilization of Colloidal Palladium Particles within Acrylamide-Based Gel Matrix

AAm (350 mg), MBAAm (20 mg), and APS (20 mg) were dissolved in 5 mL of colloid solution of palladium protected by PVP (or PVA, LPEI and PAA) under stirring. The amount of Pd nanoparticles in 5 mL of colloid solution corresponds to $3.3 \cdot 10^{-3}$ mmol or 0.35 mg. Polymerization reaction was carried out at 343 K during 30 min. The obtained monolith samples were periodically washed out by distilled water during 1 week to remove the sol fractions. Then the washed out hydrogel samples were dried in vacuum oven up to constant mass. The dried samples were thin powdered and kept in vacuum oven.

Preparation of Hydrogel-immobilized LPEI-Metal Complexes

LPEI-metal complexes were prepared by addition of aqueous solution of selected metal salts to aqueous solution of LPEI at the molar ratio of reacting components [LPEI]:[metal salts] = 6:1 mol/mol. For instance, 0.71 mL of aqueous solution of $CuSO_4 \cdot 5H_2O$ (C = 0.1 mol/L) was dropwise added to 4.29 mL of aqueous solution of LPEI (C = 0.1 mol/L) under stirring. No precipitation of LPEI-metal complexes was observed. In order to prepare hydrogel samples, the AAm (400 mg) and MBAA (20 mg) were thoroughly dissolved in 2 mL of water, then to this mixture 2 mL of aqueous solution of preliminary prepared LPEI-metal complexes and 10 mg of APS were added. The reaction mixture with total volume 4 mL and consisting of AAm, MBAA, LPEI-metal complexes and APS was bubbled with nitrogen during 10 min to remove the dissolved oxygen and then transferred to plastic syringe with diameter 1 cm and length 5 cm. Polymerization reaction was carried out at 333 K during 30 min. The obtained monolith samples were washed out, dried and powdered as described in previous section. Further the LPEI-metal complexes immobilized within PAAH are designated as PAAH/LPEI-metal complexes (where metal ions are Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Pd^{2+}, Fe^{3+}, Cr^{3+}).

Equilibrium and Dynamic Swelling Experiments

The swelling degree of SIHs was determined gravimetrically by formula $\alpha = m\text{-}m\ _0/m_0$ (where m and m_0 are the masses of swollen and dried gels respectively). The gravimetric experiments were performed with cylindrical gel samples with diameter and length 1 cm (mass ca. 600–650 mg). The weighing process was performed three times and the average weight was taken for calculation. Gel samples were carefully taken out from the solution and the excess of liquid from the gel surface was gently removed with filter paper. To exclude the evaporation of solvents from the gel volume, samples were weighed in closed vials. The errors in all gravimetric experiments did not exceed ±5%. The dynamic swelling behavior of the SIHs in aqueous solutions was measured according to procedure.[19] The swelling rate was expressed as $kt^n = M_t/M_\infty$, where k is the swelling rate constant, n is a characteristic exponent describing the mode of the penetrant (e.g. water) transport mechanism, t is the absorption time, M_t is the mass of water absorbed at time t, M_∞ is the mass of water absorbed at infinite time t_∞. The constants k and n were calculated from the slopes and intercepts of the plots of $\ln(M_t/M_\infty)$ versus $\ln t$ for M_t/M_∞ less than 0.6.

Hydrogenation of Allyl Alcohol by Polymer-Protected and Gel-Immobilized Palladium Nanoparticles

Hydrogenation of allyl alcohol was carried out in catalytic reactor at atmospheric pressure of hydrogen. 30 mg of thin powders of catalyst were dispersed in 20 mL of water and put into catalytic reactor and the system was blown by hydrogen during 1 min to remove the air from the reaction vessel. Then the catalyst was shaken and saturated by hydrogen during 30 min. 0.3 mL allyl alcohol was added into catalytic reactor taking into account that this amount of substrate corresponds to full reaction with 100 cm^3 of hydrogen. The reaction rate was measured by volumetric method, e.g. by calculating the reacted amount of hydrogen with allyl alcohol. For each experiment the amount of Pd nanoparticles in 30 mg of catalyst used for hydrogenation of allyl alcohol did not exceed 0.35 mg.

Cyclohexane Oxidation by Hydrogel-immobilized LPEI-Metal Complexes

Oxidation of cyclohexane was carried out in catalytic reactor at atmospheric pressure and 313 K. 30 mg of thin powder of catalyst was dispersed in 1.2 mL of acetonitrile, then 0.3 mL of cyclohexane was added. To this mixture 0.9 mL of hydrogen peroxide (30 wt. %) was added and the reaction mixture was stirred by magnetic stirrer. The oxidation reaction proceeded during 3 h.

Results and Discussion

Immobilization of Polyelectrolytes, LPEI-metal Complexes and Polymer-Protected Palladium Nanoparticles within PAAH Matrix

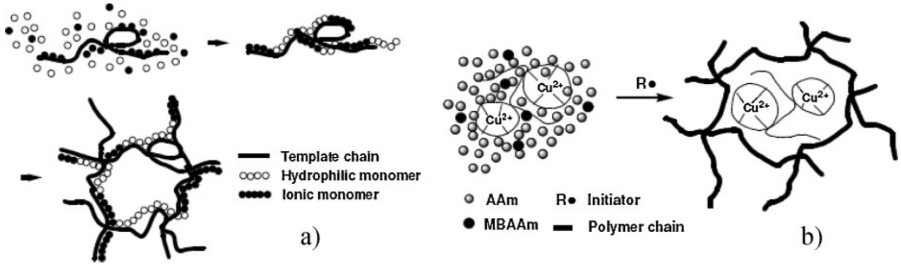
Template (co)polymerization is widely used for synthesis of SIHs.[4] In this case ionic monomers are preadsorbed by template through electrostatic interaction while neutral monomers are randomly distributed in reaction medium without interaction with template (Scheme 1). The resulting systems are composed of crosslinked network and linear template which interpenetrate each other to form SIHs. The network contains both covalent and ionic bonds. The covalent bonds retain the three-dimensional structure of hydrogel and the ionic bonds bring in the hydrogel the higher mechanical strength and stimuli-sensitivity. Immobilization of polyelectrolytes, LPEI-metal complexes or polymer-protected palladium nanoparticles within hydrogel matrix proceeds in the course of radical polymerization and simultaneous crosslinking of AAm as shown in Scheme 2.

Dynamic Swelling Properties of SIHs

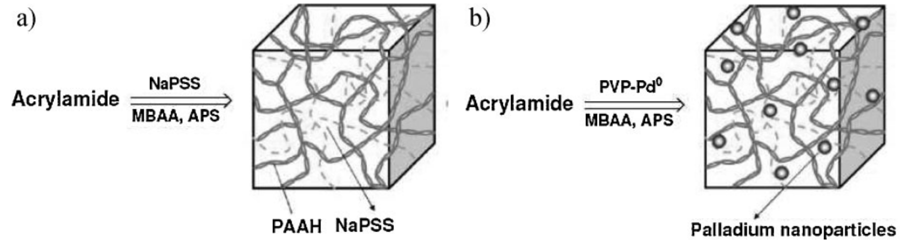
The swelling behavior of SIHs depends on network structure and nature of embedded macromolecules. Coulomb interactions or hydrogen bonds arising between the gel matrix and functional polymers have crucial effect and lead to high sensitivity and reversibility to external stimuli. Dynamic swelling curves of PAAH/LPEI-metal complexes in water are shown in Figure 1. The equilibrium swelling degree (α) of hydrogels changes in the following order: PAAH/LPEI-Fe^{3+}>PAAH/LPEI-Cr^{3+}>PAAH/LPEI-Ni^{2+}>PAAH/LPEI-Cu^{2+}>PAAH/LPEI-Co^{2+}>PAAH/LPEI-Mn^{2+}>PAAH/LPEI-Pd^{2+}. According to[19] the dynamic swelling behavior of hydrogels depends on the relative contribution of penetrant diffusion and relaxation of crosslinked polymer chains. A value of $n = 0.5$ corresponds to Fickian diffusion, e.g. the process is diffusion controlled, whereas transport is considered to be relaxation controlled for $n = 1$ and as anomalous when the value of n lies between 0.5 and 1. Table 1 summarizes the values of α and n and k that reflect the mode of water transport mechanism and the swelling rate constant respectively.

It is seen that the diffusion of water into the SIHs volume of PAAH/NaPSS, PAAH/PDMDAAC, PAAH/NaPSS-PDMDAAC, and PAAH/LPEI-Cr^{3+} is close to relaxation-controlled mechanism, e.g. $n \approx 1$ (Table 1).

For the most SIHs the values on n are close to 0.5 and correspond to Fickian diffusion. An anomalous swelling mechanism is observed for PAAH/LPEI-Fe^{3+} and PAAH/LPEI-Co^{2+} for which the values of n are equal to 0.85 and 0.84 respectively. This type of diffusion indicates that for these gels the rate of diffusion overtakes the rate of relaxation of the polymer chains, whereas it is reverse for the Fickian type of diffusion. The photos of PAAH samples containing the LPEI-metal complexes and polymer-protected palladium nanoparticles are shown in Figure 2.



Scheme 1.
Schematic representation of template (co)polymerization and formation of SIHs structure with embedded linear polyelectrolytes (a) and LPEI-metal complexes (b).



Scheme 2.
Spatial structure of PAAH-immobilized NaPSS (a) and PVP-protected palladium nanoparticles (b).

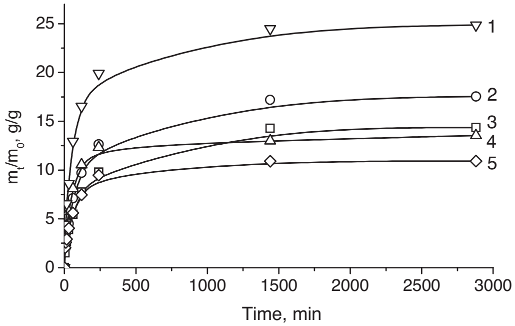


Figure 1.
Swelling kinetics of PAAH/LPEI-metal complexes (curves 1, 2, 4, 5) and PAAH (curve 3) in water. 1 – PAAH/LPEI-Fe^{3+}, 2 – PAAH/LPEI-Ni^{2+}, 4 – PAAH/LPEI-Cu^{2+}, 5 – PAAH/LPEI-Pd^{2+}.

Hydrogenation of Allyl alcohol by PAAH-Immobilized and Polymer-Protected Palladium Nanoparticles

Embedding of colloidal particles protected by hydrophilic polymers within the three-dimensional structure enables to reach the high stability and activity of gel-immobilized catalysts in the course of allyl alcohol hydrogenation. The role of hydrophilic polymers in this system is to stabilize the Pd nanoparticles and to prevent their aggregation, while the role of hydrogel matrix is restriction of diffusion of nanoparticles both inside of and outside from the gel matrix. SEM micrographs show spherical structures on the surface of the gel matrix (Figure 3). These spheres with diameter of about 60 nm can be related to PVP-stabilized spherical Pd nanoparticles or particle aggregates according to Scheme 2b.

Table 1.
Equilibrium swelling degree α and parameters of n and k calculated for various SIHs.

SIHs	α, g/g	n	$k \cdot 10^2$
PAAH/NaPSS	12.0	0.95	5.3
PAAH/PDMDAAC	10.1	0.90	7.1
PAAH/NaPSS-PDMDAAC (1:1 mol/mol)	11.7	1.00	4.1
PAAH/LPEI-Fe^{3+}	25.0	0,85	2.2
PAAH/LPEI-Cr^{3+}	17.7	0,94	4.3
PAAH/LPEI-Ni^{2+}	17.3	0,47	6.0
PAAH	14.3	0,49	5.0
PAAH/LPEI-Cu^{2+}	13.5	0,52	7.3
PAAH/LPEI-Co^{2+}	12.9	0,84	1.1
PAAH/LPEI-Mn^{2+}	11.1	0,47	8.6
PAAH/LPEI-Pd^{2+}	11.0	0,44	8.4
PAAH/PVP-Pd^{o}	22.0	–	–
PAAH/LPEI-Pd^{o}	20.0	–	–

Catalytic activity of hydrogel-immobilized catalysts in the course of allyl alcohol hydrogenation passes through the well-defined maximum (Figure 4). This is accounted for involvement at first the surface parts of gel-immobilized catalysts in the hydrogenation reaction. The further gradually decreasing of catalytic activity

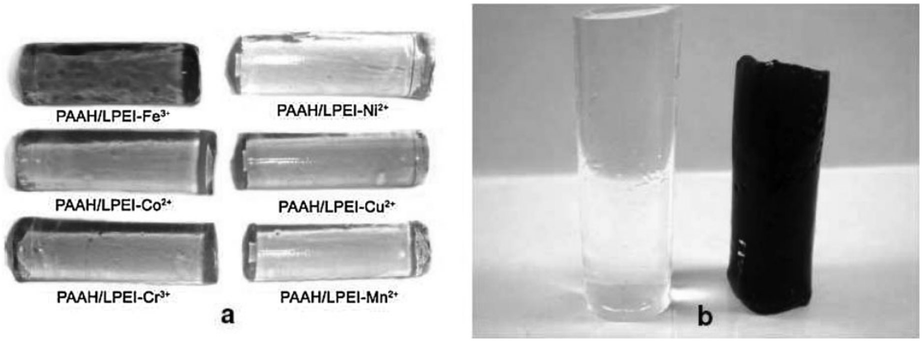


Figure 2.
PAAH samples containing the LPEI-metal complexes (a) and LPEI-Pd^0 nanoparticles (b).

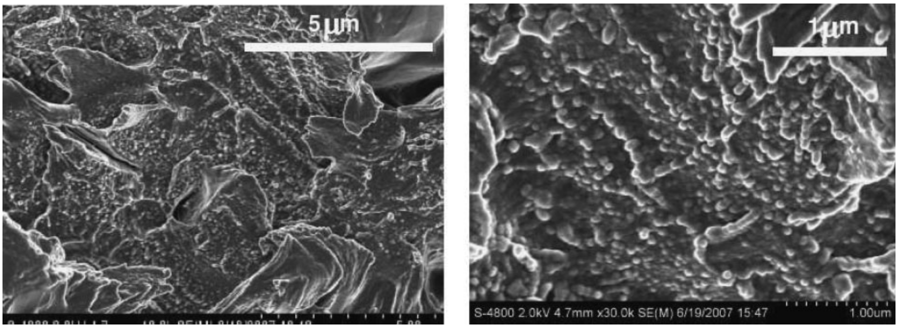


Figure 3.
SEM pictures of PVP-protected Pd nanoparticles within the PAAH matrix.

may be the result of restriction of allyl alcohol diffusion to gel volume due to step by step shrinking of hydrogels in the medium of water-alcohol that is permanently enriched by hydrogenation product – propanol.The catalytic activity of gel-immobilized Pd^0 catalysts increases in the following order: PAAH/PVA-Pd^0 >

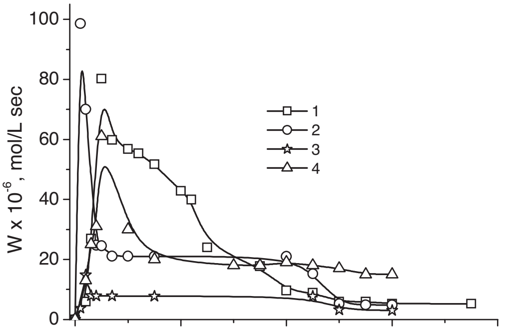


Figure 4.
Kinetic curves of allyl alcohol hydrogenation in water in the presence of Pd nanoparticles protected by PVP (1), PVA (2), LPEI (3), PAA (4) and immobilized into the PAAH matrix. $T = 40\,^{\circ}C$, $P_{H_2} = 1$ atm.

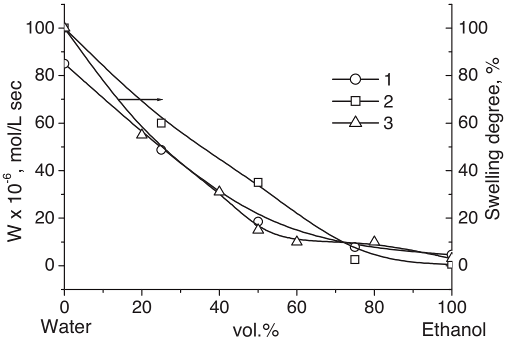


Figure 5.
Dependences of hydrogenation rate (1, 2) and swelling degree (3) of hydrogel-immobilized catalysts on composition of water-ethanol mixture. PAAH/PVP-Pd^0 (1, 3) and PAAH/PVA-Pd^0 (2).

PAAH/PVP-Pd^0 > LPEI-Pd^0 > PAAH/PAA-Pd^0. The catalytic activity of PAAH/LPEI-Pd^0, PAAH/PVP-Pd^0 and PAAH/PVA-Pd^0 catalysts preserved up to hydrogenation of 6, 10 and 12 sequential portions of allyl alcohol. To evaluate the stability of gel-immobilized catalyst in hydrogenation of allyl alcohol the so-called turnover number (TON), that is moles of substrate that a mole of catalyst can convert before inactivation, was calculated. The value of TON calculated for PAAH/PVP-Pd^0 was equal to 10^4. This indicates a stable and moderate long-lived catalyst.

The catalytic activity of hydrogel-immobilized catalysts gradually decreases with increasing of ethanol content in water-ethanol mixture (Figure 5). These results are in good agreement with the volume-phase transition of hydrogel matrix in water-ethanol mixtures. Therefore, one can conclude, that the increasing of ethanol content in the water-ethanol mixture leads to gel contraction and consequently diminish the gel pore size, and restricts the diffusion of substrate to catalytic sites of hydrogels. Examples of catalytic system acting by "on-off" mechanism are hydrogels of (co)-N-isopropylacrylamide which reversibly swells or shrinks in water-ethanol mixture[16] or reversibly turns first "off" and then "on" as the temperature is first raised and then lowered.[12] As seen from Figure 6 after hydrogenation of sequential portions of allyl alcohol the amount of Pd nanoparticles on the surface of gel matrix is considerably reduced. This is probably due to leaching out of Pd nanoparticles in the

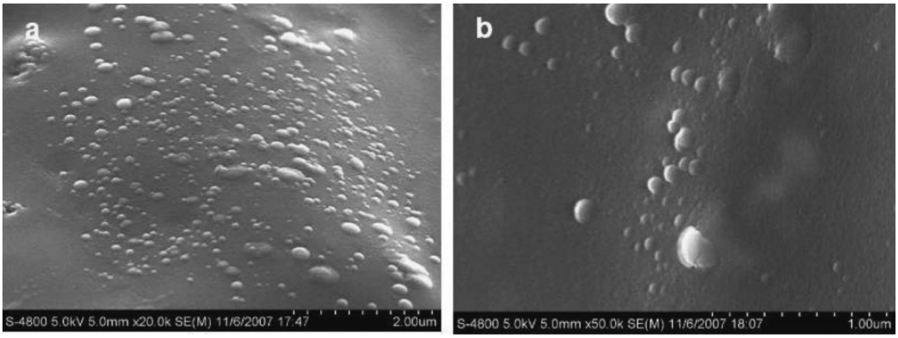


Figure 6.
SEM pictures of PVP-protected Pd nanoparticles within the gel matrix of PAAH after hydrogenation of the first (a) and twelfth (b) successive portions of allyl alcohol.

course of hydrogenation reaction. The average size of Pd nanoparticles is less than 100 nm although the bigger aggregated particles are observed.

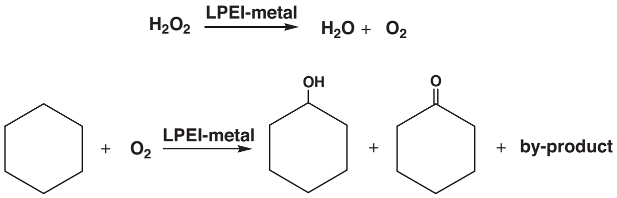
Catalytic Properties of PAAH/LPEI-Metal Complexes in Cyclohexane Oxidation

Hydrogen peroxide is considered as an ideal ‘‘green’’ oxidant due to its high oxidizing ability and lack of toxic by-products. Oxidation of cyclohexane by hydrogen peroxide in the presence of hydrogel-immobilized LPEI-metal complexes proceeds in two stages (Scheme 3).

In the first stage the decomposition of H_2O_2 takes place then the oxidation of cyclohexane occurs. Both hydrogen peroxide decomposition and cyclohexane oxidation reactions are accelerated by LPEI-metal complexes. The difference between the consumed volume of oxygen in the absence and presence of PAAH/LPEI-Cu^{2+} is in favor of cyclohexane oxidation by H_2O_2 (Figure 7).

Taking into account the catalytic properties of polyethyleneglycol-Co^{2+} and polyurethane-Co^{2+} complexes as example of liquid-phase oxidation of hydrocarbons (phenanthrene, tetralin, cyclohexene)[20,21], the following mechanism of cyclohexane oxidation for our catalytic systems can be adopted. As illustrated in Scheme 4, during the catalysis of cyclohexane oxidation, transition metal ions that are in coordination environment of ethyleneimine units interact with the molecular oxygen. As a result a partly breaking of the nitrogen-metal bonds may occur. Then the activated molecular oxygen reacts with the substrate (cyclohexane) to form cyclohexyl hydroperoxide (CHHP).

It was reported[22,23] that CHHP is the intermediate product of the cyclohexane oxidation and its formation is the rate-determining step. Two mechanisms exist for CHHP rapid decomposition: heterolytic (CHHP → cyclohexanone) and homolytic (CHHP → cyclohexanol). In addition,



Scheme 3.
Cyclohexane oxidation by hydrogel-immobilized LPEI-metal complexes.

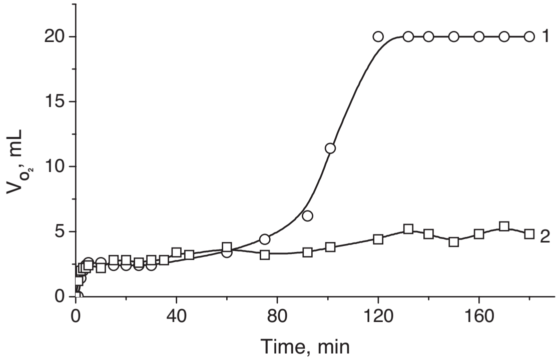
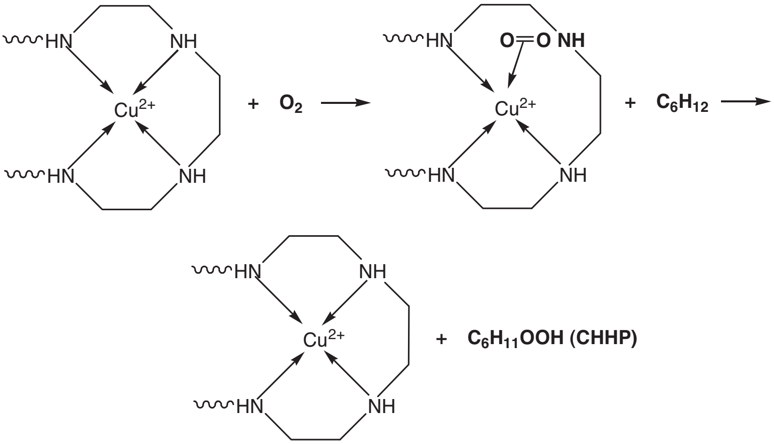


Figure 7.
Consumption of oxygen in the course of cyclohexane oxidation by H_2O_2 in the absence (1) and presence (2) of PAAH/LPEI-Cu^{2+} catalyst.



Scheme 4.
Schematic representation of cyclohexane oxidation mechanism with participation of LPEI-Cu^{2+} complex.

cyclohexanol is more active than cyclohexane under reaction conditions and can be converted to cyclohexanone easily. So there are two possible pathways for the products formation:

(1) CHHP → cyclohexanol → cyclohexanone
(2) cyclohexanone ← CHHP →
cyclohexanol → cyclohexanone

In order to distinguish the above pathways the results of Figure 8 and Table 2 should be taken into account.

As seen from Table 2 the catalytic systems Exhibit 1.5-3 times higher selectivity towards the ketone over the alcohol. Therefore, pathway (2) should be more reliable, that is, both heterolytic and homolytic mechanisms exist during CHHP decomposition. The conversion of cyclohexane to cyclohexanone and cyclohexanol is changed in the following order: PAAH/LPEI-Cu^{2+} > PAAH/LPEI-Cr^{3+} ≫ PAAH/LPEI-Mn^{2+} > PAAH/LPEI-Pd^{2+} > PAAH/LPEI-Co^{2+} > PAAH/LPEI-Ni^{2+} > PAAH/LPEI-Fe^{3+}. The best catalytic activities in

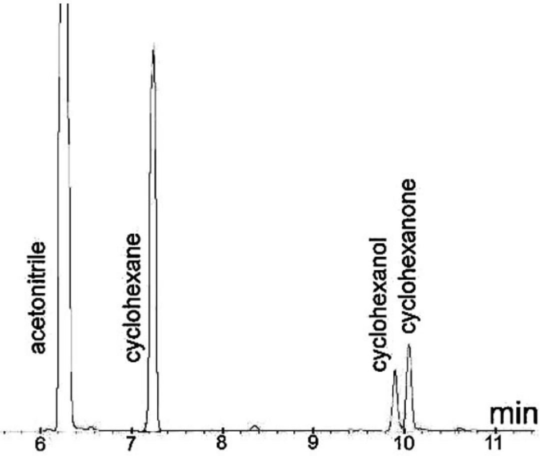


Figure 8.
Chromatogram of cyclohexane oxidation product catalyzed by PAAH/LPEI-Cu^{2+}.

Table 2.
The results of chromatographic analysis of cyclohexane oxidation products oxidated by hydrogen peroxide in the presence of hydrogel-immobilized LPEI-metal complexes.

Catalyst	Conversion, %			Selectivity, %		one/ol ratio[a]
	Total	Cyclo-hexanone	Cyclo-hexanol	Cyclo-hexanone	Cyclo-hexanol	
PAAH/LPEI-Cu^{2+}	4	1,07	0,35	26,68	8,81	3
PAAH/LPEI-Cr^{3+}	2	0,30	0,18	15,21	8,81	1.67
PAAH/LPEI-Mn^{2+}	0,8	0,13	0,07	15,74	8,95	1.86
PAAH/LPEI-Pd^{2+}	0,7	0,12	0,07	14,22	10,02	1.71
PAAH/LPEI-Co^{2+}	0,5	0,07	0,04	10,48	7,08	1.75
PAAH/LPEI-Ni^{2+}	0,4	0,21	0	52,36	0	–
PAAH/LPEI-Fe^{3+}	0,3	0,10	0,06	31,88	21,23	1.67

[a] The ratio of cyclohexanol to cyclohexanone.

oxidative conversion of cyclohexane to cyclohexanone and cyclohexanol exhibit PAAH/LPEI-Cu^{2+} and PAAH/LPEI-Cr^{3+}. In spite of low conversion degree of the PAAH/LPEI-Ni^{2+} it shows high selectivity with respect to cyclohexanone. For the rest catalysts the conversion of substrate is negligible and less than 1%.

Conclusion

Anionic and cationic polyelectrolytes and their interpolyelectrolyte complex, polymer-protected palladium nanoparticles as well as polyethyleneimine-metal complexes were immobilized into acrylamide-based hydrogel matrix. Dynamic swelling properties of hydrogels are described by Fickian and anomalous mechanism of water diffusion. The average size of Pd nanoparticles in gel volume and surface estimated by SEM is *ca.* 60 nm. The catalytic activity of hydrogel-immobilized Pd nanoparticles was studied with respect to hydrogenation of allyl alcohol. It was shown that the catalytic activity of hydrogel-immobilized catalysts passes through the well-defined maximum. The catalytic activity of gel-immobilized Pd catalysts changes in the following order: PAAH/PVA-Pd^0 > PAAH/PVP-Pd^0 > PAAH/PAA-Pd^0. Palladium nanaparticles embedded into the hydrogel volume exhibit a high catalytic stability. However the leaching out of Pd nanoparticles takes place in the course of hydrogenation of sequential portions of substrate. Good correlation between the volume-phase transition of gel matrix and catalytic activity of gel-immobilized catalysts was found in water-ethanol mixture. Hydrogel-immobilized polyethyleneimine-metal complexes exhibit catalytic activity in oxidation of cyclohexane to cyclohexanone and cyclohexanol. All tested catalysts behave 1.5-3 times higher selectivity towards the ketone over the alcohol. The best catalytic activities in oxidative conversion of cyclohexane to cyclohexanone and cyclohexanol show the linear polyethyleneimine-copper complexes immobilized into polyacrylamide gel matrix. It is suggested that cyclohexane oxidation mechanism by hydrogel-immobilized polymer-metal catalysts includes the activation of molecular oxygen by polymer-metal complexes and further formation of the intermediate product – cyclohexyl hydroperoxide (CHHP). In its turn the CHHP is converted to cyclohexanone and cyclohexanol by the pathway: cyclohexanone $\leftarrow$ CHHP $\rightarrow$ cyclohexanol $\rightarrow$ cyclohexanone.

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