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Pd Nanoparticles in Dendrimers Immobilized on Silica–Polyamine Composites as Catalysts for Selective Hydrogenation

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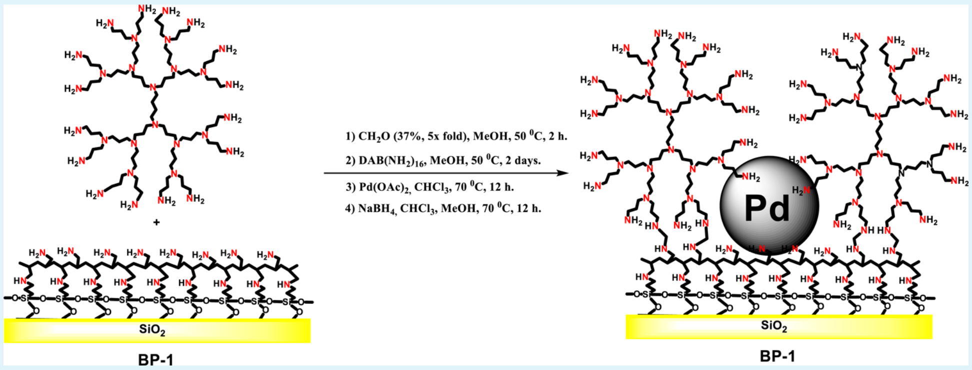
Supporting Information



ABSTRACT: New heterogeneous hydrogenation catalysts, based on Pd nanoparticles and polypropyleneimine (PPI) dendrimers of the third generation that have been covalently grafted to a silica surface modified with polyallylamine (PAA) have been synthesized. The final products were characterized by TEM, XPS, and solid-state NMR spectroscopy. The synthesized materials are effective catalysts for selective hydrogenation of dienes to monoenes and phenyl acetylene to styrene at very high substrate/Pd ratios with turnover rates higher than related Pd nanoparticle catalysts. The synthesized catalysts can be reused without any loss of activity in the case of styrene and isoprene.

KEYWORDS: *hydrogenation, Pd catalysis, hybrid-materials, amine-modified silica, dendrimers*

1. INTRODUCTION

Hydrogenation of unsaturated hydrocarbons is one of the most important processes in modern petrochemical industries. Thus, hydrogenation of olefins allows the production of stable additives for diesel fuel requiring a high octane number and permits the stabilization of gasoline pyrolysates.[1] Therefore, it is possible to avoid the polymerization of olefins, inevitable under refining and storage conditions, leading to fuel deterioration. The selective hydrogenation of phenylacetylene, which poisons polymerization catalysts, is more cost-effective than its separation from the reaction products.[1−3] Hydrogenation of dienes and acetylenic hydrocarbons also prevents further polymerization and oxidation of these products.[1,4] Thus, selective hydrogenation plays an essential role in the processing of fine organic chemicals, where it is possible to use both different metal complexes as catalysts and heterogeneous catalysts.[5,6]

The heterogeneous catalysts traditionally used in the industry often require severe reaction conditions under which a high selectivity for the product desired is very difficult to achieve, and the ratio of substrate to catalytically active metal is not high. Homogeneous catalysts used in fine organic synthesis have high specific activity; however, they possess a number of disadvantages: high cost, poor stability, and lack the ability to be regenerated and reused. In this regard, it is of interest to develop systems with properties of both homogeneous (high activity and selectivity) and heterogeneous (stability and reusability) catalysts.[4,6−13] As active components, nanoparticles of metals such as platinum, palladium, and ruthenium have been successfully used as catalysts for hydrogenation of olefins and aromatic compounds.[10,14−17]

The selective hydrogenation of conjugated double bonds to monoenes is essential for the purification of monomeric alkenes to be subsequently used in the reactions of polymerization and hydroformylation. Similarly, the selective reduction of alkynes to olefins is desirable because alkynes poison polymerization

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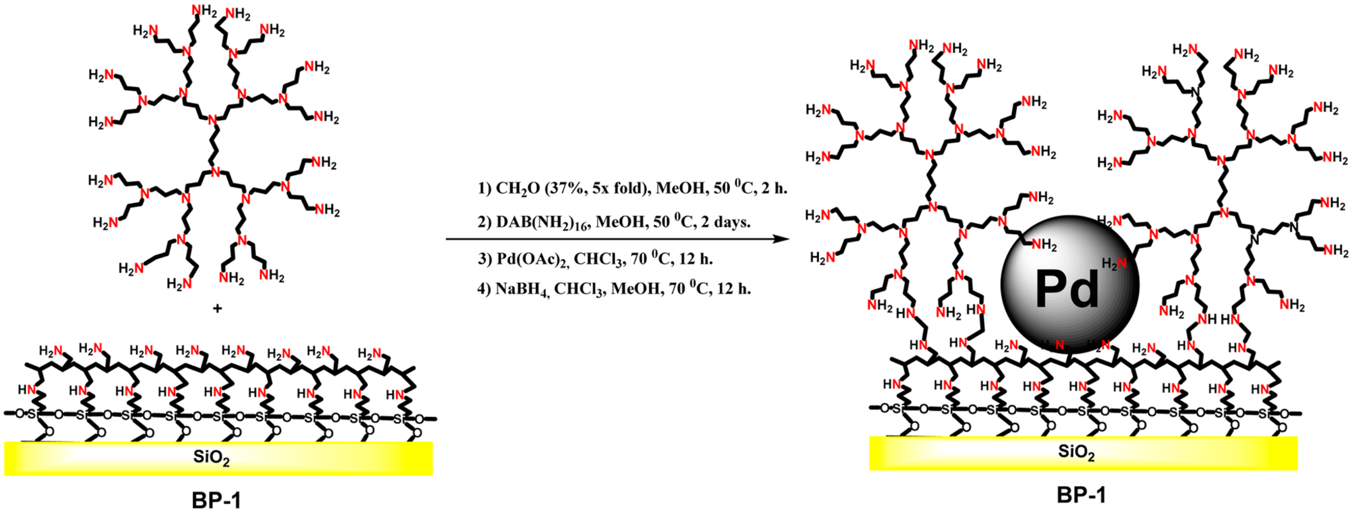
Scheme 1. Modification of BP-1 Support with PPI Dendrimers and Deposition of Palladium Nanoparticles on the SPC–Dendrimer Hybrid



catalysts. The use of nitrogen-containing additives to palladium catalysts—among them the Lindlar catalyst (palladium supported on the calcium carbonate or barium sulfate, poisoned with the lead acetate)—is known to increase the selectivity for olefins. It is achieved by changing the electronic properties of the metal surface and its partial blocking.[18,19] However, amines and other organic modifiers are gradually washed out from the catalyst surface, being easily dissolved in the organic substrates. Therefore, these additives need to be loaded in much higher amounts than the substrate for high selectivity to be achieved.[19,20] Thus, the design of catalysts where nanoparticle coordination and stabilization is achieved by the binding of nitrogen-containing ligands to inorganic carriers is a desirable goal.

The polyamine dendrimers PAMAM and PPI are good candidates for the stabilization of palladium nanoparticles.[7,21−23] The large number of donor atoms and the branched regular structure, enable them to encapsulate metal ions and nanoparticles efficiently and also provide high selectivity in various catalytic processes. The acceleration of the hydrogenation process in the presence of both homogeneous and heterogeneous catalysts based on dendrimers as compared with traditional analogues is reported elsewhere.[24−26] Palladium complexes and nanoparticles stabilized by PAMAM and PPI dendrimers can hydrogenate phenylacetylene and conjugated dienes to the corresponding monoenes selectively, and at higher rates than traditional heterogeneous nanoparticle catalysts.[21,24,25,27] Palladium–rhodium and platinum–palladium bimetallic nanoparticles stabilized with fourth generation PAMAM dendrimers selectively hydrogenated 1,3-cyclooctadiene to cyclooctene.[28,29] However, nanoparticles stabilized with dendrimers cannot be effectively separated from the reaction products and reused.[7,21]

The development of methods for immobilizing dendrimer catalysts could circumvent this problem. There are two main approaches for immobilizing dendritic catalysts described in the literature. The first approach involves the attachment of dendrons to the surface of modified amino groups on an inorganic carrier. Heterogeneous catalysts based on palladium phosphine complexes with PAMAM dendrons grafted to silica demonstrated high conversions and selectivity to the hydrogenation of both cyclic and acyclic dienes.[26] A number of authors have synthesized catalysts based on palladium and platinum nanoparticles stabilized with PAMAM dendrimers, which are covalently attached to the internal pore surface of the silica based materials SBA-15 and MCF-17. These catalysts were successfully applied in the hydrogenation of unsaturated and heteroaromatic compounds,[30−32] the reduction of organic and inorganic compounds with sodium borohydride[33] and in the Suzuki–Miyaura cross-coupling reaction.[34] Due to their regular branched structure and the large number of donor atoms, dendrimers limit the growth of metal nanoparticles and stabilize them better than direct complexation to the silica matrix. The second approach is to create three-dimensional networks by covalently linking dendrimers together using different bi- and trifunctional agents, followed by encapsulation of the noble metal nanoparticles.[27,35] Palladium nanoparticles encapsulated in the cross-linked PPI dendrimers allowed the hydrogenation of 1,3-cyclohexadiene to cyclohexene effectively, with 100% selectivity, while the selectivity for cyclooctadiene was higher than 90%, even at longer reaction times.[26,27,36]

In this paper, we report the combination of silica polyamine composite (SPC) hybrids[37,38] with PPI dendrimers to provide an easy route to stable and highly efficient selective hydrogenation catalysts based on palladium nanoparticles. The advantages of this approach are as follows: (1) easy modification of surface amino groups; (2) high density of amino groups on the support surface compared with commonly used supports such as modified SBA-17 and MCF-17; (3) the presence of multiple covalent bonds between the polyamine and the silica surface, which eliminates the probability of leaching the polymer during the reaction; (4) the availability of industrial quantities of the SPC hybrid materials (the SPC technology is currently being produced by Johnson–Matthey Ltd.).

2. EXPERIMENTAL SECTION

2.1. Materials. Solvents and reagents: benzene (IREA 2000, Purum p.a.); toluene (Chimmed, Puriss.); ethylbenzene (Reachim, Purum); styrene (Aldrich, ≥ 99%); phenylacetylene (Aldrich, 98%); 2,5-dimethyl-2,4-hexadiene (Aldrich, 98%); isoprene; 1,4-diaminobutane (Ferak); acrylonitrile (Acros Organics, 99 +%); methanol (Acros Organics, 99+%); ethanol (IREA 2000, Purum p.a.); chloroform (Ecos-1, Purum). Chloroform was purified by distillation from 4 Å molecular sieves. Solvent and reagent purity was determined by gas–liquid chromatography. The dendrimer-based catalysts were synthesized from palladium(II) acetate Pd (Aldrich, 99.9%), and the dendrimer $\mathrm{DAB(NH_2)_{16}}$ was prepared according to published literature procedures.[39] The SPC **BP-1** (Poly(allylamine) covalently bound to a silanized amorphous silica gel, Scheme 1) was synthesized according to published procedures.[37,38]

2.2. Methods. *Analysis by LS-MS-D-Trap Method Electrospray Ionization.* The degree of purity of the dendrimers synthesized was evaluated by mass spectrometry. Mass spectra were recorded on an Agilent LC-MS 1100 SL device by electrospray ionization of the sample (ESI). The analysis was performed in the positive ion mode. The samples were prepared in methanol and distilled water (~1 mg/mL). The voltage at the electrospray needle was 3.5 kV. Drying gas temperature was 250 °C, and the flow rate was 11 L/min.

Nuclear Magnetic Resonance Spectroscopy. The ^{1}H and ^{13}C Nuclear Magnetic Resonance spectroscopy was performed with a Bruker Avance spectrometer at 400.13 MHz for ^{1}H and 100 MHz for ^{13}C. Chemical shifts are reported δ (ppm) relative to TMS (0.00 ppm). DSS (3-(trimethylsilyl)-propanesulfonic acid), δ 0.015 ppm, as a standard for aqueous solutions. $\mathrm{D_2O}$, DMSO-d_6 were used as solvents.

Infrared Spectroscopy. FT-IR spectra were performed with a Nicolet IR2000 (Thermo Scientific) using multiple distortion of the total internal reflection method with Multireflection HATR accessories, containing a ZnSe crystal 45° for different wavelengths with a resolution of 4 $\mathrm{cm^{-1}}$.

Gas–Liquid Chromatography. Chromatographic analysis of the reaction mixtures was done with a ChromPack CP9001 gas chromatograph equipped with a flame ionization detector and a 30 m × 0.2 mm column containing a grafted SE-30 phase. The chromatograms were recorded and analyzed in a computer using the program Maestro 1.4. Conversion was determined by the change in the relative area (%) of substrate and product peaks. The substrates are grouped according to their boiling point. The substrates and reaction products belonging to the same group are analyzed with the same temperature program.

Transmission Electron Microscopy. Transmission electron microscopy (TEM) analysis was performed using a LEO912 AB OMEGA microscope.

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) studies were performed using a LAS-3000, equipped with a photoelectronic analyzer with retarding potential OPX-150. To excite photoelectrons, aluminum anode X-ray radiation was used (Al $K\alpha$ = 1486.6 eV) with a tube voltage of 12 kV and emission current of 20 mA. The calibration of photoelectron peaks was performed along the C 1s line with binding energy of 285 eV.

Atomic Emission Spectroscopy. Quantitative determination of palladium in the samples was performed using atomic emission spectroscopy with inductively coupled plasma (ICP-AES) on an IRIS Interpid II XPL instrument (Thermo Electron Corp., U.S.A.) in radial and axial observation modes at wavelengths of 310 and 95.5 nm.

Solid State NMR Spectroscopy. The solid state ^{13}C CPMAS NMR spectroscopy analysis was performed using a Varian NMR Systems 500 MHz spectrometer at an operating frequency of 125 MHz using TanCP at a spinning speed of 10 kHz.

2.3. Synthesis. Preparation of Dendrimer-Based Hybrid Organic–Inorganic Materials: Grafting of the Third Generation PPI Dendrimers to the Silica Polyamine Composite, BP-1. In a 10 mL single-neck round-bottom flask, equipped with a magnetic stirrer and a reflux condenser, 995 mg of the BP-1 support (1.6 mmol N/g, particle size range 250–550 μm), 300 μL of 37% aqueous formaldehyde solution (5-fold excess relative to the mmol N/g of **BP-1**) and 5 mL of methanol were combined. The reaction was carried out for 2 h with vigorous stirring, the product swelling to form a gel. The imine derivative of BP-1 formed was combined with the third generation PPI dendrimer (600 mg, 0.356 mmol) and the reaction was conducted for 24 h at 70 °C with vigorous stirring (the yellow-brown dendrimer solution was gradually discolored). The mixture was evaporated in a rotary evaporator at 50 °C. The product was isolated as a milky-white powder in 88% yield, 1.4 g.

XPS (eV): 102.2 (Si 2p, 6.0%); 285.2 (C 1s, 61.1%); 399.0 (N 1s, 16.0%); 531.2 (O 1s, 16.9%).

NMR ^{13}C (δ, ppm): 71.0 ($\mathrm{HN}\boldsymbol{CH_2}\mathrm{OH}$, $\mathrm{HN}\boldsymbol{CH_2}\mathrm{NH}$); 53.5 (br. s, $\mathrm{N}\boldsymbol{CH_2}\mathrm{CH_2}\boldsymbol{CH_2}\mathrm{N}$, $\mathrm{(CH_2)_2CH}\boldsymbol{CH_2}\mathrm{NH}\boldsymbol{CH_2}$, $\mathrm{N}\boldsymbol{CH_2}\mathrm{CH_2CH_2}\boldsymbol{CH_2}\mathrm{N}$); 41.6 (br. s, $\mathrm{NCH_2CH_2}\boldsymbol{CH_2}\mathrm{NH_2}$, $\mathrm{(CH_2)_2CH}\boldsymbol{CH_2}\mathrm{NH_2}$); 28.0 (br. s, $\mathrm{NCH_2}\boldsymbol{CH_2}\mathrm{CH_2NH_2}$, $\mathrm{NCH_2}\boldsymbol{CH_2}\mathrm{CH_2N}$); 18 (br. s, $\mathrm{NCH_2}\boldsymbol{CH_2}\mathrm{CH_2Si}$); 13 (br. s, $\mathrm{NCH_2CH_2}\boldsymbol{CH_2}\mathrm{Si}$).

^{29}Si (δ, ppm): −65.2 (br., $\boldsymbol{Si}\mathrm{(OSi)_3(CH_2)_3}$); −97.0 (br., $\boldsymbol{Si}\mathrm{(OSi)_3OH}$); −111 (br. s., $\boldsymbol{Si}\mathrm{(OSi)_4}$).

Synthesis of the Pd(II) Catalyst Precursor (1). In a single neck round-bottom flask (capacity 10 mL), equipped with magnetic stirrer and reflux condenser, 1000 mg of the PPI-BP-1 composite material and 5 mL of methylene chloride were added. 420 mg (1.87 mmol) of $\mathrm{Pd(OAc)_2}$ in 5 mL of methylene chloride was added to the resulting suspension with stirring. The reaction was carried out for 12 h at 70 °C. The color of the reaction mixture changed from red-ocher to brown-black. After reaction, the suspension was evaporated in a rotary evaporator at 50 °C. The resulting material was a black-brown powder weighing 1375 mg (97% yield).

XPS (eV): 102.2 (Si 2p, 7.1%); 285.2 (C 1s, 50.0%); 334.9 ($\mathrm{Pd^0}$ $\mathrm{3d_{5/2}}$, 1.14%); 337.2 ($\mathrm{Pd^{II}}$ $\mathrm{3d_{5/2}}$, 2.78%); 339.9 ($\mathrm{Pd^0}$ $\mathrm{3d_{3/2}}$, 0.37%); 342.1 ($\mathrm{Pd^{II}}$ $\mathrm{3d_{3/2}}$, 1.00%); 398.8 (N 1s, 18.7%); 529.2 (O 1s, O–Pd, 2.80%); 531.8 (O 1s, 16.10%); 534.0 (Pd $\mathrm{3p_{3/2}}$).

NMR ^{13}C (δ, ppm): 56.6, 51.1 ((br. s, $\mathrm{N}\boldsymbol{CH_2}\mathrm{CH_2}\boldsymbol{CH_2}\mathrm{N}$, $\mathrm{(CH_2)_2CH}\boldsymbol{CH_2}\mathrm{NH}\boldsymbol{CH_2}$, $\mathrm{N}\boldsymbol{CH_2}\mathrm{CH_2CH_2}\boldsymbol{CH_2}\mathrm{N}$); 23.9 (s, $\mathrm{NCH_2}\boldsymbol{CH_2}\mathrm{CH_2NH_2}$).

ICP-AES: 7.23% Pd.

*Reduction of the Catalyst Precursor to Give the Pd^0 Catalyst (**2**).* To a single neck round-bottom flask (capacity 10 mL), equipped with a magnetic stirrer and a reflux condenser, 685 mg of the catalyst precursor **1**, 5 mL of methylene chloride and 5 mL of methanol were added. To this suspension, 710 mg (18.7 mmol) of sodium borohydride was added portion-wise while stirring. The reaction mixture turned black while gas evolution was observed. The reaction was carried out for 12 h at 70 °C. After the reaction, the resulting solid mixture was washed with water and methanol to remove sodium tetraborate and the residue isolated by centrifugation and dried. The resulting material was a black powder weighing 553 mg (95.5% yield).

XPS (eV): 103.0 (Si 2p, 13.2%); 285.1 (C 1s, 39.9%); 335.2 ($\mathrm{Pd^0}$ $\mathrm{3d_{5/2}}$, 1.92%); 337.7 (PdO $\mathrm{3d_{5/2}}$, 0.61%); 338.9 ($\mathrm{Pd^{2+}{}_{bound.}}$ $\mathrm{3d_{5/2}}$, 0.48%); 340.3 ($\mathrm{Pd^0}$ $\mathrm{3d_{3/2}}$, 1.64%); 342.5 (PdO $\mathrm{3d_{3/2}}$, 0.81%); 342.5 ($\mathrm{Pd^{2+}{}_{bound.}}$ $\mathrm{3d_{3/2}}$, 0.22%); 399.1 (N 1s, 11.9%); 529.5 (O 1s, O–Pd, 6.72%); 531.8 (O 1s, 22.48%).

NMR ^{13}C (δ, ppm): 52.6 (br. s, $\mathrm{N}\boldsymbol{CH_2}\mathrm{CH_2}\boldsymbol{CH_2}\mathrm{N}$, $\mathrm{(CH_2)_2CH}\boldsymbol{CH_2}\mathrm{NH}\boldsymbol{CH_2}$, $\mathrm{N}\boldsymbol{CH_2}\mathrm{CH_2CH_2}\boldsymbol{CH_2}\mathrm{N}$); 44.0 br. s, $\mathrm{NCH_2CH_2}\boldsymbol{CH_2}\mathrm{NH_2}$, $\mathrm{(CH_2)_2CH}\boldsymbol{CH_2}\mathrm{NH_2}$); 26.0 (br., $\mathrm{NCH_2}\boldsymbol{CH_2}\mathrm{CH_2NH_2}$).

ICP-AES: 7.61% Pd.

2.4. Protocol for the Catalytic Experiments. The desired amount of catalyst, substrate and solvent were placed into a thermostated steel autoclave, equipped with a test tube insert and a magnetic stirrer. The autoclave was sealed, pressurized with hydrogen up 1 or 3 MPa and connected to the thermostat. The reaction was carried out at 70 °C for 1 h or 15 min. The reactor was then cooled below the room temperature and depressurized. The reaction products were analyzed by gas–liquid chromatography.

Reuse of **2** was carried out by hydrogenation of styrene and isoprene. For the styrene hydrogenation, 0.95 mg of catalyst, 1 mL of substrate, and 1.5 mL of solvent (benzene) were placed in the thermostated stainless steel autoclave, equipped with the test tube-insert and a magnetic stirrer. For the isoprene hydrogenation, 0.5 mg of catalyst, 1 mL of substrate, and 2 mL of solvent (toluene) were used. The autoclave was sealed, pressurized with hydrogen up to 3 MPa and connected to the thermostat. The reaction was conducted at 70 °C for 15 min. Then, the reactor was cooled below the room temperature and depressurized. The reaction products were separated by decantation and analyzed by gas–liquid chromatography. The

Table 1. Physiochemical Characteristics of the Hybrid Materials

			XPS, atomic content (%)							
								Pd $3d_{5/2}$ (%, eV)		
hybrid	metal content (%)	d (nm)	Si	C	N	O	Pd	Pd^0	PdO_x	Pd^{2+}
1	7.23	1.31 ± 0.02 2.31 ± 0.01 3.62 ± 0.02 4.94 ± 0.05 6.13 ± 0.06 7.34 ± 0.35	7.1	50.0	18.7	18.9	5.3	30.0 (334.9)	71.0 (337.2)	
2	7.61	1.95 ± 0.02	13.2	39.9	11.9	29.2	5.8	64.0 (335.2)	20.1 (337.7)	15.9 (338.9)

catalyst located in vitro was used without additional loading, drying, or purification in the subsequent reaction cycles.

The activity of each catalytic reaction is reported as specific activity (SA) and was calculated as the ratio of the reacted substrate to the metal loading, expressed in moles, per unit of time:

$$SA = \frac{\text{Conv.} \times n_{\text{substr}}}{n_{\text{pd}} t}$$

3. RESULTS AND DISCUSSION

3.1. Synthesis of Hybrid Catalysts Based on Dendrimers.

The polypropyleneimine third generation dendrimers were synthesized according to the literature[39] and were used to modify the SPC heterogeneous carrier. The SPC used was BP-1, made by reaction of 15 000 MW poly(allylamine) with an amorphous silica gel after silanization with 3-chloropropyltrichlorosialne.[36−38] Formaldehyde reacts with the surface amines to form a formyl-imine, which in turn, reacts with amine groups of the dendrimers, according to the Mannich reaction (Scheme 1).

The ratio of linkable groups and the sequence of adding the reactants were chosen so that grafted dendrimers should preserve their mobility and should not ligate together. For this purpose, the BP-1 support was introduced into the reaction first with an excess of formaldehyde in methanol and after 2 h the dendrimer was added to the resulting system in 1:4.2 ratio with the available formyl imine groups. As the reaction proceeds, the yellow solution containing the dendrimer gradually discolorized, indicating the dendrimer is being grafted to the support surface.

The structure and composition of the synthesized material was confirmed by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and ^{13}C solid-state NMR spectroscopy. Physico-chemical characteristics of the samples prepared are presented in the Experimental section and in the Supporting Information (See Figures S1 and S2 in the Supporting Information).

The deposition of palladium nanoparticles on the support modified by dendrimers was performed as previously described,[23,40] which includes complex formation with a transition metal salt and subsequent reduction with sodium borohydride (Scheme 1). Materials containing nonreduced palladium ions were also synthesized. Both the reduced and nonreduced catalysts were characterized by TEM, XPS, and ^{13}C solid-state NMR spectroscopy. The metal content in the samples was determined by means of ICP-AES. Physico-chemical characteristics of the Pd(II) catalyst precursor, **1**, and the Pd^0 catalyst, **2**, are given in Table 1.

According to the XPS (Table 1), both catalysts contain both Pd (0) ($3d_{5/2}$ 335 eV) and oxidized Pd (PdO_x $3d_{5/2}$ 337 eV, Pd^{2+} $3d_{5/2}$ 338.9 eV) on the surface. The atomic concentration of the metal was 5.3 and 5.8% for **1** and **2** respectively. This correlates with the palladium content in the samples (7.23 and 7.61%, respectively) obtained from ICP-AES. The slight energy displacement observed for carbon and nitrogen from the usual values (284.8 and 398.6 eV, respectively[41]) in the spectra of these samples is due to partial transfer of electrons from donor nitrogen atoms to the neutral metal particles.[42,43]

The atomic concentration ratio of Pd(0)/(PdO_x+Pd(II)) in **1** is ~0.4 according to the deconvolution spectra (Figure 1, a). The presence of Pd(0) in **1** could to be due to the reduction of metal ions by the organic ligands grafted to the support. In

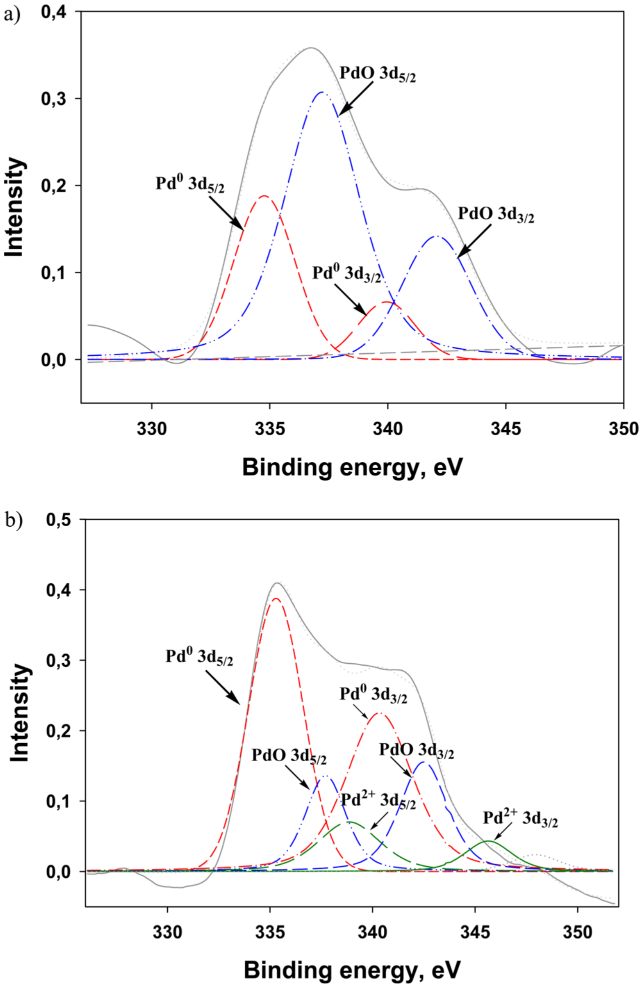
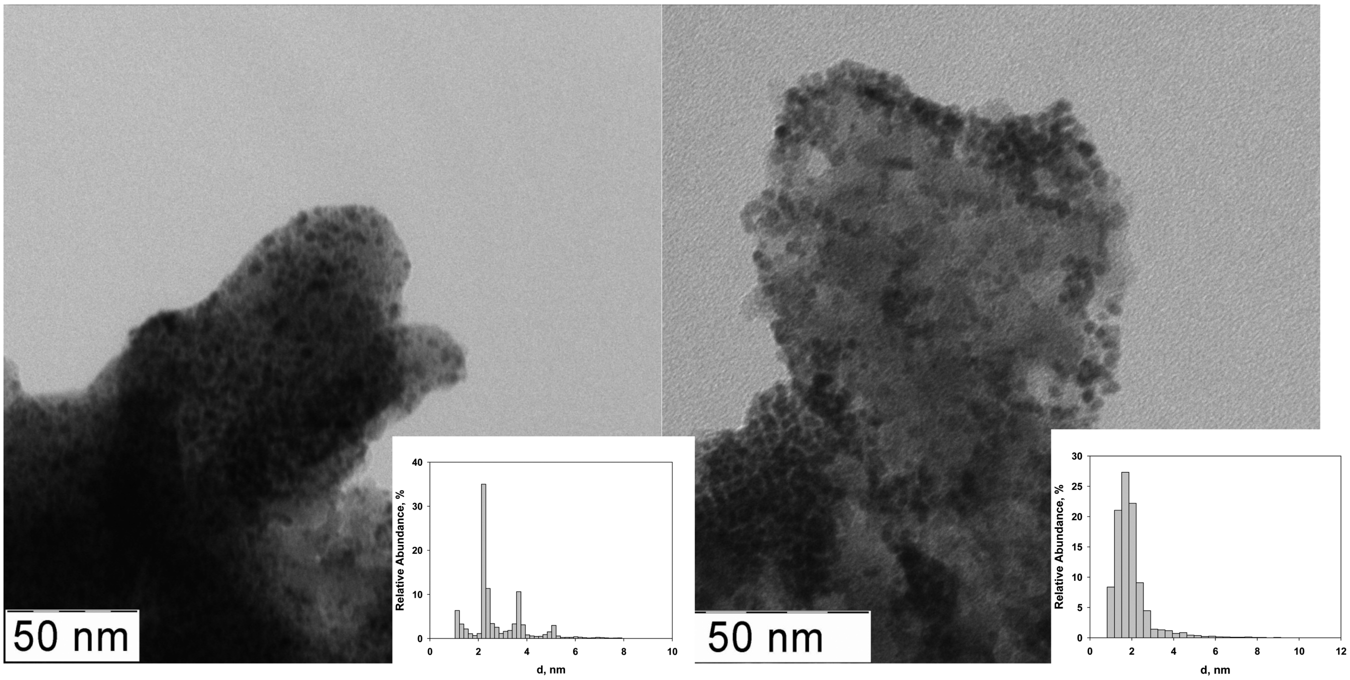


Figure 1. Deconvolution of the XPS spectra of (a) Hybrid **1** and (b) Hybrid **2**.



a) b)

Figure 2. TEM microphotographs and particle size distribution: (a) Hybrid **1** and (b) Hybrid **2**.

addition, there is an electron transfer from organic groups of the support to palladium clusters to form enamines.[44−46] In **2** the ratio of atomic concentrations of Pd(0)/(PdO_x+Pd(II)) is approximately 1.7 (Figure 1, b). In the O 1s spectra of both dendrimer-hybrids there is a signal corresponding a Pd−O bond, which correlates with the presence of surface oxide PdO_x in the Pd 3d spectra.[47] Its presence appears to be associated with the palladium nanoparticles susceptibility to air oxidation.[48]

There is an assemblage of crystalline Pd (0) clusters of different sizes (2−4 nm, 6−8 nm) in the TEM micrographs of **1** (Figure 2a). The particle size distribution is of a multimodal character (Figure 2a). The reduction processes referred to above apparently lead to the spontaneous growth of Pd(0) nanoparticles, the size of which will depend on the position of the crystallization center on the support surface and the density of dendrimer population. Smaller crystallites (1.0−1.5 nm) are likely to be formed between dendrimer branches while the particles of 2−5 nm in diameter are in the space between the dendrimers depending on the distance between them. Hybrid **2** reduced in the presence of $NaBH_4$, is characterized by a monomodal size distribution with the predominance of nanoparticles of 1.5−3 nm in diameter (Figure 2b). The major fraction of zerovalent palladium is formed during the reduction process, resulting in an increase in the number of particles with 2 nm as mean diameter. As a consequence, the fraction of large/bulk nanoparticles is essentially decreased.

3.2. Hydrogenation of Unsaturated Compounds in the Presence of Hybrid Dendrimer-Based Catalyst 2. The hybrid catalyst **2** was evaluated for the reduction of styrene, phenylacetylene, isoprene, and 2,5-dimethyl-2,4-hexadiene. As stated in the introduction, all of these unsaturated hydrocarbons are found in petroleum feedstocks and therefore efficient and selective hydrogenation is of significant importance to the petrochemical industry. The two dienes were chosen in order to evaluate how chain branching affects the product distribution of the product monoenes and the efficiency of the catalyst with more sterically demanding dienes

*3.2.1. Hydrogenation of Styrene with Hybrid Catalyst **2**.* Table 2 shows the results for the reduction of styrene at 1 and 3 MPa and at two relatively high substrate/catalyst ratios at 70 °C for 15 min. The only reaction product was ethylbenzene. In terms of percent conversion combined with substrate/Pd ratio, the optimal conditions are seen in entry 4 of Table 2. Increasing the substrate/Pd ratio further gets almost as good a percent conversion with significant increases in specific activity (entries 5 and 6 in Table 2). Further, increases in substrate to catalyst ratio lead to a decrease in conversion, whereas the specific activity still increases (entry 7, Table 2). In a separate series of experiments catalyst precursor **1** was used to reduce styrene (see Supporting Information Table S1). Specific activities were up to 30% lower, as compared with catalyst **2**, due to the need to create more Pd^0 during the short reaction period.

Table 2. Hydrogenation of Styrene in the Presence of Hybrid Catalyst 2[a]

entry	*P* (MPa)	Substrate/Pd (mol/mol)	conv. (%)	SA[b] (h^{-1})
1	1	6425	73.5	18 890
2	3	6425	100	25 700
3	1	12 845	67	34 440
4	3	12 845	100	51 400
5	3	20 345	97	78 945
6	3	30 520	94	114 755
7	3	61 040	57	139 170

[a] Reaction conditions: 1 mL of substrate, 1.5 mL of benzene, for 15 min, at 70 °C. [b] SA = specific activity, mole product/mol catalyst/t.

*3.2.2. Hydrogenation of Phenylacteylene with Hydrid Catalyst **2**.* The selectivity for styrene strongly depended on hydrogen pressure and the substrate/catalyst ratio. Thus, the selectivity for styrene was 52% at the substrate/Pd ratio = 3350, when carrying out the reaction for 1 h and at the pressure of 1 MPa, and increased up to 93%, when reducing the reaction time to 15 min, and became 97% with an additional 2-fold increase in the substrate/Pd ratio (see Table 3). Under the same conditions, the increase in hydrogen pressure to 3 MPa results in a quantitative conversion and simultaneous drop in the selectivity for styrene down to 70%. Further increases in substrate/catalyst ratio to 60 000, results in a gradual increase in the selectivity of up to 96%. The optimum conditions for carrying out the reaction are a hydrogen pressure of 3 MPa, a substrate/Pd ratio equal to 20 100, and a reaction time of 15 min. These conditions give a conversion up to 91% and selectivity for styrene of 90%.

Table 3. Hydrogenation of Phenylacetylene in the Presence of Hybrid Catalyst 2[a]

entry	*P* (MPa)	*t* (h)	substrate/Pd (mol/mol)	conv. (%)	SA (h^{-1})	selectivity on styrene (%)
1	1	1	3350	100	3350	52
2	1	0.25	3350	87.5	11 730	93.5
3	1	0.25	6700	51	13 675	97
4	3	0.25	6700	99.5	26 680	70.5
5	1	0.25	13 405	32.5	17 430	96
6	3	0.25	13 405	98	52 550	87
7	3	0.25	20 100	91	77 265	90
8	3	0.25	31 840	76	96 790	89.5
9	3	0.25	60 300	40.5	103 160	96.5

[a] The reaction conditions are 1 mL of substrate, 1.5 mL benzene, at 70 °C.

3.2.3. Selective Reduction of Dienes to Monoenes. Hybrid catalyst **2**, showed high activity for the hydrogenation of dienes to monoenes (see Tables 4 and 5). Thus, for isoprene the conversions were 83% at 3 MPa of hydrogen and 1.5×10^{-3} Pd mol % (substrate/Pd = 66240). The specific activity exceeded 200 000 h^{-1}. The main product of the reaction in all cases was thermodynamically more stable 2-methyl-2-butene formed by 1,4-addition. An increase in hydrogen pressure leads to an increase in hydrogenation rate and simultaneously to a small decrease in the total alkene selectivity, while an increase in the substrate/Pd ratio results in the opposite effect. Activity and selectivity of the catalyst **2** was significantly higher than for palladium−phosphine complexes grafted on immobilized PAMAM dendrons.[26]

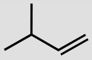
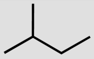
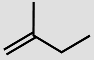
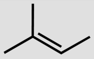
We have previously shown that SPC, modified by polyallylamine and polyethylenimine, on which platinum group metal salts have been adsorbed, are effective catalysts for the hydrogenation of terminal *n*-alkenes and cyclic dienes.[4] We have now compared these catalysts with regard to stabilizing nanoparticles as a result of their interaction with then amino groups of the immobilized polymers (polyallylamine for **BP-1**, polyethylenimine and for **WP-1**), with the activity of the catalyst **2** containing PPI dendrimers. The activity and selectivity of supported catalysts based on BP-1 and WP-1 in the hydrogenation of isoprene (Table 6) strongly depended on both hydrogen pressure and the nature of the support. Thus, under a pressure of 1 MPa conversions per hour did not exceed 25%, the total alkene selectivity was 50%, and the main reaction products were 2-methylbutane and 2-methyl-1-butene. This suggests that the reaction is under kinetic control with a predominance of 1,2-addition. Under 3 MPa the conversions exceeded 75% in an hour and the selectivity for internal alkene was more than 95%. In this case, the main product of the reaction was thermodynamically more stable 2-methyl-2-butene with a selectivity of 80−95%.

As can be seen from Tables 4 and 6, the hybrid catalysts containing dendrimers in their structure are far superior in their activity than the supported catalysts **BP-1-Pd** and **WP-1-Pd**. Thus, under a pressure of 1 MPa **BP-1-Pd** and **WP-1-Pd** give 25% conversion for an hour at the substrate/Pd ratio approximately equal to 1500−1600 (1 MPa). The substrate/Pd ratios for BP-1-Pd and WP-1-Pd were near 1500. The conversions under these ratios for 1 h were 25−26% (1 MPa). The conversions were 100% for catalyst **2** under a substrate/Pd ratio 3680 under the same conditions. So, for substrate/Pd ratio near 3000 of BP-1-Pd and WP-1-Pd catalysts the conversion will be lower than 25−26% and the specific activity is estimated to be lower than 780−790 h^{-1}. These numbers are much lower than for catalyst **2** (3680 h^{-1}). Catalyst **2** is therefore at least 5 times as fast in comparison with BP-1-Pd based on their respective specific activities.

Catalyst **2** retains high activity and selectivity for alkenes, even at very high substrate/Pd ratios (Table 4), which supports the idea that the dendrimers enhance nanoparticle catalytic activity relative to reduced Pd salts directly bound to the SPC.

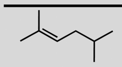
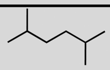
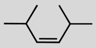
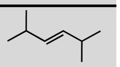
The high selectivity for monoenes with the observed high activity for the catalysts reported here suggests that this may be associated with the electronic structure of palladium nanoparticles stabilized by amine-containing polymers in the SPC.[4] High catalyst dispersion and hence small particle size as well as

Table 4. Hydrogenation of Isoprene in the Presence of 2

Entry	P, MPa.	t, h	Substrate/Pd, mol/mol	Conv.,%	SA, h^{-1}	Total selectivity on alkenes, %	Product distribution, %			
										
1	1	1	3680	100	3680	96	16.5	4	22	58
2	3	1	3680	100	3680	95	17.5	5	23.5	53
3	1	0.25	3680	100	14715	95.5	20	4.5	26	51
4	1	0.25	7360	91.5	26935	99	9	1	64.5	25.5
5	3	0.25	7360	100	29435	91	16.5	9	24	50.5
6	3	0.25	14720	100	58875	93.5	20.5	6.5	25	48
7	3	0.25	22080	100	93210	94	22	6	24.5	47.5
8	3	0.25	66240	83	232210	98.5	19	2	30	49

[a] The reaction conditions are 1 mL of substrate, 2 mL of the solvent, at 70 °C.

Table 5. Hydrogenation of 2,5-Dimethyl-2,4-hexadiene in the Presence of 2

Entry	P, MPa	t, h	Substrate/Pd, mol/mol	Conv.,%	SA, h^{-1}	Total selectivity for alkene, %	Product distribution, %			
										
1	1	1	2580	92	2375	99.5	28	< 0.5	9.5	62.5
2	1	0.25	2580	54	5575	99.5	25.5	< 0.5	5.5	69
3	1	0.25	5160	46.5	9605	98.5	25	1.5	3.5	70
4	3	0.25	5160	44.5	9190	99.5	27.5	< 0.5	2.5	70

[a]The reaction conditions are 1 mL of substrate, 1.5 mL of benzene, at 70 °C.

Table 6. [a] Hydrogenation of Isoprene in the Presence of Silica−Polyamine-Based Catalysts

entry	P (MPa)	catalyst	substrate/Pd (mol/mol)	conv. (%)	SA (h^{-1})	total selectivity for alkene, %
1	1	BP-1-Pd	1490	26	390	47
2	1	WP-1-Pd	1585	25	395	50
3	3	BP-1-Pd	1490	77.5	1155	96
4	3	WP-1-Pd	1585	77.5	1230	98

[a]The reaction conditions are 10 mg of cat., 1 mL of substrate, 2 mL of the solvent, 1 h. at 70 °C.

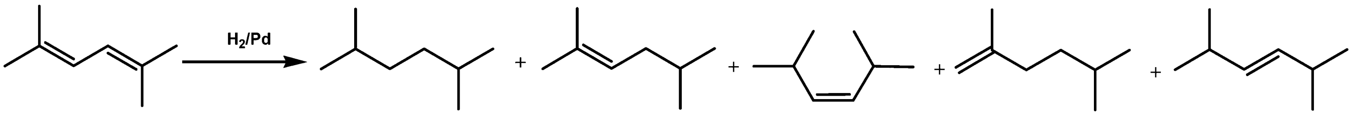
an increase in the reaction time[49,50] are known to result in a decrease in catalyst activity and selectivity for the methylbutenes. This is usually associated with coke formation and diene polymerization on the surface of the metal nanoparticles. For small particles (<200 atoms or <4 nm) partial positive charge is formed on the surface of the palladium, which leads to irreversible diene chemisorption and, consequently, to self-poisoning or substrate inhibition of the catalyst, this is a particular characteristic at high substrate/Pd ratios.[51] Addition of donor ligands leads to an increase in the reaction rate and selectivity for olefins. This effect is observed both for dienes and acetylenes in the presence of additives such as pyridine,[25,52] piperidine,[53] isopropylamine.[52] The electron-donor properties of nitrogen-containing ligands not only displace chemisorbed olefin from the palladium surface but also reduces the adsorption activity of the latter, preventing the coke formation and polymerization.[53]

It should be noted that the methylbutene isomer distribution reported here differs slightly from the classical distribution described in the literature as 1:1:2 (2-methyl-1-butene (2M1B):3-methyl-1-butene (3M1B):2-methyl-2-butene (2M2B)).[51,54] The literature articles on this theme indicated that various factors influence the ratio of methylbutenes: the feed rate in the continuous-flow reactor (which is equivalent to the substrate/catalyst ratio in the stationary reactor);[55,56] dispersion of the active metal;[49,50,53] contact time,[1] substrate nature and/or ligand environment of the active sites.[25,52,54] The ratio of isomers may be affected by two factors. First, the isomerization of terminal methylbutenes into the internal thermodynamically more stable 2-methyl-2-butene. Second, the presence of the methyl group, which influences the stability of the resulting π-allyl intermediate being formed at the first stage of the isoprene hydrogenation.[1,51,54,56−59] The maximal selectivity for 2-methyl-2-butene is observed when heterogeneous catalysts on inorganic supports are poisoned by various organic compounds (pyridines, tertiary amines, phosphines, arsines[57]). This is also observed when using polar organic supports, such as nylon-6.6,[60] and with homogeneous catalysts such as palladium complexes with diphosphinic ligands.[52] In addition, it has been reported[58] that an increase in substrate/Pd ratio leads to a gradual decrease in the 2-methyl-2-butene selectivity to approximately 50%. It should be pointed out that specific activity of the catalyst prepared (entry 8, Table 4, 232 210 h^{-1}) is much higher than the activity of Pd/C (23 000−8000 h^{-1}) and the Lindlar catalyst (11 500 h^{-1}).[57]

The 2-methyl-2-butene selectivity for **2** in the range of 40−50% indicates a high electron density on the nanoparticle surface. Higher selectivity for 2-methyl-1-butene as compared with 3-methyl-1-butene appears to be associated with a higher probability of addition of the first hydrogen atom to the sterically less hindered C=C double bond, due to the presence of dendrimers in the catalyst structure. The increase in the 3-methyl-1-butene content in the final mixture with increasing the substrate/catalyst ratio is likely due to competitive adsorption of electron-rich isoprene, which, being in large excess, easily replaces the alkene formed. As a result the latter is desorbed without undergoing further hydrogenation or isomerization.[55,58]

Increasing the size of the substrate and/or its branching at double bonds in the diene molecule leads to a significant drop in activity (Table 5). The 2,5-dimethyl-2,4-hexadiene conversion for 1 h is less than 100% for **2**. Decreasing the reaction time or increasing the substrate/Pd ratio leads to even lower yields, while an increase in hydrogen pressure does not affect the catalyst activity. The total alkene selectivity is 98−99% regardless of the hydrogen pressure or the substrate/Pd ratio (Table 5, Scheme 2). The main reaction product was trans-2,5-dimethyl-3-hexene, the more thermodynamically stable product

Scheme 2. Product Distribution in the 2,5-Dimethyl-2,4-hexadiene Hydrogenation with the Dendrimer-Containing Pd Catalysts



$DAB(NH_2)_{16}*Pd^0@BP1$	0.5-1.5%	25-30%	5-10%	0%	60-70%
$DAB(NH_2)_{16}*Pd^{II}@BP1$	0.5-1%	25-30%	2-10%	0-25%	60-72%

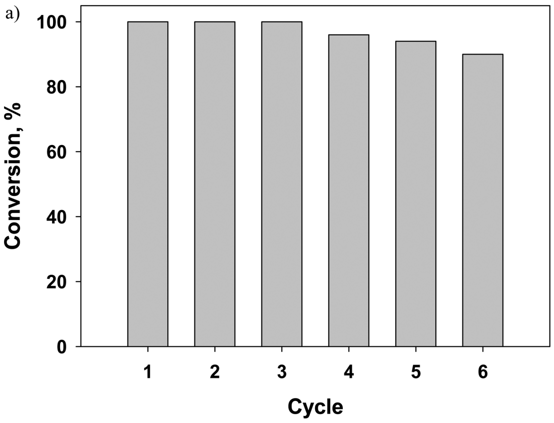
of 1,4-addition, with the selectivity being 60–70%. This suggests a decrease in the degree of kinetic control as compared with the less sterically hindered isoprene. The high ratios of *trans*/*cis*-isomers are generally a characteristic of Pd catalysts and corresponds to the thermodynamic stability of the corresponding compounds.[26,61]

Simultaneous coordination of both double bonds on two different atoms Pd can be possible for 2,5-dimethyl-2,4-hexadiene for the Pd nanoparticles and large clusters, the molecule being parallel to the tangent plane of the nanoparticle.[5] Initially 1,2-addition is most likely due to steric hindrance created by the terminal methyl groups.[5,62] The resulting intermediate then undergoes isomerization to the most stable π-allyl radical by migration of a hydrogen atom (Supporting Information Scheme S1). In this case, palladium appears to act as an intermediate electrophilic agent being subsequently replaced by hydrogen. Terminal alkenes can be isomerized into the more stable internal ones at the stage of π-allyl complex formation without preliminary desorption.[51,59] Before the isomerization stage, the rotation of trisubstituted cation-radical around the double bond is possible; therefore, the reaction products may include 2,5-dimethyl-2-hexene, 2,5-dimethyl-*cis*-3-hexene and 2,5-dimethyl-*trans*-3-hexene, the latter being the most stable thermodynamically. Dendrimers appear to create special steric factors (the substrate must accept the most "streamlined" conformation for approaching the catalytic center) and electronic factors (partial positive charge on the surface of palladium nanoparticles due to their small size), which not only prevent further hydrogenation of the alkenes produced, but also promote the formation of the thermodynamically most stable isomer. In this case, their activity was several times higher than activity of palladium catalysts based on the triazole-containing dendrimers.[63]

It should be noted that in spite of the pressure of 1–3 MPa and temperature of 70 °C the catalysts keep high selectivity for monoolefins while for the traditional palladium hydrogenation catalysts, under these conditions, the selectivity falls significantly.[1,57] For example, with the Lindlar catalyst hydrogenation of isoprene at 1.7 MPa, has a selectivity for olefins of 88–92% with conversions of 90–99%. For catalyst **2**, selectivity reaches 94–99% with similar percent conversions.

3.3. Catalyst Recycling.

The recyclability of **2** was examined in the styrene and isoprene hydrogenation. The phenylacetylene reduction to styrene showed significant leaching of Pd and therefore was not evaluated. At the end of the reaction period, the reaction mixture was decanted and the remaining catalyst was reused without additional loading. The results for **2** in the styrene and isoprene hydrogenations are shown in Figure 3, a and b. The total turnover number for six cycles was ≈78485 for styrene and 86730 (four cycles) for isoprene. It should be noted that after the reaction with styrene there was no darkening of the reaction mixture and dissolution of the catalyst was not observed, suggesting the absence of palladium leaching. The slight decrease in conversion is likely due to mechanical losses of catalyst during the decantation procedure. Hence, the dendritic catalyst **2** can be reused without significant loss of activity.



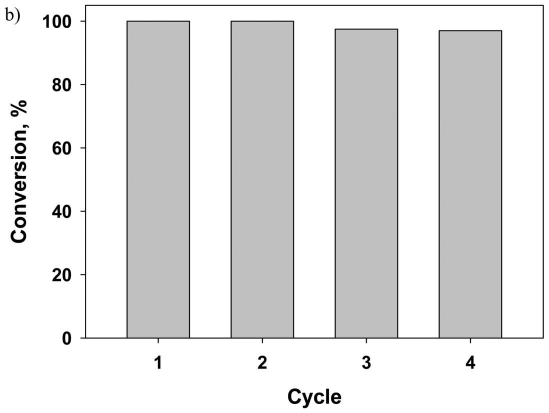


Figure 3. Recycling of the hybrids: (a) **1** in the styrene hydrogenation (reaction conditions are 0.95 mg of catalyst 1 mL of styrene, 1.5 mL of benzene (styrene/Pd ≈ 12845), 3 MPa of H_2, 15 min, 70 °C); and (b) **2** in the isoprene hydrogenation (reaction conditions are 0.5 mg of catalyst 1 mL of isoprene, 2 mL of toluene (styrene/Pd ≈ 29445), 3 MPa of H_2, 15 min, 70 °C).

4. CONCLUSIONS

The hybrid organic–inorganic catalysts, based on PPI dendrimers grafted to a silica polyamine composite support containing Pd^0 nano particles were synthesized. The materials obtained were characterized by TEM, XPS, and solid-state ^{13}C NMR spectroscopy. It was found that the presence of dendrimers on the polyamine/silica surface contributes to the formation and growth of metal nanoparticles. The synthesized catalyst **2** was shown to be effective in the hydrogenation of styrene, phenylacetylene and dienes (isoprene, 2,5-dimetyl-2,4-hexadiene) and their specific activities exceeded 100 000 h^{-1} even at the substrate/Pd ratio more than 20 000. The total selectivity for alkene in the hydrogenation of dienes reached 95–99%. All of the reported reductions are of significance to the petroleum feedstock and refining industries.

The hybrid materials based on the palladium nanoparticles and dendrimers exhibited resistance to metal leaching and can be reused for several cycles. Overall, these catalyst systems showed higher activity than Pd nanoparticles combined with PPI dendrimers alone[35,36] as well as the Lindlar catalyst.[57] They were also much more active and selective than Pd nanoparticles or complexes bound directly to the silica polyamine composite support.[4] Thus, there appears to be an important synergism between the dendrimers and the silica polyamine support. The origin of this synergism is likely related to maintaining the individual integrity of the dendrimers as a result of their multianchor-point immobilization on the SPC support. Studies extending these results to other reactions and catalytic metals are currently underway in our laboratories.

ASSOCIATED CONTENT

Ⓢ Supporting Information

^{13}C CPMAS NMR spectra of the materials PPI dendrimers on **BP-1** and **2** the mechanism proposed for the 2,5-dimethyl-2,4-hexadiene and the results for styrene reduction with the precatalyst **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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