

Metal-Polymeric Nanocatalysts of Selective Oxidation and Hydrogenation

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Introduction

Catalysis is a key methodology for the efficient industrial production of important biologically active compounds, thus the application of new methods and technologies in catalysis is very important [1].

In this work we report a comparative study of two types of nanoparticulate catalytic systems based on two amphiphilic block copolymers (polystyrene-*b*-poly(4-vinyl pyridine) (PS-*b*-P4VP) and poly(ethylene oxide)-*b*-poly(2-vinyl pyridine) (PEO-*b*-P2VP)) and a nanoporous polymer, hypercrosslinked polystyrene (HPS). Nanostructures in polymers (block copolymer micelle cores or nanopores) control nanoparticle (NP) formation and location while polymeric environment (functional groups) influences the catalytic performance. Catalytic properties of these nanocomposites were studied in selective hydrogenation of triple bond of dehydrolinalool (DHL) and in direct selective oxidation of both L-sorbose and D-glucose. The product of the DHL selective hydrogenation, linalool (LN), is a fragrant substance and an intermediate product of isophytol (IP) synthesis, which, in turn, is an intermediate product of vitamins E and K. Dihydrolinalool (DiHL) is the side product. L-sorbose is used for the synthesis of 2-keto-L-gulonic acid, which is an intermediate in vitamin C production. D-glucose is used for calcium gluconate synthesis.

Materials and Methods

PS-*b*-P4VP was a gift from Max Plank Institute of Colloids and Interfaces (Potsdam/Golm, Germany). PEO-*b*-P2VP was purchased from Polymer Source Inc., Canada, and used as received. The HPS (MN270 type) was purchased from Purolite Int. (UK). Dehydrolinalool (99% purity) was supplied by pharmaceutical company OAO "Belgorodvitamin" (Belgorod, Russia) and distilled under vacuum. D-glucose and L-sorbose were provided by Fluka.

Mono- (Pd and Pt) and bimetallic (PdAu, PdPt and PdZn) colloid catalysts were synthesized by solubilization of appropriate metal salts into the P4(2)VP micelle cores followed by reduction. Bimetallic based catalysts contained 1.5-2 nm NPs with a narrow particle size distribution, but with different NP morphology: cluster-in-cluster for PdPt and PdZn and core-shell for PdAu [2]. In the case of HPS the monometallic (Pd, Pt and Ru) catalysts were synthesized by the impregnation method.

Hydrogenation of a triple bond of DHL was carried out at ambient pressure in a glass batch isothermal reactor installed in a shaker and connected to a gasometric burette as described elsewhere [2]. In the case of micellar catalysts based on amphiphilic block copolymers, different organic solvents providing the better swelling of micelle corona and access of the substrates to catalytic sites were used. The oxidation of monosaccharides was conducted batchwise at ambient pressure in PARR 4592 apparatus in water [3].

Results and Discussion

Pt compound NPs formed in HPS pores were remarkably active and selective in L-sorbose oxidation. We demonstrated that 2-keto-gulonic acid (the target product) modifies the NP surface leading to its excellent stability and most likely high selectivity (up to 98%), while accessibility of the NPs in the pores allows exceptional activity. Ru-containing catalysts based on HPS were the most active and selective (99% of selectivity) catalysts in D-glucose oxidation. PS-*b*-P4VP-Pt showed lowest activity and selectivity in both monosaccharides oxidation, because the catalytic NPs are likely buried under the PS corona, which is insoluble in water, and the substrate is too polar to penetrate the P4VP core. For PEO-*b*-P2VP-Pt containing water-soluble corona, the catalytic activity was higher by a factor of 2.0-2.5, but the selectivity of L-sorbose was still low. Ru-containing catalysts based on both amphiphilic block copolymers behaved in a similar way.

The selectivity of PEO-*b*-P2VP-Pd in DHL hydrogenation in optimal conditions was slightly lower than that of PS-*b*-P4VP-Pd (98% versus 99%). We ascribe this decrease of selectivity to less efficient modification of the NP surface with 2VP units (nitrogen is located near the polymer chain) than with 4VP ones. In DHL hydrogenation with HPS-Pd the catalytic activity is remarkably high, while selectivity was upsettingly low (94.2%) due to the absence of proper NP particle modification. It is noteworthy that the catalytic activity for bimetallic samples was higher than for Pd NP. This can be explained by the modifying influence of Au, Pt and Zn towards Pd. Moreover, the highest activity was observed for the PdPt-containing catalyst due to synergy of catalytic activity of both metals in hydrogenation, while Zn and Au were not catalytically active in this reaction.

Significance

We provided a comparative study of the catalytic properties of the systems based on two types of nanostructured polymers, amphiphilic block copolymers and nanoporous HPS, in selective hydrogenation of DHL and selective oxidation of monosaccharides. The modifying influence of second metal-modifier was revealed, and synergy of activity of both metals was shown. Besides, the modification of the NP surface with pyridine units was found to take place. For both hydrogenation and oxidation reactions the enhanced activity, selectivity and stability were provided.

References

1. Bonrath, W., Eggersdorfer, M., Netscher, T., *Catal. Tod.* 121, 45 (2007).
2. Bronstein, L.M., Chernyshov, D.M., Volkov, I.O., Ezernitskaya, M.G., Valetsky, P.M., Matveeva, V.G., Sulman, E.M., *J. Catal.* 196, 302 (2000).
3. Sulman, E., Doluda, V., Dzwigaj, S., Marceau, E., Kustov, L., Tkachenko, O., Bykov, A., Matveeva, V., Sulman, M., Lakina, N., *J. Mol. Catal. A*: 278, 112 (2007).