



Editor's choice paper

Palladium nanoparticles on dendrimer-containing supports as catalysts for hydrogenation of unsaturated hydrocarbons



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ABSTRACT

A method for the synthesis of encapsulated palladium nanoparticles of size to 5 nm in the pores of specially prepared supports, which are polymer networks based on poly(amidoamine) (PAMAM) and poly(propylene imine) (PPI) dendrimers, is proposed. It was found that particle size distributions, as well as catalytic activity and selectivity of the resulting materials in hydrogenation of unsaturated compounds significantly depend on the structure features of the support (nature and generation of dendrimer, size and rigidity of a crosslinking agent, and the use of a template in the synthesis). The best values of specific activity were achieved for styrene (86,000 h⁻¹), phenylacetylene (103,700 h⁻¹) and 1,3-cyclohexadiene (65,000 h⁻¹). It was established that the catalysts based on PAMAM dendrimers, synthesized in the presence of template, were superior to their analogues, synthesized without template, in terms of activity. An inverse relationship was observed for catalysts, based on PPI dendrimers, for all substrates with the exception of phenylacetylene. The catalysts based on palladium nanoparticles, encapsulated into dendrimer networks, can be repeatedly used without a noticeable loss of activity.

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1. Introduction

Hydrogenation of unsaturated compounds is one of the most important processes in the current petrochemical industry. Thus, hydrogenation of olefins allows to obtain stable diesel fuel additives with high cetane numbers and to stabilize gasoline pyrolyzates [1,2] in order to avoid the polymerization of olefins, which is inevitable at operation and storage and accompanied by fuel performance degradation. The selective hydrogenation of phenylacetylene, which is a poison for polymerization catalysts, is more preferential from economics point of view, than its separation from reaction products [1,3–5]. Hydrogenation of acetylene and diene fragments in C₂–C₅ hydrocarbons allows to avoid the subsequent polymerization and oxidation of these products [1,3–6]. Selective hydrogenation also plays an important role in the processes of fine organic synthesis, where both various metal complexes and heterogeneous catalysts can be used [7,8].

In this connection development of efficient and selective hydrogenation catalysts that can be easily recycled used is a problem of considerable current importance. Heterogeneous catalysts, that

are traditionally used in industry, often require severe reaction conditions, under which it is very difficult to reach high selectivity for a required product, and high metal loading in system. The homogeneous catalysts, used in fine organic synthesis, are characterized by high values of specific activity and selectivity; at the same time, they have a number of disadvantages, such as high costs, low stability and impossibility for recycling. Thus, the promising is development of the systems that simultaneously combine advantages of both homogeneous and heterogeneous catalysts. Systems based on noble metal nanoparticles encapsulated into dendrimers, being spherically symmetrical macromolecules with a regular branched structure, may appear as catalysts of this kind.

Dendrimers as matrices for the synthesis of metal nanoparticles have a number of advantages [9], such as the possibility to obtain materials with a uniform particle distribution in the volume and control the size of nanoparticles being formed. In applications to catalysis, the separation and recycling of dendrimer-stabilized nanoparticles can be realized due to the fractional solubility of the dendrimer ligand [10–12].

Recently catalysts, based on dendrimer-encapsulated nanoparticles, have been widely used in petrochemical and organic synthesis. They were applied to the hydrogenation of C=C double bonds [13–16] and reduction of nitro- and carbonyl groups [16,17]; in reactions of hydroformylation [18,19], amination [20], oxida-

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tion [16] and carbonylation [21]; and Suzuki [22–25], Heck [26,27] and Sonogashira cross-coupling reactions [28], as well as various cycloaddition, condensation and alkylation reactions [16,17,29]. Nevertheless, these catalysts have their own disadvantages: they can be stored and used only as colloidal solutions, and they rapidly lose activity at recycling [22]. Therefore, heterogenization of dendritic catalysts is a problem of considerable interest. Thus, there was proposed an approach, suggesting chemical immobilization of poly(propylene imine) (PPI) or poly(amidoamine) (PAMAM) dendrimers in pores or on surfaces of silica [22,30–35], carbon nanotubes [12] or insoluble polymers, as cross-linked poly(styrene) [36–38].

Earlier we have developed an approach for synthesis of heterogeneous supports based on PPI and PAMAM dendrimers by their crosslinking with the use of special agents (diisocyanates and diepoxides), whose size and rigidity are responsible for the final properties of the resulting materials [39–45]. The possibility of regulating the particle size (from 1 to 2.5 nm) in these materials was reached by varying the size and rigidity of the linker, and the generation of dendrimers. Here, we report the results of the use of another approach, allowing to synthesize catalysts with a large particle size: the initial supports of PPI and PAMAM networks are prepared in the presence of a block-copolymer of ethylene oxide and propylene oxide as a template. We present data on the synthesis of these materials and on their efficiency in the hydrogenation of unsaturated compounds. For comparison, we also consider the results obtained with catalysts synthesized using non-templated networks.

2. Experimental

2.1. Materials

The following reagents were used as initial and reference substances: 1-octene C_8H_{16} (Reachim, Reagent Grade); styrene $C_6H_5CH=CH_2$ (Aldrich, $\geq 99\%$); *p*-methylstyrene $p-CH_3C_6H_4CH=CH_2$ (Aldrich, 96%); *p*-*tert*-butylstyrene $p-(CH_3)_3CC_6H_4CH=CH_2$ (Aldrich, 94%); phenylacetylene (Aldrich, 98%); 2,5-dimethyl-2,4-hexadiene $(CH_3)_2C=CH-CH=C(CH_3)_2$ (Aldrich, 98%); and dicyclopentadiene $C_{10}H_{12}$ (Aldrich, 97%). Their purity was monitored by gas–liquid chromatography (GLC).

Methanol CH_3OH (Acros Organics, 99+); ethanol C_2H_5OH (IREA 2000, analytical grade); chloroform $CHCl_3$ (Ekos-1, Reagent Grade); tetrahydrofuran (THF) C_4H_8O (Chimmed, 99.5%); dimethylformamide (DMF) $HC(=O)N(CH_3)_2$ (Chimmed, Chemical Grade) were used as solvents. Chloroform was purified by distillation from molecular sieves 4 Å; THF was distilled over calcium hydride, and DMF was distilled over molecular sieves in a vacuum with the azeotropic distillation of water in the presence of benzene.

The following substances were used for the synthesis of catalysts based on dendrimers: second-generation poly(amidoamine) dendrimer with an ethylenediamine core (PAMAM-G2, PAMAM(NH_2)₁₆, MW ~ 3256.18) synthesized in accordance with a published procedure [46]; third-generation poly(propylene imine) dendrimer with a diaminobutane core (PPI-G3, DAB(NH_2)₁₆, MW ~ 1686.79) synthesized in accordance with a published procedure [47]; 3,3'-dimethoxy-4,4'-diphenyl diisocyanate $p-(H_3COC_6H_3NCO)_2$ (DMDPDI) (Aldrich, tech., 85%); poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic 123) $(C_2H_4O)_{20}(C_3H_6O)_{70}(C_2H_4O)_{20}$ with the number average molecular weight $M_n \approx 5800$ (Aldrich); poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic 127) $(C_2H_4O)_{101}(C_3H_6O)_{56}(C_2H_4O)_{101}$ with the average-number molecular weight $M_n \approx 12,000$ (Aldrich); and palladium(II) acetate $Pd(OAc)_2$ (Aldrich, 99.9%). They were used without additional purification. Dispersities of dendrimers used

were calculated as ratio of number-average molecular weight (M_n) to weight-average molecular weight (M_w), retrieved from the corresponding mass-spectra, and achieved 99% for DAB(NH_2)₁₆ and $\sim 100\%$ for PAMAM(NH_2)₁₆ respectively.

2.2. Methods and instrumentations

1H and ^{13}C NMR spectroscopic analysis was performed on Avance Bruker instrument with operating frequency of 400.13 MHz. The chemical shifts δ (ppm) are given with reference to TMS (0.00 ppm). For aqueous solutions, 3-(trimethylsilyl)propanesulfonic acid (DSS) was used as an internal standard (δ 0.015 ppm). D_2O and $DMSO-d_6$ were used as solvents.

Mass spectrometry was used for the determination of the purity of synthesized PPI dendrimers and the conversion of *N*-isopropylacrylamide. Mass-spectra were recorded on Agilent LC–MS 1100 SL instrument with electrospray ionization (ESI), in positive ion detection mode. Samples were prepared as solutions in methanol (Acros Organics, 99+%) and distilled water with a concentration of ~ 1 mg/mL. The electrospray needle voltage was 3.5 kV. The drying gas temperature was 250 °C, and the flow rate was 11 L/min.

Fourier transform IR spectroscopic analysis was performed on Nicolet IR2000 instrument (Thermo Scientific) with the use of a horizontal attenuated total reflectance (HATR) accessory supplied with a 45° ZnSe crystal for different wavelength ranges with a resolution of 4 cm^{-1} .

X-ray photoelectron spectroscopy (XPS) analysis was carried out on Kratos Axis Ultra DLD and LAS-3000 instruments equipped with an OPX-150 hemispherical retarding-field electron-energy analyzer. The X-radiation of an aluminum anode (Al $K\alpha = 1486.6$ eV) was used for the excitation of photoelectrons at a tube voltage of 12 kV and an emission current of 20 mA. Photoelectron peaks were calibrated on the C 1s line of carbon with a binding energy of 284.8 eV.

The quantitative determination of palladium in the samples was performed by inductively coupled plasma atomic emission spectrometry (ICP AES) with the aid of an IRIS Interpid II XPL instrument (Thermo Electron Corp., USA) with both radial and axial viewings at wavelengths of 310 and 95.5 nm.

The studies by transmission electron microscopy (TEM) were carried out on LEO912 AB OMEGA transmission electron microscope. Micrographs were processed and average particle sizes were calculated with the Image J software.

A ChromPack CP9001 gas chromatograph, equipped with a capillary column (SE-30 grafted phase, 30 m \times 0.2 mm) and flame-ionization detector, was used for analysis of substrates and reaction products. Chromatograms were recorded and analyzed on a computer with the use of the Maestro 1.4 software. Conversion was determined by changes in the relative peak areas (in%) of the substrates and products.

2.3. Synthesis of dendrimers-based hybrid materials

2.3.1. Synthesis of the DAB-PPI-G3-DMDPDI(1/1) material [34]

DAB(NH_2)₁₆ dendrimer (1 g, 0.6 mmol) and 50 mL of THF were placed into a 100-mL round-bottom flask, equipped with a magnetic stirrer and a reflux condenser. Then, 1.4 g (4.75 mmol) of 3,3'-dimethoxy-4,4'-diphenyldiisocyanate was added while stirring. The reaction was carried out at 70 °C for 12 h. After the reaction completed (the complete dissolution of the cross-linking agent and the appearance of light yellow precipitate at the bottom instead of the red-brown dendrimer particles), the mixture was evaporated on a rotor evaporator with the formation of 2.07 mg of milk-white powder (yield of 86%).

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