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Physico-chemical and catalytic properties of polymer-protected and hydrogel-immobilized gold, silver and palladium nanoparticles

Abstract
Gold (AuNPs), silver (AgNPs) and palladium (PdNPs) nanoparticles stabilized by various hydrophilic polymers are considered. Embedding of polymer-protected AuNPs, AgNPs and PdNPs within hydrogel matrix restricts the diffusion of nanoparticles both inside of and outside of gel matrix. Catalytic properties of metal nanoparticles supported onto either metal oxides or immobilized within hydrogel matrix have been studied in model reaction – decomposition of hydrogen peroxide. The influence of catalyst amount (m_{cat}), concentration of substrate (H_2O_2) and temperature (T) was studied in order to find the optimal conditions of H_2O_2 decomposition. Examples of hydrogel-based catalytic system acting by "on-off" mechanism are demonstrated. The catalytic activity of gel-immobilized metal nanoparticles is proved to be much lower than deposited on the metal oxides due to lesser accessibility of active centers in hydrogel matrix to substrate molecules.

Keywords: Gold, silver, palladium, nanoparticles, hydrophilic polymers, hydrogel, immobilization.

Introduction

Gold (AuNPs) and silver (AgNPs) nanoparticles have attracted significant attention of researchers due to their unique optical, electrical, biomedical and catalytic properties [1-4]. A lot of polymers possessing nonionic [5-8] anionic [9], cationic [10,11] and amphoteric [12-14] nature are widely used as protecting agents of AuNPs and AgNPs in aqueous solution or organic solvents for preventing of nanoparticles aggregation [15,16] (Fig. 1).

Figure 1 - Samples of AuNPs stabilized by sodium citrate (1), by PVP with M_n = 10 kD (2), 40 kD (3) and 350 kD (4), and AgNPs protected by PVP with M_n = 40 kD in DMF (5) and DMSO (6)

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Size of poly(N-vinylpyrrolidone) (PVP) protected AuNPs ranging from 10 to 110 nm was easily controlled by varying the concentration (0.01-10 g/dL) [17] or the average-number molecular weight of PVP (M_n = 10-350 kD). Shape, size, and optical properties of the AuNPs and AgNPs are tuned by changing the employed PVP/metal salt ratio [18]. It is proposed that PVP acts as the reducing agent suffering a partial degradation during the nanoparticles synthesis. Two possible mechanisms are proposed to explain the reduction step: direct hydrogen abstraction induced by the metal ion and/or reducing action of macroradicals formed during degradation of the polymer. Initial formation of the macroradicals might be associated with the metal-accelerated decomposition of low amounts of peroxides present in the commercial polymer. Gold catalysts have recently been attracting rapidly growing interests due to their potential applicabilities to many reactions of both industrial and environmental importance [19]. Typical examples are the low-temperature catalytic combustion, partial oxidation of hydrocarbons, hydrogenation of carbon oxides and unsaturated hydrocarbons, reduction of nitrogen oxides, and so forth [20]. Recent review [21] describes the size-, shape-, structure- and composition-dependent behavior of AuNPs employed in alkylation, dehydrogenation, hydrogenation, and selective oxidation reactions for the conversion of hydrocarbons (with main emphasis on fossil resources) to chemicals. The perspectives of substituting platinum group metals for automobile emission control with gold were outlined by authors [22].

Immobilization of polymer-protected AuNPs and AgNPs within hydrogel matrix

Hydrogels are chemically stable and interlocked polymeric network retain vast amounts of water without dissolving, therefore they are feasible for preparation of metal nanoparticles in situ and readily applicable in the catalysis of various aquatic and non-aquatic reactions. The functional groups in the hydrogel network can act as both chelating and capping agents for metal nanoparticle preparation from metal ions and for their stabilization; thus, the metal particles are protected from the atmosphere hindering the oxidation/deactivation and aggregation, allowing an increase in their stability and longevity. Various synthetic methods have been reported to produce AuNPs–hydrogel composites [23]: 1) preparation of the nanoparticles and hydrogels separate or in combination [24,25]; 2) mixing and polymerization of the pre-formed nanoparticles with monomer precursor(s) [26-30]; 3) embedding of metal salts into a hydrogel matrix followed by a reduction process in presence of reducing agents [31]. The role of hydrophilic polymers in this system is to stabilize the metal 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. Typical example of embedding of PVP protected AuNPs, AgNPs and PdNPs within hydrogel matrix is shown in Figure 2.

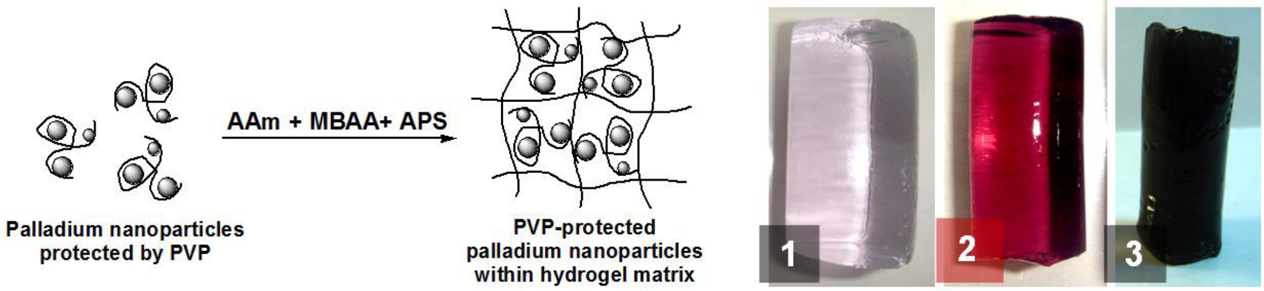


Figure 2 – Immobilization protocol of polymer-protected nanoparticles within hydrogel matrix and PAAH samples with immobilized AgNPs (1), AuNPs (2) and PdNPs (3)

Average size of AgNPs, AuNPs and PdNPs in the volume of PAAH was equal to 20-30, 10-50, and 10-60 nm respectively [32]. Metal ions with different oxidation state to be loaded into the hydrogel matrices can be reduced/precipitated to their metallic particle forms inside hydrogels of different dimensions using green chemicals (those with no hazardous impact on the environment) or nontoxic chemical reducing agents such as $NaBH_4$, H_2, citrate, ethylene glycol, etc., depending upon the nature of the metal ions. Reduction of polyethyleneimine-protected and immobilized within PAAH AuNPs by $NaBH_4$ is shown below [33] (Fig.3):

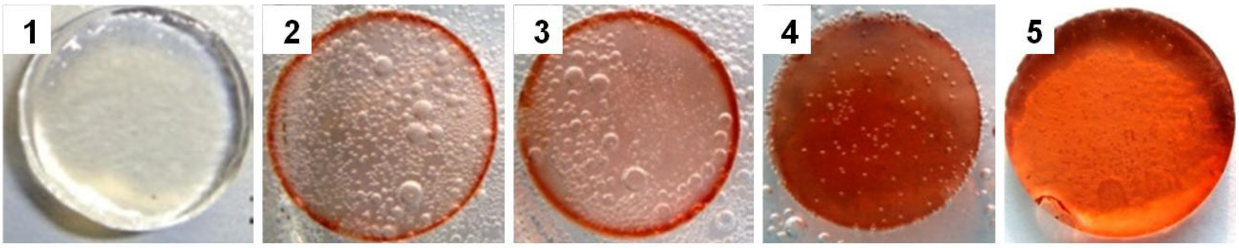


Figure 3 - Swollen in water PAAH/PEI-$HAuCl_4$ (1) in the course of reduction by $NaBH_4$ (C=0.1 $molL^{-1}$) during 5 min (2), 15 min(3), 60 min(4) and 1 day (5)

Reduction of PEI-Au^{3+} complexes to Au^0 within hydrogels is accompanied by formation of thin colored layer on the gel surface that is gradually moves into the gel volume. The driving force of this process is constant diffusion of reducing agent $NaBH_4$ deeply into the gel volume. Narrow-dispersed gold nanospheres and single crystals were prepared, respectively, by reducing $HAuCl_4$ within the hydrogel matrix [34, 35]. Authors [35] described a unique strategy to prepare discrete composite nanoparticles consisting of a large gold core (60–150 nm) surrounded by a thermoresponsive hydrogel derived from the polymerization of NIPAM or copolymerization with acrylic acid. The growth of AuNPs in the presence of preformed spherical hydrogel particles allows precisely to control the size of composite nanoparticles between 200 and 550 nm. The most of hydrogel immobilized palladium nanoparticles (PdNPs) exhibited good catalytic activity in both Heck and Suzuki reactions [36, 37] and Suzuki-Miyaura cross-coupling reaction [38-42].

Decomposition of hydrogen peroxide by polymer-protected AuNPs and AgNPs deposited on inorganic supporters

The literature survey shows that the most investigated AuNPs systems with respect to catalytic activity are nonprotected by hydrophilic polymers AuNPs, e.g. colloidal gold nanoparticles themselves or deposited on the surface or volume of various inorganic supporters. Information on polymer protected AuNPs and supported on metal oxides nanocatalysts is less available. The catalytic activity of AuNPs loaded on the supports (ZnO, Al_2O_3 and MgO) by a colloidal deposition method in benzene conversion was compared [42]. The catalytic activity of AuNPs/ZnO was much greater than that of AuNPs/Al_2O_3 and AuNPs/MgO. The high catalytic activity of the AuNPs/ZnO was attributed to the effects of strong metal-oxide interaction which is possibly originated from the small lattice parameter difference between Au and ZnO lattice planes. The liquid-phase selective oxidation cyclohexane to cyclohexanol and cyclohexanone over AuNPs in mesoporous materials catalyst was carried out in a solvent-free system, in which oxygen was the only oxidant and the reaction conditions are very moderate [43]. A series of organo-soluble spherical AuNPs prepared through the reduction of $HAuCl_4$ by $NaBH_4$ in the presence of amphiphilic hyperbranched polyethylenimine core and a hydrophobic palmitamide (C16) shell were used as efficient catalysts for the biphasic catalytic reduction of 4-nitrophenol by $NaBH_4$ [44]. Earlier [45] we have studied the catalytic activity of polymer protected AuNPs with respect to hydrogenation of 4-nitrophenol. It was found that polymer-protected AuNPs convert 4-nitrophenol to 4-aminophenol with high yield (97-99% conversion). The catalytic activity of PVP-AuNPs supported on the surface of aluminum oxide was evaluated with respect to decomposition of hydrogen peroxide [46-48] (Fig4).

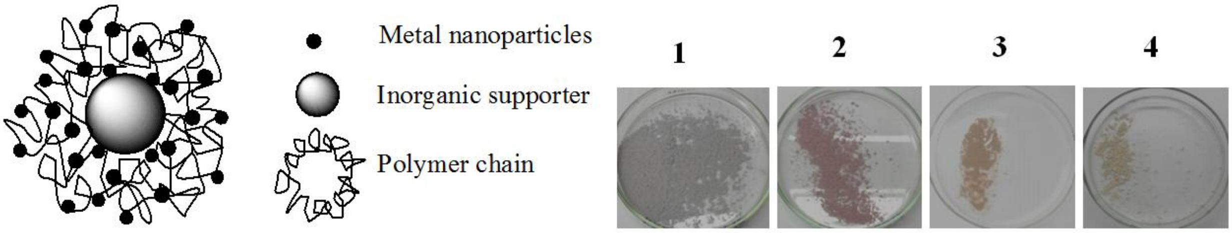
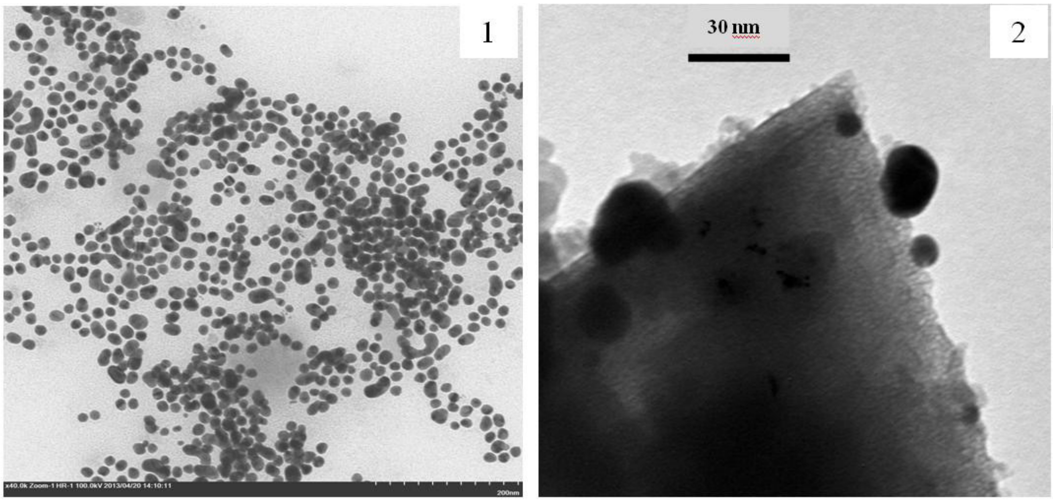


Figure 4 – Supporting of polymer-protected nanoparticles on the surface of inorganic oxides and samples of Al_2O_3 with immobilized PVP-AuNPs (1,2) and PVP-AgNPs (3,4)

TEM image of AuNPs-PVP deposited onto Al_2O_3 reveals that there are no big agglomerates of the gold nanoparticles (Fig. 5). TEM micrograph clearly shows the attached to the surface of Al_2O_3 gold nanoparticles with average size varying from 10 to 25 nm. The concentration of AuNPs deposited on Al_2O_3 and ZnO is equal to 0.07-0.1%. TEM results are in good agreement with SEM results and hydrodynamic sizes of AuNPs measured by DLS.



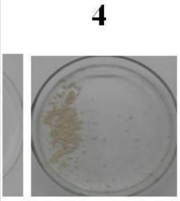


Figure 5 – TEM image of pristine PVP-AuNPs (1) and PVP-AuNPs supported on Al_2O_3 (2)

In the presence of Al_2O_3/AuNPs-PVP the rate of H_2O_2 decomposition increases in the following order PVP-10 kD > PVP-40 kD > PVP-350 kD [48]. Decomposition of H_2O_2 in the presence of Al_2O_3/AuNPs-PVP-10 kD starts immediately while the same reaction in the presence of Al_2O_3/AuNPs-PVP-350 kD is much slower. This is probably explained by less accessibility of gold nanoparticles to substrate due to surrounding of catalytic centers by high molecular weight PVP. The catalytic activity of Al_2O_3/AgNPs-PVP-10 kD was also checked with respect to H_2O_2 decomposition. The PVP-AgNPs deposited on Al_2O_3 has much lower catalytic activity than that of AuNPs. The catalytic activity of PVP-protected AuNPs supported on the surface of ZnO was also evaluated with respect to decomposition of hydrogen peroxide. The influence of catalyst amount (m_{cat}), concentration of substrate [H_2O_2] and temperature (T) was studied in order to find the optimal conditions of H_2O_2 decomposition. At concentration of [H_2O_2] = 30 wt.% and T = 318K the decomposition rate of hydrogen peroxide increases with increasing of the m_{cat} (Fig.6). As seen from Figure 6a, the rate of decomposition of H_2O_2 at m_{cat} = 30 mg is higher than at m_{cat}=50 mg. Thus the optimal amount of catalyst for H_2O_2 decomposition is 30 mg. At m_{cat} = 30 mg, the decomposition rate of hydrogen peroxide gradually increases with increasing of temperature (Figure 6b).

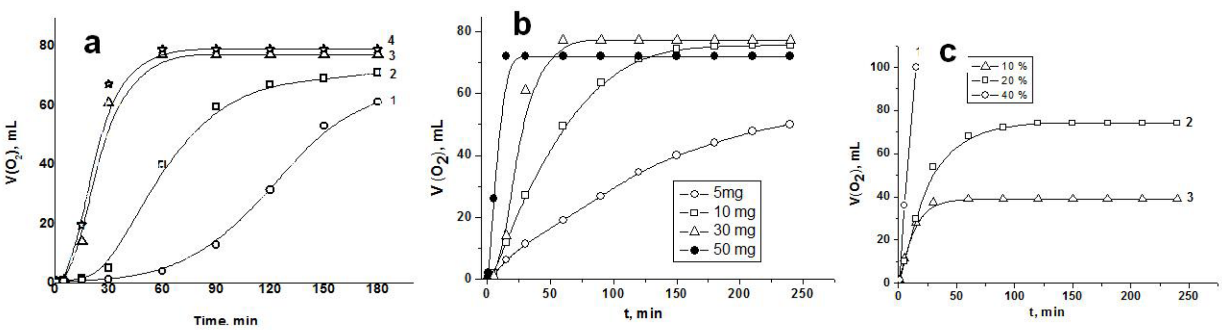


Figure 6 - Decomposition rate of hydrogen peroxide in dependence of the m_{cat} on ZnO/AuNPs-PVP-10 kD. T = 318 K, $[H_2O_2]$ = 30 wt.% (a).
Decomposition of hydrogen peroxide in the presence of ZnO/AuNPs-PVP-10 kD at different temperatures. T = 298 (1), 308(2), 318(3), and 328 K (4). m_{cat} = 30 mg, $[H_2O_2]$ = 30 wt.% (b).
Decomposition rate of hydrogen peroxide in dependence of the H_2O_2 concentration. The catalyst is ZnO/AuNPs-PVP-10 kD. $[H_2O_2]$ = 40 (1), 20 (2) and 10 wt.% (3), m_{cat} = 30 mg. T = 318 K (c)

However the rate of H_2O_2 decomposition at T = 328 is very close to T = 318 K meaning that the latter is optimal temperature. At T = 318 K and m_{cat} = 30 mg the rate of H_2O_2 decomposition increases with increasing of H_2O_2 concentration (Figure 6c). However at $[H_2O_2]$ = 40 wt.% a very fast decomposition of hydrogen peroxide taking places during several minutes is not effective for further oxidation of organic substrates. Therefore it is accepted that the optimal concentration of H_2O_2 for oxidation is 30 wt.%. Thus the optimal conditions of H_2O_2 decomposition were the following: the amount of catalyst is m_{cat}= 30 mg, the substrate concentration is $[H_2O_2]$ = 30 wt.% and T = 318 K. In dependence of reaction conditions decomposition of H_2O_2 is completed during 10-100 min.

Catalytic properties of polymer-protected PdNPs and AuNPs immobilized within hydrogels

The combination of natural catalytic abilities with the in situ metal nanocatalyst preparation capability make hydrogels indispensable multifunctional materials for unique applications [49-53]. The recent review [54] summarizes application aspects of metal nanoparticles within hydrogel templates in catalysis. Of special interest is homo- and copolymers of NIPA that undergo a sharp volume transition around the body temperature [55]. Many researchers have examined the potential application of NIPA-based polymers for immobilization of AuNPs [56,57]. Examples of catalytic system acting by "on-off" mechanism are NIPA-based hydrogels which reversibly swells or shrinks in water-ethanol mixture [58] or reversibly turns first "off" and then "on" as the temperature is first raised and then lowered [59]. The "smart" behavior of PNIPA/PVP-Pd(0) system was demonstrated in the course of allyl alcohol hydrogenation [60-63]. Swelling-deswelling of PNIPA at temperature interval 25-40°C causes the release or inflow of PVP-Pd(0) outside or inside of hydrogel matrix. This in its turn leads to periodic increase or decrease of the hydrogenation rate of allyl alcohol (Fig.7).

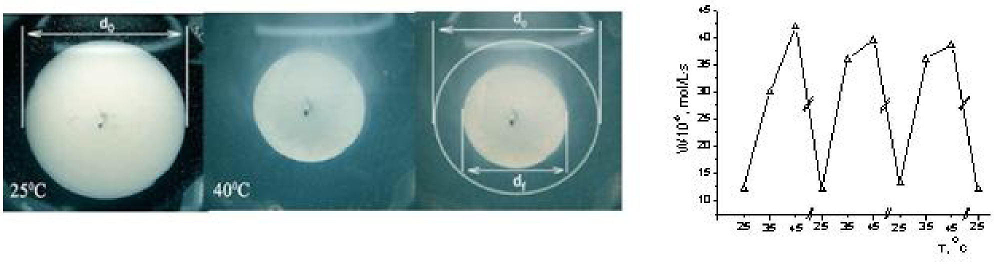


Figure 7 – Reversible changing of size (a) and catalytic activity of PNIPA/PVP-Pd(0) (b) at 25 и 40°C

The catalytic activity of polymer-protected and PAAH-immobilized Pd(0) catalysts increased in the following order: PAAH/PVA-Pd(0)>PAAH/PVP-Pd(0)>PAAH/PEI-Pd(0)>PAAH/PAA-Pd(0). The catalytic activity of PAAH/PEI-Pd(0), PAAH/PVP-Pd(0) and PAAH/PVA-Pd(0) catalysts preserved up to hydrogenation of 12 sequential portions of allyl alcohol [64]. Turnover numbers (TON) for PAAH/PEI-Pd(0) and PAAH/PVP-Pd(0) were equal to 4•103 и 7•103 respectively indicating a stable and long-lived behavior of catalysts. After hydrogenation of sequential portions of allyl alcohol the amount of Pd(0) on the surface of gel matrix is considerably reduced (Fig.8). This is probably due to leaching out of Pd nanoparticles in the course of hydrogenation reaction. The average size of Pd nanoparticles is less than 100 nm although the bigger aggregated particles are observed. While SEM micrographs of pristine PAAH/PVP-Pd(0) show spheres with average diameter of about 60 nm that are related to PVP-stabilized spherical Pd nanoparticles or particle aggregates (Fig.8).

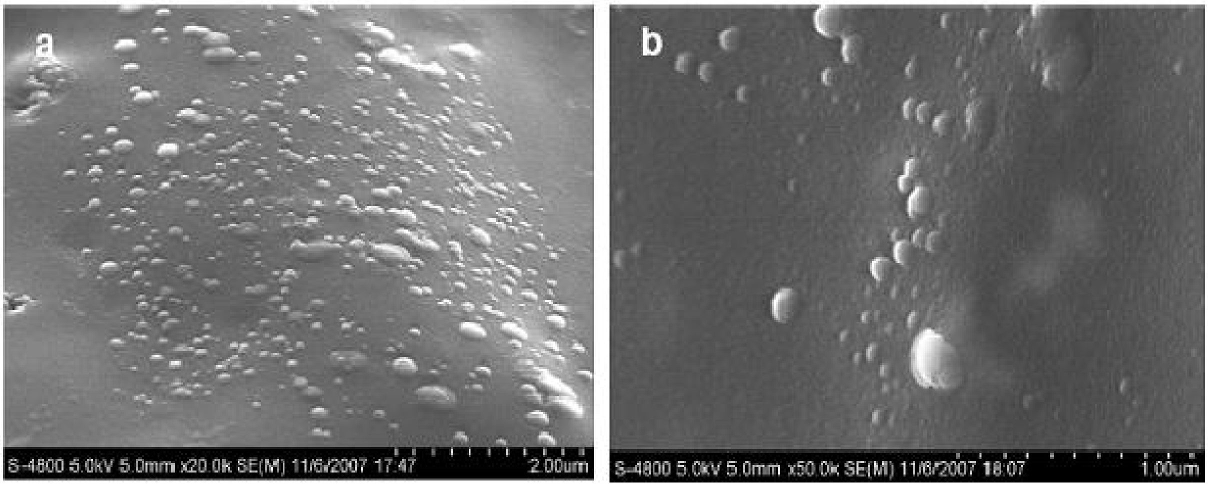


Figure 8 – SEM pictures of PVP-protected Pd nanoparticles within the gel matrix of PAAH after hydrogenation of the first (a) and twelfth (b) successive portions of allyl alcohol

The PVP and PEI stabilized AuNPs were embedded within thermosensitive copolymer gels of NIPAM and AAm (3:1mol/mol). The NIPAM-AAm hydrogels containing PVP-AuNPs and PEI-AuNPs demonstrated the thermosensitivity at the interval of temperature 308-333K (Fig.9).

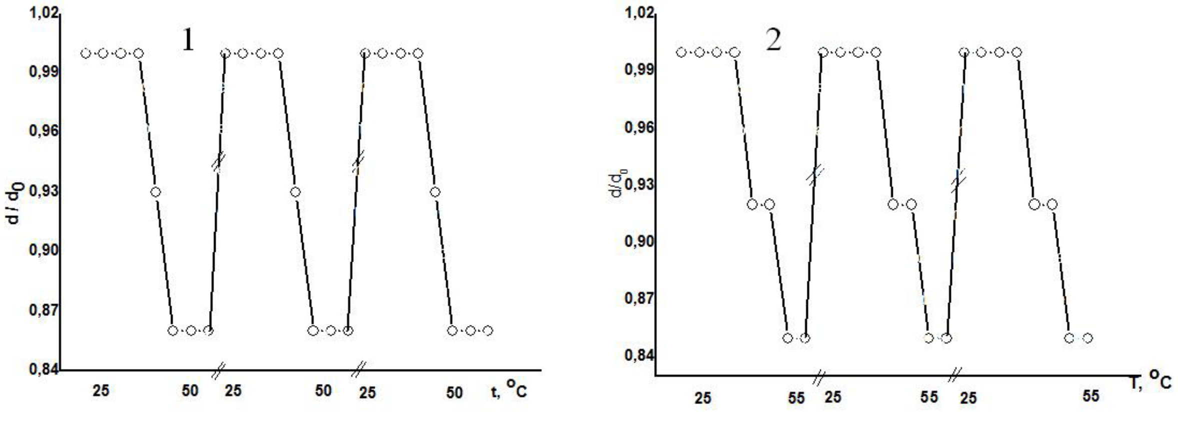


Figure 9 – Thermosensitive character of NIPAM-AAm with immobilized PEI-AuNPs (a) and PVP-AuNPs (b)

The catalytic activity of gel-immobilized AuNPs was evaluated with respect to hydrogen peroxide decomposition. The influence of 1) substrate concentration (C=10-40 wt.%) at constant temperature (T=328K) and constant mass of catalyst (mcat= 30 mg); 2) temperature (T=308-323) at constant substrate concentration ([H2O2] = 30 wt.%) and constant mass of catalyst (mcat= 30 mg); 3) mass of catalyst (mcat= 15-50 mg) at constant temperature (T=328K) and constant substrate concentration ([H2O2] = 30 wt.%) on the decomposition rate of H2O2 was studied (Fig.9). In each experiment the volume of substrate was kept constant and equal to 1 mL.

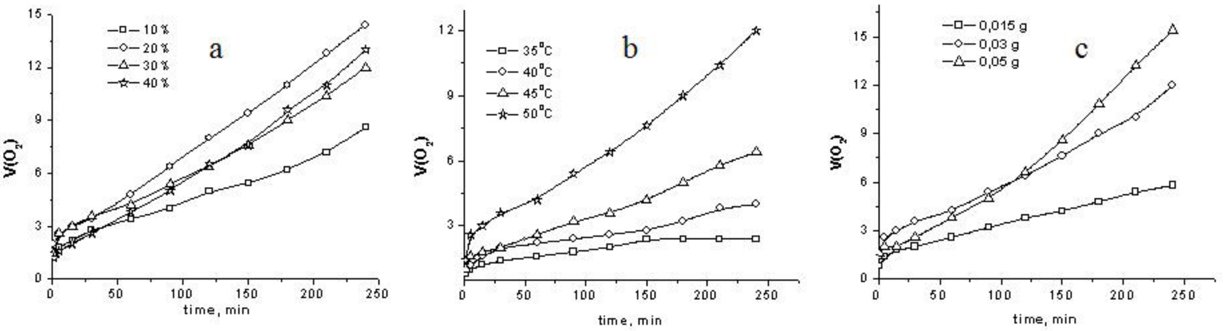


Figure 10 – Influence of substrate concentration (a), temperature (b), and mass of catalyst (c) PVP-AuNPs/NIPAM-AAm on decomposition rate of hydrogen peroxide

Comparison of figures 6 and 10 shows that the catalytic activity of gel-immobilized AuNPs is much lower than deposited on metal oxides. This is probably accounted for the less accessibility of catalytic centers in gel matrix to substrate molecules, e.g. entrapment of polymer-protected AuNPs within hydrogel networks may restrict diffusion of substrate inside of gel.

Conclusions

Gold, silver and palladium nanoparticles stabilized by various hydrophilic polymers were supported onto metal oxides and incapsulated within stimuli-responsive hydrogel matrix. Polymer-protected AuNPs and AgNPs deposited on inorganic supporters showed much higher catalytic activity in decompoisiton of hydrogen peroxide than that of metal nanoparticles immobilized within hydrogel network. The optimal conditions of H2O2 decomposition in dependence of substrate concentration, catalysts amount and temperature were established. “On-off” catalytic behavior of NIPA-based “smart” hydrogels in hydrolysis of p-nitrophenyl caprylate as a function of water-ethanol mixture and NIPA-immobilized PdNPs in the course of allyl alcohol hydrogenation as a function temperature was demonstrated.

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