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Oxidation of Cyclohexane Mediated with Gel-Immobilized Gold Nanoparticles

This paper reports the study of hydrogen peroxide decomposition and oxidation of cyclohexane catalyzed by polymer-protected gold nanoparticles (AuNPs) immobilized within polyacrylamide hydrogel. The stabilization of AuNPs was achieved using nonionic, anionic and cationic polymers. Embedding of AuNPs stabilized with various polymers into polyacrylamide hydrogels was carried out using threeways: «in situ» polymerization, sorption and boronhydride methods. Size, shape and morphology of AuNPs were characterized by various physicochemical methods. Application aspects of polymer-protected AuNPs in catalysis are outlined.

Key words: gold nanoparticles, hydrogels, hydrophilic polymers, stabilization, catalysis.

Introduction

Hydrogels have found numerous applications due to their unique properties such as high water content, softness, flexibility, biocompatibility and ease of synthesis.Their resemblance to living tissue opens up many opportunities for applications in biomedical areas. Nowadays, hydrogels are used for manufacturing contact lenses, hygiene products, tissue engineering scaffolds, drug delivery systems and wound dressings [1, 2].

Hydrogels are three-dimensional, hydrophilic, polymeric networks capable of absorbing large amounts of water or biological fluids. Due to their high water content, porosity and soft consistency, they resemble natural living tissues, more so than any other class of synthetic biomaterials. Hydrogels may be chemically stable or they may degrade and eventually disintegrate and dissolve. There are numerous original papers, academic reviews and monographs focused on the synthesis, properties and applications of hydrogels [1-4].

New technologies rely on the development of modern materials, and these may simply be the innovative combination of known components. The structural combination of a polymerichydrogel withnanoparticles (metals, nonmetals, metal oxides, and polymers) often provides superior functionality to the composite materialswith potential applications in various fields, including catalysis, electronics, biosensing, drug delivery, nanomedicine, and environmental remediation. This mixing may result in a synergistic property enhancement of each component: for example, the mechanical strength of the hydrogel could be improved with embedded nanoparticles and concomitantly the aggregation of nanoparticles could be prevented within a polymeric network. These mutual benefits and the associated potential applications have seen a surge of interest in the past decade from multi-disciplinary research groups. Recent advances in nanoparticle–hydrogel composites are herein reviewed with a focus on their synthesis, design, potential applications, and the inherent challenges [5-13].

This paper reports the study of oxidation of cyclohexane catalyzed by polymer-protected gold nanoparticles (AuNPs) immobilized within polyacrylamide hydrogel (PAAH).

Experimental part

Materials

Poly-N-vinylpyrrolidone (PVP, MW 40 kDa), branched polyethylenimine (PEI, MW 25 kDa) and

NaOH werepurchased fromSigma – Aldrich (USA). $HAuCl_4$ was purchasedfrom Altey (Kazakhstan). $NaBH_4$ was purchased from AppliChem (Germany). All chemicals were used without further purification.

Synthesis of AuNPs

AuNPs were synthesised bymixing 4mL 0.5M KOH with5mL4 w/v % PVP or 5 mL 4 w/v % PEI, then addition of5 mL of 100 mg/L $HAuCl_4$solution into the mixture and heating it at 100°(1) «in-situ» immobilization method: Gel-immobilized AuNPs were prepared by polymerizing the mixture of 500 mg acrylamide dissolved in 5 mL PEI- or PVP-protected AuNPsaqueous dispersionsin the presence of 10 mgmethylene bisacrylamide as a crosslinking agent and 10 mg ammonium persulfate as an initiator. The reaction mixture was purged with argonfor 5 min; then it was kept at 60^0C. The hydrogels were formed within 30 min of the reaction and then they were washed in distilled water for 3-4 days to get rid of unreacted monomers.The purified hydrogel samples were crushed and dried in air to a constant mass.

(2) Sorbtion method:

Pure polyacrylamide hydrogels were synthesized using three-dimensional polymerization of 500 mg acrylamide in 5 mL waterin the presence of 10 mg of methylene bisacrylamide and 10 mg of ammonium persulphate. This solution mixture was held at 60°C for 30 min to form hydrogels. These hydrogels were purified as described above. Then these materials were air dried and 1 g of dry sample was immersed in 10 mL AuNPs aqueous dispersion for 24 hours. After washing and grinding, the hydrogels were dried to a constant mass. The sorption of AuNPs by dry hydrogelsresulted in colouredsamples, which were subsequently dried in air.

(3) Borohydride method: The preparation of AuNPs immobilized hydrogels in this method was carried out by immersing dried hydrogel samples into 100 mg/L solution of $HAuCl_4$ for 24 hours. After sorption the hydrogel samples were placed into 5 mL 0.1 M solution of sodium borohydride for 20 min, which resulted in colored samples indicatingthe formation of AuNPs. These hydrogels were cut into smaller pieces and dried in air to a constant mass.

Dynamic Light Scattering

Particle size distributions and zeta-potential of gold nanoparticles (AuNPs) in aqueous dispersions were measured using dynamic light scattering (DLS, MalvernZetasizerNanoZS90, UK).

Transmission electron microscopy (TEM)

Transmission electron microscopyimages of gold nanoparticles in aqueous dispersions and in gels were recorded using JEM-1011 (Japan) at an accelerating voltage of 80 kV. The samples for investigation were applied as a dispersion of AuNPs dripped onto standard copper grid with subsequent drying in air. Gel samples were micronized and a drop of microgel aqueous suspension was placed on TEM grid and air dried.

Gas-liquid chromatography (GLC)

Products of oxidation the cyclohexane were identified using GLC «MasterGCGasChromatograph» (DANIMaster, Italy) using DN-5 column with the length of 30m, diameter of 0.25 mm, thickness of phase 0.45 μm, and a flow rate of 1 mL/s.

Cyclohexane oxidation using gold nanoparticles

The oxidation of cyclohexane was carried out in a closed reactor BuchiLimbo (Switzerland). 0.07 g of a dry hydrogel with AuNPs were placed into the reactor, followed by addition of 4 mL of acetonitrile, 1 mL of cyclohexane and 0.59 mL of 30% hydrogen peroxide. Cyclohexane oxidation was carried out at 70°C for 6 hours. In these experiments the oxidant was taken in an equimolar amount relative to the substrate (cyclohexane). In this case, the theoretical amount of oxygen obtained during decomposition of hydrogen peroxide was 112 mL.

Results and Discussion

The hydrogel samples for UV-Vis analyses were prepared as following: the gel-immobilized hydrogel samples were prepared in quartz cuvettes by «in-situ» method. The AuNPs solutions were diluted for UV-Vis: 0.5 mL of AuNPs solution was added 2.5 mL water. In this diluted solution the hydrogels were synthesized: red – AuNPs/PEI, purple – AuNPs/PVP (Fig. 4).

Synthesis and characterization of AuNPs

AuNPs were synthesized by reduction of $HAuCl_4$ in aqueous solutions containing either 4 w/v % of PVP or 4 w/v % PEI under alkali conditions (achieved by addition of 4 mL 0.5M KOH to the reaction mixture). The reaction was initiated by increasing temperature up to 100°C, which resulted in the aqueous mixtures becoming colored within a few minutes. The change of solution color indicated the formation of AuNPs sols. The synthesized nanoparticles were initially characterized using dynamic light scattering and TEM (Fig. 5).

The use of different water-soluble polymers for reduction of $HAuCl_4$ results in formation of nanoparticles substantially differing in their sizes as measured by dynamic light scattering: the hydrodynamic diameters are 46 ± 10 nm and 128 ± 20 nm for AuNPs synthesized in the presence of PVP and PEI, respectively. It is interesting to note that the comparison of DLS data with TEM images of the nanoparticles reveals a significant difference in sizes. The analysis of TEM results using ImageJ software indicates that the nanoparticles formed in PEI have diameters of 8.170 nm. This dramatic discrepancy between DLS and TEM results is explained by different physical principles used by these two sizing techniques. DLS is a technique that measures light scattered by the objects present in solutions and will be able to detect individual macromolecules. AuNPs formed in the presence of water-soluble polymers have a core-shell structure with the core made of gold and a hydrophilic shell made of macromolecules of a water-soluble polymer. DLS measurements in this case will provide the size distribution for the nanoparticles together with a hydrated shell. TEM, on the contrary, is based on transmission of accelerated electrons through the sample and, in the absence of specific staining agents, this technique will be able to detect only dense objects such as gold-based core. The comparison of both DLS and TEM data allows establishing the structural features of AuNPs prepared in the presence of PVP and PEI.

Hydrogel immobilized gold nanoparticles were prepared using three approaches: (1) «in-situ» immobilization method; (2) sorption method; and (3) borohydride method. Figure 6 shows the images of selected hydrogel samples with immobilized AuNPs prepared using «in-situ» and sorption methods.

Table 1 presents the comparison of the dimensions and other physicochemical properties of AuNPs in aqueous dispersions and immobilized within hydrogels. Analysis of TEM images of AuNPs immobilized within a hydrogel indicates that the size of gold core has a diameter very similar to the sizes of the nanoparticles before their incorporation into the hydrogels. Zeta-potential measurements indicate that of AuNPs formed in the presence of PVP and PEI in aqueous dispersions have slightly negative values (-10.52 mV and -9.31 mV, respectively).

Figure 1 – PVP (purple)- and PEI (red)-protected gold nanoparticles

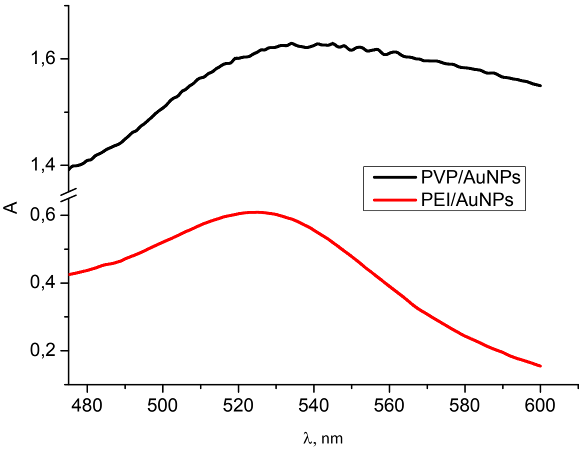

Figure 2 – UV-Vis spectra of AuNPs solutions

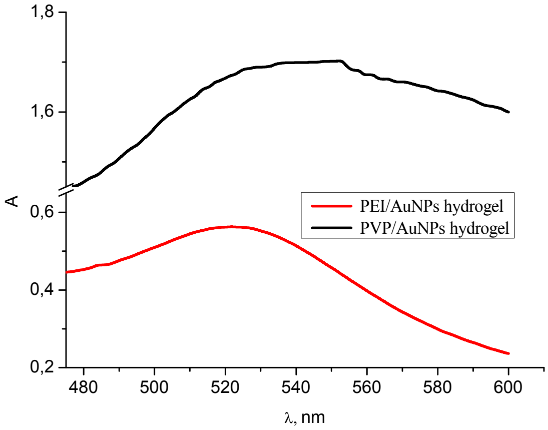

Figure 3 – UV-Vis spectra of AuNPs hydrogels

Considering that these nanoparticles are very stable in dispersion, it could be concluded that their stabilization is related to the sterical effects caused by highly hydrated macromolecules forming their shell rather than their charge interactions.

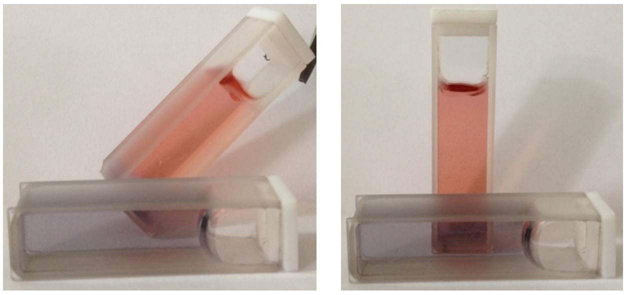

Figure 4 – Gel-immobilized AuNPs

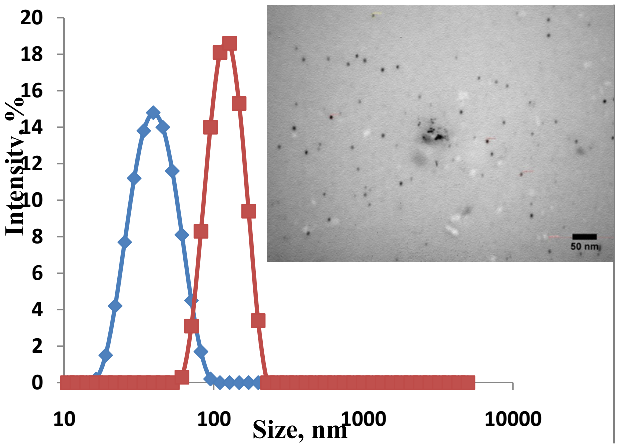

Figure 5 – Size distributions of gold nanoparticles as measured by dynamic light scattering. AuNPs were synthesized in the presence of PVP (1) and PEI (2). Insert: Exemplary TEM image of AuNPs synthesized in the presence of PEI.

Oxidation of cyclohexane by AuNPs immobilized within PAAH

Catalytic conversion of saturated hydrocarbons to oxygenated compounds has been studied intensively in the last decade due to the important industrial synthesis of a plurality of organic compounds. Among oxygenation process the alkane oxidation is of greatest interest, because reaction products of cyclohexane – cyclohexanol and cyclohexanone are the basis for the production of adipic acid using in the further for polyamide materials and plastics, foams, and the acid itself is used in the food industry and as lubricant materials.

In this case, the process proceeds in acetonitrile having weakly basic character, which basifiesthe solution that prevents the complete decomposition of hydrogen peroxide.

When using the gel-immobilized catalyst expected to show «catalase» (enzyme catalase promotes the decomposition of hydrogen peroxide to water and oxygen), and the «oxidase» (group peroxidase enzymes allows oxygenation alkanes with hydrogen peroxide) activity.

After the reaction mixture was filtered and the reaction products were analyzed by gas chromatography Dani Master GS (Italy). Figure 2 (supplementary materials) shows the chromatogram of the oxidation products of cyclohexane. AuNPs immobilized in hydrogel only catalyze the oxidation of cyclohexane to cyclohexanol and cyclohexanone with minimal formation of oxygenated products. According to the results of the chromatographic investigations revealed that the yield of cyclohexanol and cyclohexanone in the presence of a catalyst Au / PEI (adsorption method) is 55.1 and 44.9% respectively (Table 1). By using this catalyst conversion of reactionis a maximum which is 37%.

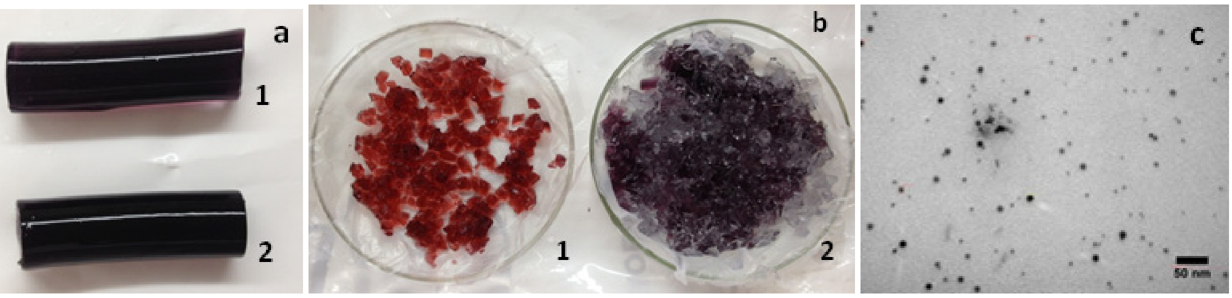

Figure 6 – Hydrogel samples with immobilized AuNPs, prepared using «in-situ» method (a) and sorption method (b). PVP (1) and PEI (2) were used for stabilization of nanoparticles. TEM image of PEI-protected AuNPs immobilized within a hydrogel using «in-situ» method (c).

Table 1 – Physicochemical properties of AuNPs in dispersions and in hydrogels

Samples	TEM, nm	DLS, nm	PDI	Zeta potential, mV
PEI-protected AuNPs (solution)	7.0±0.53	128±20	0.427	-9.31
PVP-protected AuNPs (solution)	*	46 ± 10	0.553	-10.52
PEI-protected AuNPs within a hydrogel	7.310±0.005	*	*	*

* – not measured.

In the presence of catalysts Au / PVP (adsorption method), Au / PEI (method «in-situ»), Au-$NaBH_4$ (method borohydride), conversion varies between 5-7% and the yield of the cyclohexanol being within 47,6-55,4% and cyclohexanone – 44,6-52,4%.

Thus, the best catalyst for the oxidation of cyclohexane to cyclohexanol and cyclohexanone is stabilized with polyethyleneimine (PEI), and immobilized in a polyacrylamide hydrogel matrix gold nanoparticles, obtained by sorption method. In the presence of Au / PEI matrix immobilized in a polyacrylamide hydrogel by sorption method, the yield of cyclohexanol and cyclohexanone is 55.1 and 44.9% respectively (conversion 37%).

Table 2 – The yield of cyclohexane oxidation according to chromatographic analyses

Catalyst	Compounds	Conversion, %	Selectivity, %
Au/PEI «in-situ» method	Cyclohexanol	7.2	55.4
	Cyclohexanon		44.6
Au/PVP sorption method	Cyclohexanol	6.37	47.6
	Cyclohexanon		52.4
Borohydride method	Cyclohexanol	5.15	53.6
	Cyclohexanon		46.4
Au/PEI Sorption method	Cyclohexanol	37	55.1
	Cyclohexanon		44.9

Conclusions

Gold nanoparticles stabilized by various hydrophilic polymers incapsulated within hydrogel matrix. The catalytic properties of gel-immobilized gold nanoparticles were investigated in oxidation of cyclohexane. The physico-chemical properties of prepared gold nanoparticles were studied by TEM, UV-Vis an DLS measurements.The best catalyst for the oxidation of cyclohexane to cyclohexanol and cyclohexanone is stabilized with polyethyleneimine (PEI), and immobilized in a polyacrylamide hydrogel matrix gold nanoparticles, obtained by sorption method. In the presence of Au / PEI matrix immobilized in a polyacrylamide hydrogel by sorption method, the yield of cyclohexanol and cyclohexanone is 55.1 and 44.9% respectively (conversion 37%).

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