Palladium Nanoparticles on Dendrimer-Containing Supports as Catalysts for Hydrogenation of Unsaturated Hydrocarbons

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Abstract—A new method has been proposed for encapsulation of palladium nanoparticles with a size of up to 2.5 nm in the matrix of special supports, the polymer networks based on poly(propylene imine) dendrimers, synthesized for this purpose. It has been shown that the particle size distribution of the materials obtained and their catalytic activity in the hydrogenation reactions of unsaturated compounds substantially depend on the specific features of the support structure. A high activity (TOF up to 15000 h⁻¹) has been observed in the hydrogenation of styrene. The catalysts can be repeatedly used without loss of activity.

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Catalysts that contain metal nanoparticles as active components have found wide application in petrochemical and organic synthesis. They are used in double-bond hydrogenation, hydrodechlorination, cross coupling, and other reactions [1-5]. As a rule, the synthesis of heterogeneous catalysts of this type is fraught with the necessity of reaching a regular arrangement of nanoparticles on the support and a narrow particle-size distribution [5-8].

One of the most interesting approaches to the synthesis of catalysts based on metal nanoparticles is the use of dendrimers as a stabilizing agent [9-12]. We have proposed a method for synthesizing heterogeneous supports from poly(propylene imine) dendrimers by their bonding to one another with special crosslinking agents, such as diepoxides and diisocyanates. Using this method, we prepared effective hydrogenation catalysts based on crosslinked dendrimers and ruthenium nanoparticles [13]. The material exhibited a high activity in hydrogenation of double bonds of olefins and aromatic compounds.

In this paper, we report some results on the design of catalysts based on palladium nanoparticles using the same approach.

EXPERIMENTAL

First- and third-generation poly(propylene imine) dendrimers **DAB-PPI-G1 (DAB(NH₂)₄)** and **DAB-PPI-G3 (DAB(NH₂)₁₆)** synthesized according to the procedure described in [14] were used as starting materials. The crosslinking agents were 1,6-hexame-thylene diisocyanate (**HMDI**) and 1,4-butylene diisocyanate (**BDI**), both from Aldrich.

IR spectra of the samples were recorded on a Nicolet IR-200 spectrometer in the attenuated total reflection mode with an HATR Multi-reflection accessory using a ZnSe 45° crystal for different wavelength ranges with 4-nm resolution. An X-ray photoelectron spectroscopy (XPS) study of the samples was performed with a LAS-3000 instrument equipped with an OPX-150 retarding-field photoelectron analyzer. Photoelectrons were excited by X-rays from an aluminum anode (Al $K\alpha = 1486.6$ eV) at a tube voltage of 12 kV and an emission current of 20 mA. Photoelectron peaks were calibrated by the C 1s carbon line with a binding energy of 285 eV.

Palladium in the samples was quantified by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an IRIS Interpid II XPL instrument (Thermo Electron, the United States) with radial and axial detection at wavelengths of 310 and 95.5 nm. Transmission electron microscopy (TEM) studies of the samples were performed with a LEO912 AB Omega electron microscope.

Synthesis of Catalysts

Synthesis of DAB₃-HMDI polymer. A 125-mg portion of DAB(NH₂)₁₆ (0.074 mmol) and 50 ml of absolute THF were placed into a 100-ml one-neck flask equipped with a magnetic stirrer and a reflux condenser. Under these conditions, the dendrimer swelled but did not dissolve. Then, 63 μ L (0.4 mmol) of hexamethylene diisocyanate was added with stirring. The reaction was run at 70°C over 12 h. The product mixture was evaporated to dryness in a rotary evaporator, the residue was washed with water and methanol, centrifuged, and dried in a rotary evaporator at 50°C. The product was obtained in the form of ocher colored, loose, sticky lumps. The product yield was 191 mg. Synthesis of DAB₃-BDI polymer. The synthesis was conducted according to the same procedure. The reactants were DAB(NH₂)₁₆ (500 mg, 0.3 mmol) and butylene diisocyanate (0.11 μ L, 0.79 mmol) in 50 ml of absolute THF. The product was ocher colored, loose, sticky lumps. The yield was 1.25 g.

IR, cm⁻¹: 3300 (N–H_{st} in NH–C(=O)); 2930 (C– H_{st}); 2850 (C–H_{st}, CH₂–N_{st}); 1750, 1620, 1570 (C=O_{st} in NH–C(=O); 1480, 1460 (N–H_{δ}, CH_{2 δ}, X–N–H_{δ}); 1420 (CH_{2 δ}); 1380, 1340, 1270, 1240, 1160, 1030 (C–N_{st} in NH–C(=O); 990, 930, 860, 795 (N–H_{δ}); 750 (CH_{2 γ}).

Synthesis of DAB_3 -HMDI₂ polymer. The reaction was conducted according to the same procedures as described above. The reactants were $DAB(NH_2)_{16}$ (1.75 g, 1.04 mmol) and hexamethylene diisocyanate (4 mL, 25.5 mmol) in 60 ml of absolute THF. The product was a light yellow powder. The yield was 5 g (83%).

IR, cm⁻¹: 3334 (N–H_{st} in NH–C(=O)); 2934 (C– H_{st}); 2587 (C–H_{st}, CH₂–N_{st}); 1685, 1619, 1573 (C=O_{st} in NH–C(=O); 1478 (N–H_{δ}, CH_{2 δ}, X–N– H_{δ}; 1420 (CH_{2 δ}); 1372, 1252, 1215, 1145, 1039 (C– N_{st} in NH–C(=O); 771 (N–H_{δ}); 735 (CH_{2 γ}).

XPS, eV: 1193.1 (C–N), 11.99.2 (C=O) (E_{kin} C 1s, 65.0%), 404.3 (N 1s, 20.9%), 944.1 (O–N), 949.1 (C=O) (E_{kin} O 1s, 14.1%).

Synthesis of DAB_1 -HMDI₂ polymer. The reaction was conducted according to the same procedures. The reactants were $DAB(NH_2)_4$ (2 g, 6.33 mmol) and hexamethylene diisocyanate (6 mL, 37.5 mmol) in 40 mL of absolute THF. The yield was 7 g (84%).

IR, cm⁻¹: 3335 (N–H_{st} in NH–C(=O)); 2928 (C– H_{st}); 2855 (C–H_{st}, CH₂–N_{st}); 1686, 1620, 1538 (C=O_{st} in NH–C(=O); 1463 (N–H_{δ}, CH_{2 δ}, X–N– H_{δ}); 1410 (CH_{2 δ}); 1342, 1259, 1223, 1141, 1053, 1009 (C–N_{st} in NH–C(=O); 780 (N–H_{δ}); 733 (CH_{2 γ}).

XPS, eV: 1192.9 (C–N), 1195.5 (C=O) (*E*_{kin} C 1s, 62.2%), 399.5 (N 1s, 17.9%), 531.5 (O 1s, 19.9%).

Synthesis of DAB₃-HMDI-Pd. The reactant was 191 mg of DAB₃-HMDI in 40 mL of absolute THF. To this suspension, 133 mg (0.59 mmol) of $Pd(OAc)_2$ was added with stirring. The reaction was run at 70°C for 12 h. At the end of the reaction, the suspension was cooled to room temperature and separated from chloroform by centrifuging. The resulting dry powdered black precipitate obtained in an amount of 199 mg was suspended in a mixture of 9.5 mL of methanol and 28 mL of chloroform. Sodium borohydride in an amount of 225 mg (5.9 mmol) was added with stirring to this slurry. The reaction mixture immediately turned black, and violent gas evolution was observed. The reaction was conducted at 60°C over 12 h. At the end of the reaction, the precipitate was separated from the solvents by centrifuging, washed with water and methanol, and dried. The yield of the product was 169 mg.

XPS, eV: 286.8 (C 1s, 77.5%); 336.1 (Pd $3d_{5/2}$, 2, 2.9%), 340.9 (Pd $3d_{3/2}$), 399.3, 401.7, 405.3 (N 1s, 10.7%); 531.9 (O 1s, 9.0%).

ICP-AES: 8.87% Pd.

Synthesis of DAB₃-BDI-Pd. The reactant was 122 mg of DAB₃-BDI in 25 mL of absolute chloroform. To this slurry, 133 mg (0.59 mmol) of palladium(II) acetate was added with stirring. The reaction was run at 70°C for 12 h. At the end of the reaction, the slurry was evaporated to dryness in a rotary evaporator. The intermediate product, which was a dark brown powder in an amount of 275 mg, was then suspended in a mixture of 30 mL of chloroform and 10 mL of methanol. Sodium borohydride (225 mg, 5.9 mmol) was added to the resulting suspension and allowed to react for 12 h at 60°C. The yield of the dry product was 75 mg.

XPS, eV: 285.0 (C 1s, 63.0%); 336.1 (Pd $3d_{5/2}$, 7.4%); 340.9 (Pd $3d_{3/2}$); 398.7, 402.6 (N 1s, 7.7%); 530.6 (O 11s, 21.9%); 534.6 (Pd $3\mathbf{p}_{3/2}$, 9.0%).

ICP-AES: 22.58% Pd.

Synthesis of DAB₁-HMDI₂-Pd. The reactants were 500 mg of DAB₁-HMDI₂ and 50 mL of absolute chloroform. To this suspension, 160 mg (0.7 mmol) of Pd(OAc)₂ was added with stirring. The reaction was run at 70°C for 12 h. At the end of the reaction, the suspension was evaporated in a rotary evaporator. The resulting dark brown powder obtained in an amount of 745 mg (100% yield) was placed in a flask and suspended in a mixture of 35 mL of methanol and 25 mL of chloroform. Sodium borohydride in an amount of 266 mg (7 mmol) was added by portions with stirring to this slurry. The reaction was conducted at 70°C over 12 h. The yield of the dry product was 355 mg (62%).

XPS, eV: 285.8 (C 1s, 58.8%); 335.8 (Pd $3d_{5/2}$, 4.0%), 341.4 (Pd $3d_{3/2}$), 399.6 (N 1s, 18.4%); 531.5 (O 1s, 18.6%). ICP-AES: Pd, 12.06%.

Synthesis of DAB₃-HMDI₂-Pd. The reactants were 1 g of DAB₃-HMDI₂ and 320 mg (1.4 mmol) of Pd(OAc)₂ in 50 mL of chloroform. The yield of the product DAB₃-HMDI₂-Pd^{II} was 1.31 g (99%).

XPS, eV: 284.8 (C 1s, 63.4%); 335.8 (Pd $3d_{5/2}$, 5.4%), 341.6 (Pd $3d_{3/2}$), 399.4 (N 1s, 16.5%); 531.5 (O 1s, 13.9%). ICP-AES: Pd, 9.37%.

Catalyst Testing Procedure

A catalyst and a substrate taken in the ratio of 1 mg of the catalyst to 2.2–2.3 mmol of the substrate were placed in a thermostated steel autoclave equipped with an insert test tube and a magnetic stirrer. A solvent was added when necessary. The autoclave was tightly sealed, filled with hydrogen to have a pressure of 10 or 40 atm, and connected with a thermostat. The reaction was run with vigorous stirring at 80°C for 1 h or 30 or 15 min; after that, the autoclave was cooled down below room temperature. The products were determined by GLC on a ChromPack CP9001 gas chro-

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Dendrimer	Crosslinker	NCO/NH ₂ ratio	Catalyst notation	Metal content, %
DAB(NH ₂) ₄	OCN(CH ₂) ₆ NCO	$NCO/NH_2 = 2/1$	DAB ₁ -HMDI ₂ -Pd	12.06
DAB(NH ₂) ₁₆	OCN(CH ₂) ₆ NCO	$NCO/NH_2 = 2/1$	DAB ₃ -HMDI ₂ -Pd	9.97
DAB(NH ₂) ₁₆	OCN(CH ₂) ₆ NCO	$NCO/NH_2 = 1/3$	DAB ₃ -HMDI-Pd	8.87
DAB(NH ₂) ₁₆	OCN(CH ₂) ₄ NCO	$NCO/NH_2 = 1/3$	DAB ₃ -BDI-Pd	22.88

Table 1. Supports and catalysts synthesized in this work

matograph with a flame-ionization detector using a $30 \text{ m} \times 0.2 \text{ mm}$ column with the bonded SE-30 phase. Chromatograms were recorded and processed with the use of the Maestro 1.4 software.

RESULTS AND DISCUSSION

To prepare network polymer matrices as supports for palladium nanoparticles, we used the first- and third-generation poly(propylene imine) (DAB) dendrimers **DAB(NH₂)₄** and **DAB(NH₂)₁₆**, respectively. The crosslinking agents were 1,4-butylene diisocyanate **OCN(CH₂)₄NCO (BDI)** and 1,6-hexamethylene diisocyanate **OCN(CH₂)₆NCO (HMDI)**, compounds that form conformationally labile links between the dendrimers. It was assumed that the size and rigidity of the cross linkers would have an effect on the activity and selectivity of the catalysts, as well as their polarity. To compare the effect of the size of the reactant dendrimer on the properties of the catalysts, two supports based on **DAB(NH₂)₄** and **DAB(NH₂)₁₆** with **HMDI** taken in a ratio of NCO/NH₂ = 2 : 1 were synthesized. To compare the dependence of the properties of the final hybrid material on the size of the crosslinking entity, **DAB(NH₂)₁₆**-based materials with an NCO/NH₂ ratio of 1 : 3 were synthesized (Table 1).

The IR and XPS data suggest that the process follows the conventional mechanism of the reaction of isocyanates with amines yielding -NH-C(=O)-NH- fragments (Scheme 1).



Scheme 1. Synthesis of polymer materials based on crosslinked dendrimers.

Material	Pd 3d _{5/2} , 3d _{3/2} , eV	At. concn., %	C 1s, eV	At. concn., %	N 1s, eV	At. concn., %	O 1s, eV	At. concn., %
DAB ₃ -HMDI-Pd	336.1; 340.9	2.9	286.8	77.5	399.3; 401.7; 405.3	10.7	531.9	9.0
DAB ₃ -BDI-Pd	336.1; 340.9	7.4	285.0	63.0	398.7	7.7	530.6	21.9
DAB ₁ -HMDI ₂ -Pd	335.8; 341.4	4.0	285.1	58.8	399.6	18.4	531.5	18.8
DAB ₃ -HMD ₂ -Pd	335.8; 341.6	5.4	284.8	63.4	399.4	16.5	531.5	13.9

Table 2. XPS data for the materials

The polymer matrices based on diisocyanatecrosslinked dendrimers were used to prepare palladium catalysts. Metal nanoparticles were encapsulated in the dendrimers according to the procedure reported in [11], which involves complexation with a transition metal salt followed by reduction with sodium borohydride (Scheme 2). The metal deposition step was conducted in chloroform because of good solubility of palladium acetate in this solvent and its swelling power with respect to polymers containing urethane groups. The reduction to Pd(0) was achieved with the use of sodium borohydride.



Scheme 2. Encapsulation of palladium nanoparticles in crosslinked dendrimer matrices.

It was found that the amount of the metal deposited on the polymer depends on the dendrimer structure, the crosslinker nature, the crosslink density, and the procedure for isolation of the intermediate and final products. The metal content in % as determined by ICP-AES for each of the materials is given in Table 1.

The materials obtained were characterized using the XPS and TEM techniques. The XPS data are presented in Table 2.

The binding energies for Pd $3d_{5/2}$ and Pd $3d_{3/2}$ are 336 and 341 eV, respectively; i.e., they are somewhat

higher than for zero-valence metallic palladium (Pd: 335.6, 341.1 eV [15]) and lower than for divalent palladium (PdO: 37.0, 342.2 [15]), thereby confirming the presence of metal nanoparticles coordinated to nitrogen or oxygen atoms in the materials. It was found that only a small portion of the metal occurs on the surface ($Cs/Cv \approx 0.3-0.5$). The carbon and nitrogen energy shifts relative to the usual values (284.8 and 398.6 eV, respectively [15]) in the spectra of the samples are due to partial electron transfer to neutral metal particles.



Fig. 1. TEM data and particle-size distribution for DAB₃-HMDI-Pd.

According to the TEM data, the nature of the crosslinker in the case of low-crosslink-density composites with Pd nanoparticles affects the particle size distribution pattern, rather than the size per se (Figs. 1, 2). In the samples prepared with the use of hexamethylene diisocyanate, the proportion of particles with the diameter above the mean (2.3–5.0 nm) is high. This difference is substantially lower for the samples prepared with butylene diisocyanate.

In the case of highly crosslinked samples (Figs. 3, 4), the density of metal nanoparticles per unit area/volume of the support noticeably increases owing to their better retention in the matrix and coordination to the amino groups of not only dendrimers but also the crosslinking agents. In addition, both the size and the distribution pattern of particles are strongly affected by the crosslinker nature and the matrix preparation procedure. Thus, the density distribution of



Fig. 2. TEM data and particle-size distribution for DAB₃-BDI-Pd.



Fig. 3. TEM data and particle-size distribution for DAB₁-HMDI₂-Pd.

particles noticeably increases in the **DAB₁-HMDI₂-Pd** and **DAB₃-HMDI₂-Pd** catalysts, correlating with both the increased palladium content of the samples and the particle size.

The **DAB**₁-**HMDI**₂-**Pd** material is characterized by a bimodal particle size distribution with maximums at 1.3 and 2.2 nm, a feature that may be due to the presence of cavities with the corresponding dimensions in the structure of the dendritic matrix. In addition, small particles ($d \le 1.5$ nm) can be accommodated in between dendrimer branches, being stabilized by tertiary nitrogen atoms.

The **DAB₃-HMDI₂-Pd** catalyst is characterized by a narrower distribution with maximums at 1.8 and 2.3 nm, which can be explained in terms of not only a smaller size of cavities compared with the material based on the first-generation dendrimer, but also their rigidity due to the dense crosslinking of the dendrimers by hexamethylene diisocyanate. In this case, the size of a particle has the upper bound due to its surrounding crosslinks and dendrimer branches—a steric



Fig. 4. TEM data and particle-size distribution for DAB₃-HMDI₂-Pd.

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Fig. 5. Dependence of (a) the conversion and (b) the activity of palladium catalysts on the substrate chain length.

limitation—and the lower bound as the minimal distance between the nearest donor atoms ($\sim 0.6-0.7$ nm for dendrimers and 1 nm for diisocyanate units in the approximation that the carbon chain envelopes the particle).

The synthesized materials were tested as catalysts for hydrogenation of unsaturated compounds. In the case of hydrogenation of terminal linear olefins in the presence of the materials based on dendrimers and Pd nanoparticles, the activity of all the catalysts with a low crosslink density decreases with an increase in the chain length of the substrate, as shown in Fig. 5, a development that can be attributed to diffusional constraints on alkene passing through the crosslinked dendritic matrix.

Simultaneously, the proportion of double-bond isomerization products in the reaction mixture increases: the longer the chain, the greater the proportion. Note that the double-bond isomerization is easy to proceed in the presence of palladium (Scheme 3) and affords internal alkenes, which are thermodynamically more stable. Being sterically more hindered than terminal alkenes, the internal isomers cannot take the conformation required for the reaction in the existent ligand microenvironment of the catalytic center and, as such, are hydrogenated with a low yield.



Scheme 3. Positional isomerization of the olefin double bond exemplified by octene-1.

The yield increases in the order DAB_3 -HMDI-Pd $\ll DAB_3$ -BDI-Pd in agreement with the increase in the Pd content on passing from one catalyst to another. The activity of the catalysts, calculated as the turnover frequency (TOF), an amount of substrate converted per mole of metal per unit time, drops in the opposite order.

Regardless of the Pd content, the activity of all the catalysts declines on passing to a bulkier substrate. It decreases by a factor of 2 on passing from hexane-1 to octene-1. On passing from octene-1 to decene-1, the

DAB₃-**BDI-Pd** or **DAB**₃-**HMDI-Pd**, respectively. The specificity of the process in this case seems to be associated with the enhancement of diffusional constraints for large substrate molecules. Note that despite their sterically hindered dendrite matrix, these catalysts turned out to be more active than the conventional Pd/C catalyst used in the industry, its TOF is 190 or $130 h^{-1}$ for hexene and cyclohexene, respectively [12], values that are a few times below those obtained in this work.

activity further drops by a factor of 2 or 1.6-1.7 for

Catalyst	Conversion, %	TOF, h^{-1}
DAB ₃ -HMDI-Pd	22	480
DAB ₃ -BDI-Pd	35	240
DAB ₁ -HMDI ₂ -Pd	27	380
DAB ₃ -HMDI ₂ -Pd	32	545

Table 3. Hydrogenation of octene-1 in the presence of dendrimer-based Pd catalysts

In the presence of the catalysts with a high crosslink density, the product yield and the activity per Pd atom significantly increase, a fact that can be explained by both a high affinity of the substrate for nonpolar crosslink chains, whose number is substantially greater in the case of denser crosslinking, and the stability of the nanoparticles themselves during the reaction. On passing from the generation one to generation three dendrimer, the specific activity increases despite a somewhat greater size of the particles (Table 3).

The materials based on Pd nanoparticles and crosslinked dendrimers showed a high activity in the hydrogenation of styrene and its derivatives to corresponding ethylbenzenes (Tables 4–6), with the TOF value being very high; it approaches 10000–15000, i.e., is substantially higher than that for 1-alkenes. The activity of the catalysts considerably increases with temperature in this case.

Note that there is a relationship between the product yield and the substrate size for this class of catalysts. Thus, a regular fall in activity because of steric hindrances with an increase in the substrate size was observed for **DAB₃-HMDI-Pd**, whereas **DAB₃-BDI-Pd** is characterized by a parabolic dependence of the activity on the substrate size with a maximum at *p*-methylstyrene (Fig. 6, Table 5). It is likely that there is an optimal substrate size for this material to correspond to the distance between branches of the dendritic matrix.

The catalysts based on highly crosslinked dendrimers appeared to be less active than their counterparts with a low crosslink density at similar Pd/substrate ratios (Table 4, Fig. 7). This difference is evidently due to steric hindrances by the dendritic matrix and the crosslinks, since all dendrimer amino groups are involved in the formation of amide bonds with the diisocyanate crosslinks.

The data in Table 6 show that the activity of the catalysts in the case of styrene drops with an increase in both the palladium content and the average substrate size. The decrease in the activity on passing from DAB₃-HMDI-Pd to DAB₃-HMDI₂-Pd is determined by enhancement of steric hindrances from the densely crosslinked dendritic matrix. The activity also dropped as the size of the substituent in the *para*-position to the vinyl group further increased (*p*-vinylstyrene) or substituents appeared at the double bond (trans-stilbene), with the yields being comparable on DAB₁-HMDI₂-Pd and DAB₃-HMDI₂-Pd (55 and 50%, respectively) and considerably below those on DAB₃-HMDI-Pd (100%). However, the stilbene hydrogenation activity of the catalysts based on densely crosslinked dendrimers was higher by a factor of approximately 1.5–1.7 than that of DAB₃-HMDI-Pd (Tables 4-6), possibly, because of enhanced hydrophobicity of the dense dendritic matrix and, as a consequence, a higher affinity for stilbene compared with the rarely crosslinked supports, which are mainly composed of hydrophilic PPI dendrimers in DAB₃-HMDI-Pd.

The catalysts prepared in this work can be repeatedly used without loss of activity. For example, the conversion of styrene almost does not decrease for six catalytic cycles. The turnover number (TON, the

Table 4. Hydrogenation of styrenes in the presence of dendrimer-based Pd catalysts							
		DAB ₂ -HMDI-Pd	DAB ₂ -BDI-Pd	DAB2-HMDI2-Pd			

	DAB ₃ -HMDI-Pd		DAB ₃ -BDI-Pd		DAB ₃ -HMDI ₂ -Pd			DAB ₁ -HMDI ₂ -Pd				
Substrate	time, min	conver- sion, %	TOF, h ⁻¹	time, min	conver- sion, %	TOF, h ⁻¹	time, min	conver- sion, %	TOF, h ⁻¹	time, min	conver- sion, %	TOF, h ⁻¹
Styrene	30	100	5240	60	100	1025	60	100	2330	60	100	1930
	10	79	12420	_	—	_	15	100*	18630	15	100*	15450
<i>p</i> -Methylstyrene	30	100	4560	60	100	895	60	100	2025	60	95	1600
	10	69	9440	—	—		15	48	3890	15	66	5300
<i>p-tert</i> -Butylsty-	60	100	1645	60	100	645	60	84	1960	60	18	350
rene	30	81	2680	—	—	_	15	9	840	15	5.5	425
trans-Stilbene	60	100	670	—	—	_	60	50	1185	60	55	1080

Reaction conditions: 1 mg of catalyst, 250-400 µL of substrate, 80°C, 1 h, 5-10 atm H₂.

* 0.5 mg of catalyst.

Table	5.	Hydrogenation	of	styrenes	in	the	presence	of
DAB ₃	-B	DI-Pd at lower to	emp	peratures			-	

Substrate	<i>T</i> , °C	Conversion, %	TOF, h^{-1}
Styrene	60	74	9110
Styrene	50	48	5910
<i>p</i> -Methylstyrene	60	95	10180
<i>p</i> -Methylstyrene	50	90	9645
<i>p-tert</i> -Butylsty- rene	60	26	2010
<i>p-tert</i> -Butylsty- rene	50	20	1540

Table 6. Comparison of activities of catalysts with the hexamethylene diisocyanate crosslinker in hydrogenation of styrenes

Catalyst	Styrene	<i>p</i> -Methyl- styrene	<i>p-tert</i> -Butylsty- rene
DAB ₃ -HMDI-Pd	12420	9840	2680
DAB ₃ -HMDI ₂ -Pd	9315	3890	1960
DAB ₁ -HMDI ₂ -Pd	7490	5300	425

Reaction conditions: 0.5 mg of catalyst, 250 μL of substrate, 10 min, 5 atm $H_2.$

Reaction conditions: 1 mg of catalyst, 250–400 μL of substrate, 10 atm $H_2,\,80^\circ C,\,10{-}15$ min.



Fig. 6. Hydrogenation of styrenes in the presence of DAB₃-BDI-Pd: (a) conversions and (b) activities.



Fig. 7. Effect of the crosslink density and dendrimer generation on the catalyst activity.

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amount of product per mole of Pd) is 13590 in this case.

In summary, the use of nanostructured assemblies based on crosslinked dendrimers and palladium nanoparticles makes it possible to synthesize high-performance selective catalysts for hydrogenation of unsaturated compounds. The activity and selectivity of such systems is directly related to the nature and structure of the dendritic matrix and its affinity for the substrate. The maximal yields and activity are attained in the hydrogenation of styrene to corresponding ethylbenzenes.

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