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Nanostructured Macromolecular Metal Containing Materials in Catalysis

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Summary: Nanostructured regular materials based on cross-linked polypropylene imine (PPI) dendrimers and silica-gel polyamine composites were used as a support for the synthesis of Pd nanoparticles. The materials were tested as catalysts and displayed a high activity and selectivity for the hydrogenation of conjugated double bonds.

Keywords: dendrimer; hydrogenation; nanoparticles; silica gel polyamine composites; supramolecular catalysts

Introduction

Designing novel materials, having a regular structure and capable of binding the substrate molecule selectively, could be considered as one of the most promising area for creating of new selective catalysts.[1] The related catalysts are zeolite-based one and also catalysts, based on molecular receptors, such as cyclodextrins and calixarenes, which allow to conduct reactions with high substrate and regioselectivity, typical of homogeneous metallocomplex systems.[2–5] Important methodology for the straightforward preparation of catalysts with molecular recognition ability is molecular imprinting.[6,7]

Another approach to such materials implies the linkage of spherical symmetric dendrimer molecules[8] into a regular macromolecular "megamers", having a three-dimensional structure. The formation of such materials is a result of connecting dendrimer molecules by covalent or coordination bonds between surface functional groups of adjacent molecules[9,10] (Scheme 1).

Dendritic fragments of megamers could be regarded as nanocapsules, which are able to bind ions of one or several metals by surface functional groups. A distance between dendrimer molecules would define a specific pore size of the materials obtained and, therefore, determine the substrate selectivity of megamer-based catalysts. Varying the size, flexibility and polarity of the cross-linking agent allows to control spacing between dendrimer molecules and the binding selectivity of organic ligands and nanoparticles by such materials. As for coordination bonding, it is usually performed via complex formation between metal ions and surface functional groups of different dendrimers. In the first part of the manuscript we present our results on the hydrogenation of unsaturated compounds with the use of catalysts based on such megamers and Pd nanoparticles.[10,11]

The second approach presented deals with the synthesis of the catalyst based on Pd nanoparticles with the use of hybrid material. Such materials are obtained via immobilization of polyamine polymers, particularly polyethyleneimine (WP-1) and polyallylamine (BP-1) on silica gel according to[12] (Figure 1).

Further modification allows to synthesize corresponding materials, containing chelate groups similar to carboxylamines. In the second part of this work, we present

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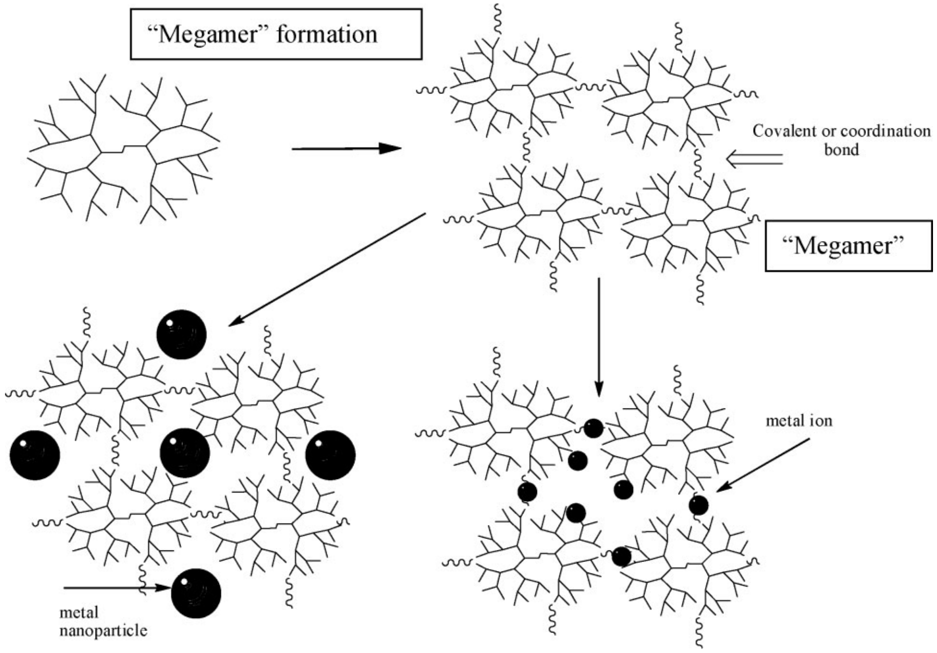


Scheme 1.
The formation of cross-linked materials based on dendrimers.

the results demonstrating catalytic properties of such Pd –base materials in hydrogenation.

Catalysts Based on Dendrimer Megamers in Hydrogenation of Double Bonds

The common method to synthesize metal nanoparticles is reduction of initial metalloprecursor in presence of corresponding ligand.[13–18] Reaction medium depends on nature both ligand and metalloprecursor. Stabilization occurs by means of donor-acceptor interactions between metal nanoparticles and donor atoms of ligands. As usual, particles size is controlled by micelles being formed, the last preventing particles aggregation. Using of macromolecular ligands for stabilization of metal nanoparticles allows to combine advantages of both

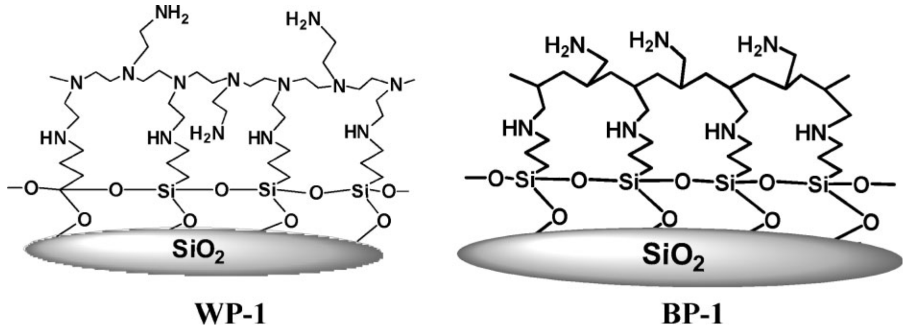


Figure 1.
Hybrid materials based on polyamine-silica composites.

traditional heterogeneous carriers and organic donor ligands. In this case ordering and stabilization of nanoparticles is achieved due to regular location of functional groups of polymer.[19] Amphiphilic nature of functionalized polymers, when the last can interact with substrate and with metallocenter simultaneously, provides high activity of catalyst, substrate and metal occurring together in micellar microreactor, formed by polymer.[18] Another advantages of polymers as stabilization ligands are simplified procedure of metal deposition (high reaction temperatures and calcinations are not required) and relatively simple recovery of catalyst (precipitation with bad solvent following by filtration).

The common method to obtain polymer-stabilized metal nanoparticles suggests wet impregnation of polymer with organic or inorganic metalloprecursor following by the reduction by hydrogen or sodium borohydride.[18,20] Among macromolecular ligands as peculiar for synthesis of metal nanoparticles should be noted dendrimers,[21–26] The majority of papers, dealing with dendrimers and metal nanoparticles, are devoted to synthesis of Pd nanocatalysts and their use in hydrogenation and cross-coupling reactions, the same catalyst being able to be used in both types of reactions. For instance, catalysts based on Pd nanoparticles and modified dendrimers of 3rd, 4th and 5th generations were successfully applied in hydrogenation of alkene and appeared to be very selective for polar substrates.[21]

We applied the polypropylene amine dendrimer with diaminobutane core ($DAB(NH_2)_{16}$) as a dendrimer scaffold for megamer synthesis. Two supports (G3-HMDI and G3-PDI) based on $DAB(NH_2)_{16}$ and two spacers with different size and flexibility ($OCN(CH_2)_6NCO$ (HMDI) and p-OCN-C_6H_4-NCO (PDI)) were synthesized with the ratio $NCO/NH_2 = 1/3$.

Dendrimer cross-linked polymer matrixes were used for the preparation of palladium catalysts with the ratio $Pd/DAB(NH_2)_{16} = 8/1$ (G3-HMDI-Pd and G3-PDI -Pd). The introduction of metal was carried out in chloroform, as it solves palladium acetate effectively and urethane polymers could swell in it. Samples with the metal content varying from 3.55 for G3-PDI-Pd to 8.87% Pd for G3-HMDI-Pd were obtained. The materials were studied by the X-Ray photoelectronic spectroscopy and transmission electron microscopy. The XPS results are presented in Table 1.

It could be seen that binding energy values for Pd $3d_{5/2}$ and Pd $3d_{3/2}$ are 336.1–336.3 eV and 340.9–341 eV, which is slightly more than for zero-valent metal palladium (Pd: 335,8; 341,1 eV[27]), but less than energy values for Pd(II) (PdO: 337.0, 342.2[27]). Data on binding energies confirms the presence of metal nanoparticles coordinated by nitrogen or oxygen atoms.[15] Notably, in G3-PDI-Pd metal is located partly on the material surface (Cs(surface concentration)/Cv(volume concentration) = 1.4 from XPS data). The surface concentration of metal was higher for G3-HMDI-Pd ($Cs/Cv \approx 3$ from XPS data).

The TEM data confirm that the nature of the spacer used in Pd-based composites influences the distribution character more than it influences particle sizes (Figures 2 and 3).

Table 1.
XPS data of the samples

	G3-HMDI-Pd	G3-PDI –Pd
Pd $3d_{5/2}$, $3d_{3/2}$, eV	336,1; 340,9	336,3; 341,0
Atomic concentration, %	2,9	4,9
C 1s, eV	286,8	285,1
Atomic concentration, %	77,5	69,3
N 1s, eV	399,3; 401,7; 405,3	400,6; 404,1
Atomic concentration, %	10,7	15,9

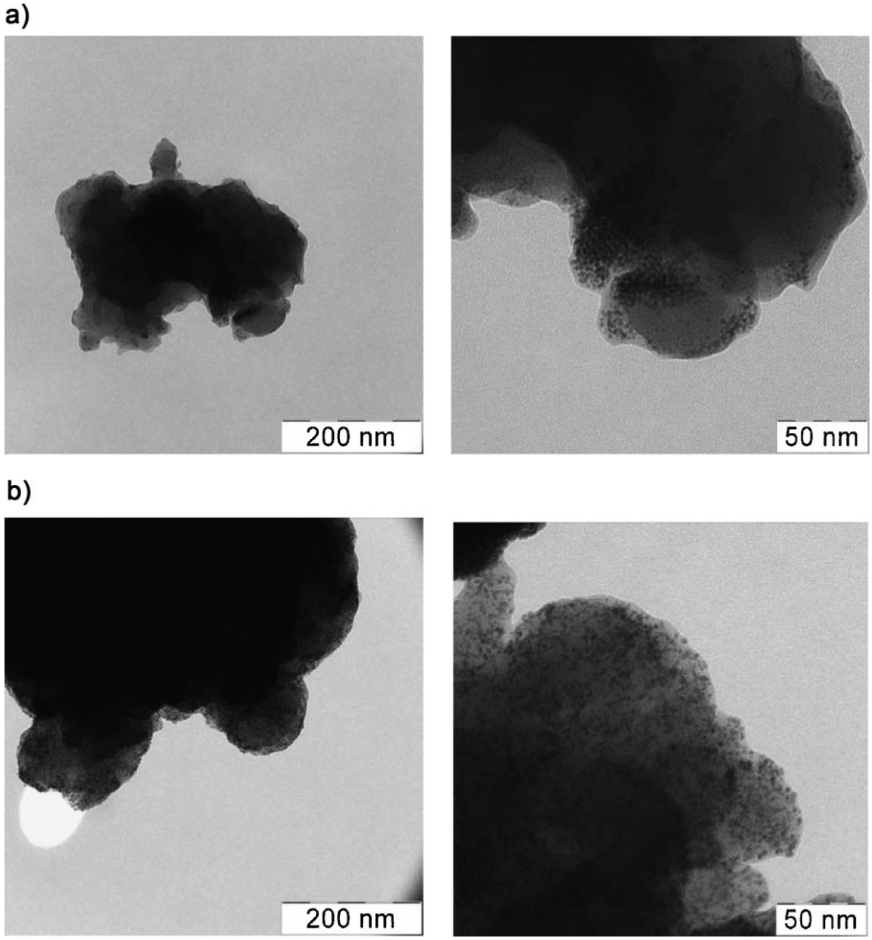


Figure 2.
Microphotographs ofG3-HMDI-Pd material (I) (a) and G3-PDI-Pd(1/8) material (b).

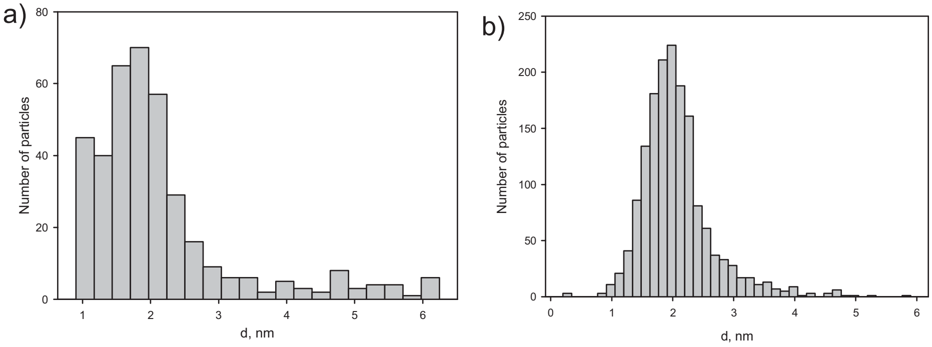


Figure 3.
Particle size distribution (a) G3-PDI-Pd(1/8); (b) G3-HMDI-Pd.

Materials cross-linked with flexible hexamethylenediisocyanate have a greater portion of 0.9–1.7 nm particles compared with particles with a size above the average (2.3–5 nm). The samples obtained with the use of rigid *p*-phenylenediisocyanate have a symmetrical particle size distribution. The average size of metal nanoparticles is about 2.1 nm.

As it can be seen from Table 2, catalytic activity in the hydrogenation of terminal linear alkenes decreases with the increase of the number of carbon atoms in the substrate. That phenomenon may be explained by diffusion difficulties occurring at the progression of the substrate through the cross-linked dendrimer matrix.

Also the quantities of double bond isomerization products are increased with the length of the carbon chain. It should be noted that the isomerization of double bonds occurs readily in the presence of Pd, resulting in the formation of thermodynamically stable internal alkenes.[1] The structure of the latter is sterically hindered, and the substrate molecule could not achieve the conformation required by the ligands of the catalytic centre. Therefore, only low yields of the hydrogenation product were observed.

The yields of the hydrogenation product increase in the row G3-PDI-Pd <G3-HMDI-Pd. The catalyst activity, which is considered in terms of the quantity of substrate transformed per mol of the metal per time unit (TOF = turnover frequency), decreases in the following order G3-PDI-Pd >> G3-HMDI-Pd that only to a lesser extent can be explained by difference in particle size distributions.[28] It is possible that the diffusion of the substrate to the catalytic centre is become easier for rigid and plane *p*-phenylene spacer compared with the material obtained by using a flexible hexamethylene cross-linker. Decrease in Pd catalyst activity is observed for all hybrid materials, when substrates with bulker structure are used. Although the dendrimer matrix caused several sterical hindrances, hybrid metal-polymer catalysts turn out to be more effective compared with Pd/C, characterized by TOF for 1-hexene and cyclohexene 190 and 130 h^{-1} [10,16] correspondingly, which was several times as little as the values obtained for dendrimer materials.

Dendrimer based materials containing palladium nanoparticles also turn out to be effective catalysts in the hydrogenation of styrene and its derivatives (Table 3), demonstrating high values of TOF, approaching to 10 000–12 000, which is considerably higher than TOF for terminal alkenes. The dependence of yield on a substrate molecule size is also observed. The expected decrease in activity, related to increase in a substrate molecule size, is demonstrated for both catalysts. G3-PDI-Pd has slightly different rates of styrene and *p*-methylstyrene hydrogenation, which could be explained by significant rigidity of its structure.

A high activity of the hybrid palladium catalyst is also observed in the hydrogenation of dienes to alkenes (Figure 4). Non-conjugated dienes undergo the isomerisa-

Table 2.
Hydrogenation of alkenes in the presence of dendrimer-based Pd catalysts (TOF - turnover frequency - the quantity of substrate transformed per mol of the metal per time unit).

Substrate	Time, min.	G3-HMDI-Pd		G3-PDI-Pd	
		Conversion, %	TOF, h^{-1}	Conversion, %	TOF, h^{-1}
1-Hexene	60	35	850	32	1950
1-Octene	60	23	440	19	920
1-Octene	180	47	295	37	584
1-Decene	60	19	365	16	640

Reaction conditions: 80 °C, 5 atm. H_2, 1 h, 2,50 ml of substrate, 10 mg of catalyst.

Table 3.
Hydrogenation of styrene derivatives in the presence of dendrimer-based Pd catalysts (TOF - turnover frequency - the quantity of substrate transformed per mol of the metal per time unit).

Substrate	Time, min	G3-HMDI-Pd		G3-PDI-Pd	
		Conversion, %	TOF, h^{-1}	Conversion, %	TOF, h^{-1}
Styrene	60	100	2620	100	6590
Styrene	10	79	12420	84	33220
p-Methylstyrene	60	100	2280	100	5735
p-Methylstyrene	10	69	9440	96	33040
tert-Butylstyrene	60	100	1645	91	3785

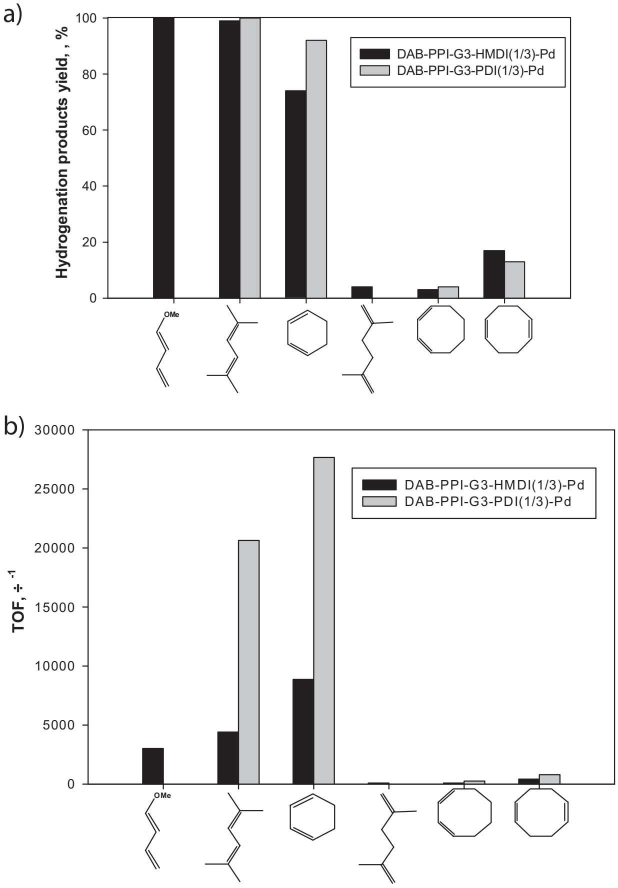
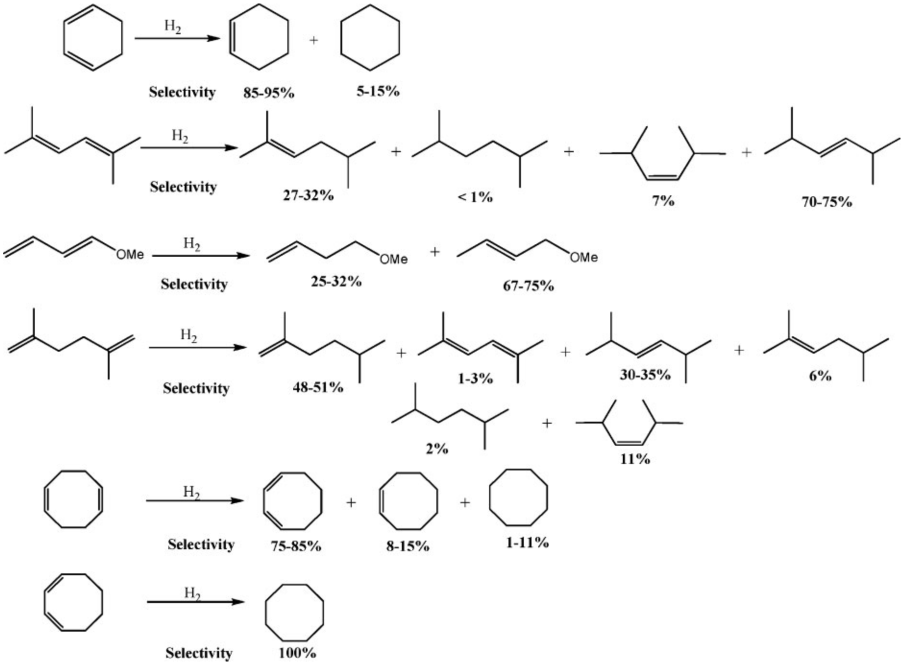


Figure 4.
Hydrogenation products yield (a) and activity (b) of hybrid Pd catalysts in diene hydrogenation.

tion of substrate molecules resulting in the formation of conjugated dienes and their hydrogenation products. Among the products of the hydrogenation of 2,5-dimethyl-1,5-hexadiene the content of products formed due to the isomerisation of substrate (2,5-dimethyl-3-cys-hexene and 2,5-dimethyl-3-trans-hexene) is approximately 50% (Scheme 2). Generally, decrease in activity in the hydrogenation of conjugated



Scheme 2.
Distribution of diene hydrogenation products in presence of Pd catalysts.

dienes is observed when the size and number of substitutes at double bonds increase.

The conversion of 1,3-cyclohexadiene is 70–90% with selectivity on cyclohexene 85–95%. The yield of hydrogenation products does not exceed 20% for of relatively bulk substrate - 1,5-cyclooctadiene. The selectivity on cyclooctene is 85%, while the content of 1,3-cyclooctadiene in equilibrium concentration is more than 50%. As for the hydrogenation of 1,3-cyclooctadiene, the only reaction product registered is cyclooctane and the conversion does not exceed 5% for all the catalysts. It could be supposed that the isomerization of 1,5-cyclooctadiene does not proceed as easily as for 2,5-dimethyl-1,5-octadiene due to cycle conformation, and, therefore, hydrogenation can only occur at the initial double bond. Sterical hindrances inside the catalyst cavities do not allow 1,3-cyclooctadiene to be converted into the corresponding monoene. In comparison with conventional Pd/C catalyst, the reactivity of substrates increases with elongating the carbon chain in the cycle (TOF was 565 h^{-1} for 1,3-cyclohexadiene and 575 h^{-1} for 1,5-cyclooctadiene[22]), and hydrogenation occurs exhaustively for both double bonds of the substrate.

Thus, the dendrimer based materials impregnated with palladium nanoparticles turn out to be highly active and selective catalysts for conjugated systems in comparison with other alkenes.

Hydrogenation Catalysts Based on Hybrid Materials

The synthesis of Pd nanoparticles immobilized on hybrid polymer materials was carried out by treating the material with solution of palladium acetate in chloroform with subsequent solvent separation. The initial composites contained 3.79 mmol of nitrogen per 1 g of material (WP-1) or 1,64 mmol of nitrogen per 1 g of composite

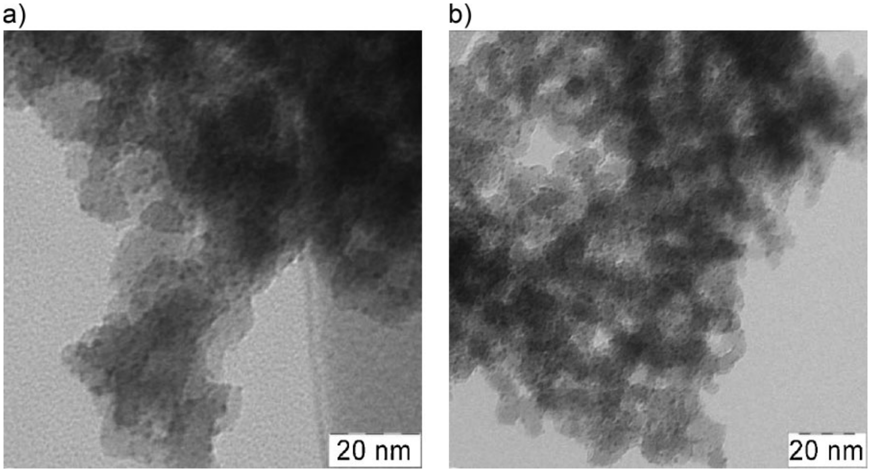


Figure 5.
Microphotographs of BP-1-Pd (a) and WP-1-Pd (b).

(BP-1). After the completion of the reaction materials with a varied content of Pd were obtained. Microphotographs of the obtained samples are given in Figure 5.

The photos confirm the formation of 1–2 nm Pd particles after the treatment, apparently, as a result of reaction with trace amounts of reducing agents present in the chloroform solution.

The XPS data (Table 4) confirm the formation both of palladium nanoparticles and Pd(II) ions, although the quantity of the latter was significantly higher. The ions present, supposedly, are bound by aminogroups of the grafted polymer. The ratio amine/metal is considerably higher for the WP-1 sample (9.7) compared with the BP-1 one (2.6). This fact indicates a peculiar enveloping of the metal ion by branched polymer chains.

The hydrogenation of unsaturated compounds was carried out under conditions similar to those in the reactions performed with the use of dendrimer-based catalysts. The substrates used were 1-hexene, 1-octene, 1-decene (Table 5).

As it is seen, the BP-1 catalyst is more active than the catalyst obtained from WP-1 material. Notably, the reaction with that catalyst occurs with the formation of larger Pd nanoparticles (up to 50 nm) (Figure 6). This process is not observed for the WP-1 catalyst. A significant number of smaller nanoparticles is retained in the matrix of branched polyethyleneimine. Branched PEI fixes nanoparticles more efficiently than linear polyallylamine, preventing aggregation.

The hydrogenation of 1,3-cyclohexadene occurs with the conversion 64% and the selectivity on monoene 95% when the WP-1-Pd is used as a catalyst. The presence of polymer amino groups in the system, coordinating with Pd nanoparticles, leads to

Table 4.
XPS data on the obtained hybrid materials

	BP-1-Pd	WP-1-Pd
Pd $3d_{5/2}$, $3d_{3/2}$, eV	336.8, 338.5	337, 338.8
Atomic concentration, %	1.5	0.8
C 1s, eV	285	285
Atomic concentration, %	29.7	31.4
N 1s, eV	400,0	400,1
Atomic concentration, %	3.7	7.8

Table 5.
Formation of hydrogen products in reactions with alkenes catalysed by composite materials.

Substrate	T, °C	Yield, %	
		BP-1-Pd	WP-1-Pd
1-Hexene	70	44	26
1-Octene	90	96	82
1-Decene	90	91	72

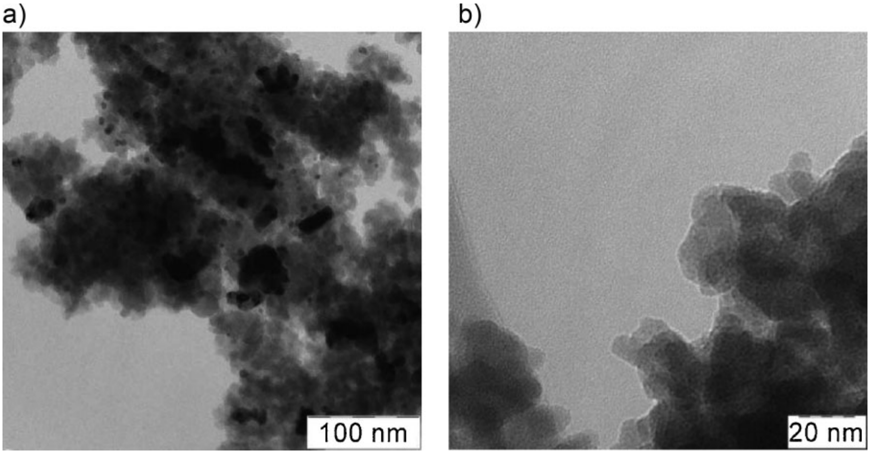


Figure 6.
Microphotographs of BP-1-Pd (a) and WP-1-Pd (b) after hydrogenation.

increase in electron density and considerable drop in activity in monoene hydrogenation, just as in the case with dendrimer materials. Moreover, the effect was primarily observed for smaller nanoparticles. For the catalyst obtained from the BP-1 material, in which large crystallites of Pd are formed during the reaction, the activity observed is considerably higher. The conversion is 86%, however, the selectivity on monoene is only 75%. Apparently, larger palladium particles, formed as a result of the aggregation process during hydrogenation, are more active in the hydrogenation of cyclohexene to cyclohexane.

Conclusion

The use of metal-containing dendrimers and polyallylamines based hybrid materials has been demonstrated to be a promising approach for the synthesis of new hydrogenation catalysts with adjustable activity and selectivity. The properties of such catalysts can controlled via the selection of suitable macromolecules and their structural organization.

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