Nanostructured catalysts for the synthesis of vitamin intermediate products

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A great challenge in nanotechnology is to design a highly selective catalyst comprising an active site with the correct ensemble of metal atoms and other active components. The advantages of the nanocatalyst prepared in organic functional polymers are not only the “nanoscale” size control of metal crystallites, but also the easy tailoring via variation of the polymer nature. Nanostructures in a polymeric composite are defined as regular nanosized heterogeneous domains (i.e., certain regions of the polymeric material that are separated by some interface). Due to the presence of nanostructures one can control the growth of nanoparticles, the particle size distribution and interfacial interactions [1].

Nanocomposites containing metal nanoparticles are widely developed to replace regular heterogeneous catalysts for many organic reactions [2] since they are characterized by high activity, selectivity and stability. Their high activity is due to huge surface area of nanoparticles and selectivity can be provided when a particle surface is properly modified.

Here, we report on the synthesis and catalytic properties of Pd and Pt nanoparticles in nanostructured polymers. The methods used for nanoparticle formation in nanostructured polymers will be divided into three groups depending on the polymer medium: (i) amphiphilic block copolymer, (ii) ultrathin polyelectrolyte layers, and (iii) nanoporous hypercrosslinked polystyrene (HPS).

The synthesis of metal nanoparticles in block copolymer micelle cores in an organic medium was reported in the middle of 90-s [2–6]. The studies on the formation of palladium, platinum and other metal nanoparticles in amphiphilic block copolymer based micelles revealed that the nanoparticle morphology strongly depends on the type of the reducing agent. With sluggish reducing agents only one particle can be formed in the micelle core in the absence of inter-micellar exchange reactions. Using fast working reducing agents, the nucleation and growth of a large number of particles occur simultaneously; therefore, each micelle contains many small particles. This morphology is most preferable for the catalysis [7]. As an amphiphilic block copolymer, we chose poly (ethylene oxide)-block-poly (2-vinylpyridine) (PEO-b-P2VP), giving micelles in an aqueous medium [8]. The structure of PEO-b-P2VP is shown in figure 1.

The synthesis of metallated micellar catalyst was carried out similar to the method described earlier [8]. The catalyst on the basis of amphiphilic block copolymer PEO-b-P2VP was prepared by immobilization of inorganic precursors (Na2PdCl4 or Na2PtCl6) into micelle cores of this polymer with the metal reduction followed. According to the obtained AFM images of colloidal solutions of metal-containing catalysts (PEO-b-P2VP-Pd, PEO-b-P2VP-Pt) micelles diameter of about 30 nm, metals particle size of 1–3.5 nm were determined.

Polyelectrolytes are able to form mono- or multilayers on various charged support particles. Such restricted layers can serve as nanoreactors for metal nanoparticles formation. The formation of metal nanoparticles in ultrathin polyelectrolyte systems was carried out using polydiallyldimethyl ammonium chloride (PDADMAC). The structure of PDADMAC is shown in figure 2.

We carried out one-layer deposition using PDADMAC. Metal compounds (Na2PdCl4 or Na2PtCl6) incorporation and subsequent reduction with NaBH4 were performed when the layer of polyelectrolyte were already formed on alumina. TEM images of platinum (or palladium) nanoparticles stabilized in PDADMAC revealed that the polyelectrolyte layer thickness is within the limits of 70–100 nm and nanoparticle size is 2–3 nm.

Metal nanoparticle formation in cavities (pores) of a polymer matrix was carried out with the use of HPS. The controlled growth of metal nanoparticles in a...
polymer matrix is possible if it occurs in cavities or pores. In this case, the size of the growing particles can be limited to the cavity size [9]. HPS is the representative of cross-linked polymers that gives the possibility for nanoparticle growth control. The first step of the catalyst synthesis is HPS immobilization of metal salts (Na$_2$PdCl$_4$ or Na$_2$PtCl$_6$) in a chosen solvent. The second step is the reduction of metal salt and nanoparticles formation (figure 3).

The study of the characteristics of platinum (or palladium) hypercrosslinked polystyrene nanocomposites by Transmission electron microscopy resulted in the determination of Pt (or Pd) particles mean diameter of 1–2 nm [10, 11].

PDADMAC (Aldrich) polydiallyldimethyl ammonium chloride
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Figure 2. Structure of polydiallyldimethyl ammonium chloride.

The Pd-containing nanostructured catalytic systems discussed above were studied in selective hydrogenation of acetylene alcohols. These processes are of particular interest because the products are the intermediates in the synthesis of vitamins (A, E, K) and fragrant substances.

The selective (partial) hydrogenation of triple carbon–carbon bond to double one is normally catalyzed on palladium and used in the synthesis of linalool (3,7-dimethylocta-1,6-diene-3-ol, LN) [12]. Linalool is a fragrant substance of the terpenic series used in several scent compositions and cosmetic preparations. According to [13], linalool is produced in an amount of 6000 tonnes per year. It is also an intermediate in the syntheses of Vitamins A and E, geraniol, citral. Linalool can be produced via selective hydrogenation of dehydrolinalool (3,7-dimethyloct-6-ene-1-yne-3-ol, DHL) (figure 4). If hydrogenation goes on non-selectively, dihydrolinalool (3,7-dimethyloct-6-en-3-ol, DiHL) forms as well.

The catalysts samples (PEO-b-P2VP-Pd, PDADMAC-Pd and HPS-Pd) were tested in hydrogenation of dehydrolinalool to linalool (selective hydrogenation of triple bond to double one).

Some results are shown in table 1. The turnover frequency (TOF) values (table 1) for nanostructured catalytic system show that, for PDADMAC-Pd, the catalytic activity is higher than that for PEO-b-P2VP-Pd and HPS-Pd, which can be explained by more quantity of active sites on the catalyst surface.

In case of PEO-b-P2VP-Pd and HPS-Pd some part of Pd-nanoparticles is not probably accessible. It accounts for the different methods of nanoparticles stabilization by polymers described above. The lower value of PEO-b-P2VP-Pd catalyst selectivity can be explained by the nature of the polymer and high metal content of the catalyst.

Figure 5 shows the kinetic data as the dependence of DHL conversion on time for PEO-b-P2VP-Pd. One can see the existence of the initial phase (induction period) characterized by a low reaction rate (up to approx. 20% DHL conversion). During this phase the selectivity remains 100% with the following drop to 98.0 ± 0.5%; then the selectivity remains constant. In case of alkyne hydrogenation over Pd catalyst the induction period shows the formation of the reaction complex [14].

The Pt-containing nanostructured catalytic systems (PDADMAC-Pt, PEO-b-P2VP-Pt, HPS-Pt)