Nanocatalysts based on dendrimers*

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Abstract: Nanostructured regular materials based on dendrimers bound by covalent or coordination bonds between surface functional groups were synthesized. Bimetallic Cu(II) and Pd(II) metal complexes with nitrile-based dendrimers demonstrated high activity in Wacker oxidation of terminal alkenes along with good selectivity for methylketone formation. New heterogeneous catalysts based on Pd nanoparticles and cross-linked polypropylene imine (PPI) and polyamidoamine (PAMAM) dendrimers were prepared and examined for selective hydrogenation of unsaturated compounds.

Keywords: catalysis; dendrimer complexes; hydrogenation; palladium nanoparticles; Wacker oxidation.

INTRODUCTION

Substitution of classical stoichiometric methodologies with cleaner catalytic alternatives plays a crucial role in green chemistry. The design of novel materials having a regular structure and the ability to bind the substrate selectively could be considered as one of the most promising approaches. Catalysts based on zeolites or organic receptors with molecular recognition abilities, such as cyclodextrins, are examples of such materials. Common features of such catalysts are high regio- and substrate selectivity [1–6]. A promising approach in the synthesis of nanostructured materials is the use of hyperbranched regular macromolecules with highly symmetrical structure (dendrimers) [7]. A particular interest to design catalysts based on dendrimers is determined by the regular branched structure of the latter along with their monodispersity and size range of 1–10 nm. With the sizes of the macromolecules being predictable, controlled, and reproducible, dendrimers offer a unique possibility for designing immobilized regular metallocomplex catalysts for various processes, e.g., hydrogenation, hydroformylation, cross-coupling, metathesis, etc. [7–11]. Adjustment of a catalyst's properties could be achieved by placing the metal ions either inside the molecule (in the core or on the branches) or on its surface (due to modification of the terminal residues). It should be mentioned that dendrimers provide a possibility of synthesis of immobilized nanoparticles [12–15]. Because of its structure, a dendrimer molecule could bind a strictly definite number of metal ions, thereby ensuring that particles of almost the same size are obtained. Such particles were demonstrated to have a high activity in homo- and two-phase hydrogenation and cross-coupling of various substrates.

Our approach to dendrimer-based catalysts implies linkage of spherically symmetrical dendrimers into a regular macromolecular "megamer", having 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 (Scheme 1).
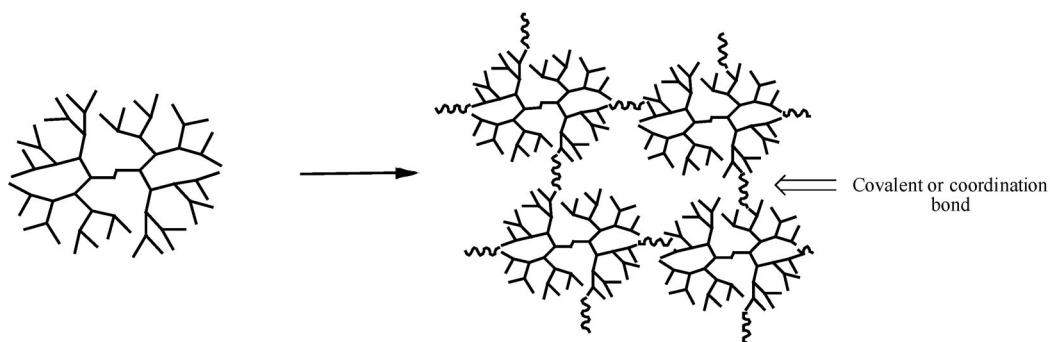
Scheme 1 Formation of cross-linked dendrimer-based networks via covalent or coordination bonding.

Dendritic fragments (areas) of megamers could be regarded as singular nanocapsules which are able to bind ions of one or several metals due to the surface functional groups and, therefore, enhance formation of the metal nanoparticles. Various bifunctional compounds, such as diisocyanates, diepoxides, etc., may be used for covalent binding of dendrimers.

Varying the size, flexibility, and polarity of the cross-linking molecule controls the spacing between dendrimer molecules and selectivity of organic ligands and nanoparticles binding in 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 same way that conventional coordination polymers are formed. 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.

In the present work, we demonstrate uniting dendrimers into superstructures to influence regio- and stereoselectivity in the processes of Wacker oxidation and hydrogenation of unsaturated compounds. Polypropylene imine (PPI) and polyamidoamine (PAMAM) dendrimers, along with dendritic ligands, derived from biscinchoninic acid, were used as building blocks for synthesis of such structures (Fig. 1).
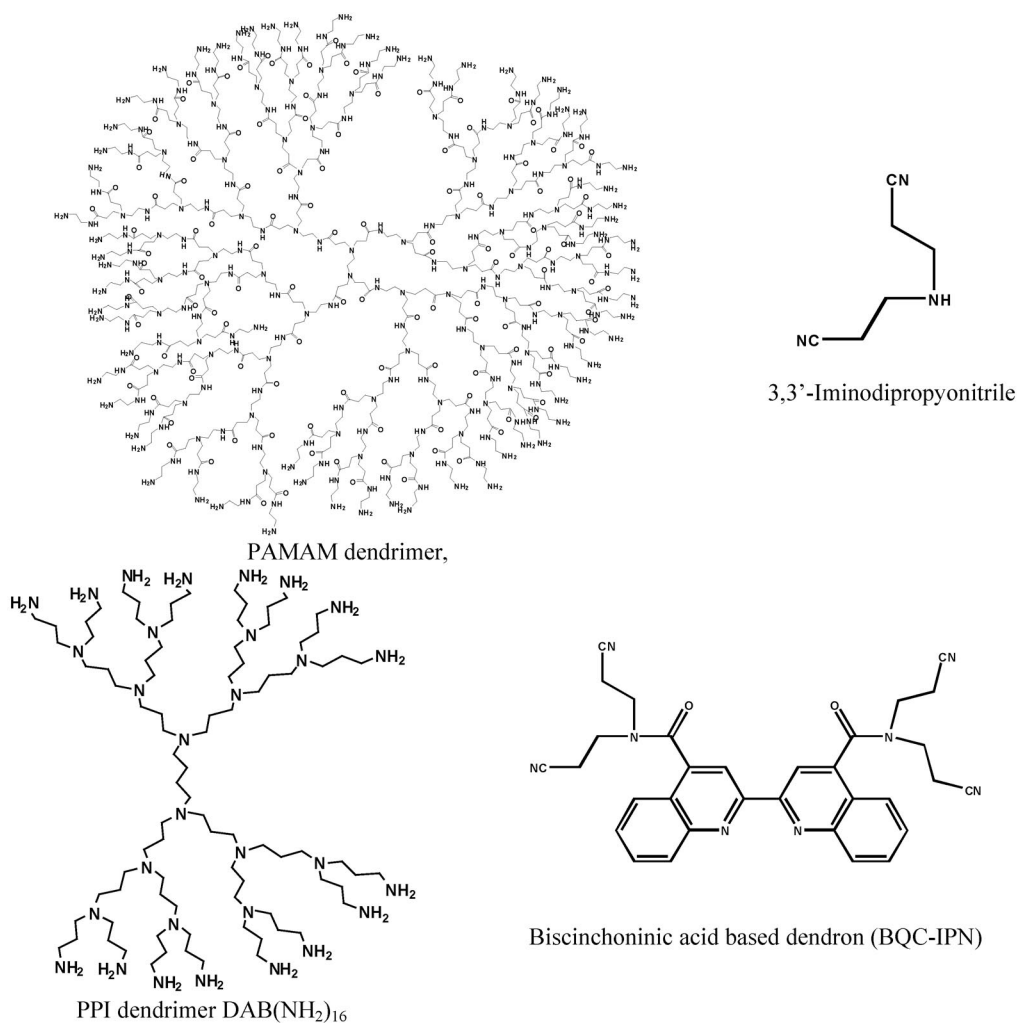
PAMAM dendrimer,

3,3'-Iminodipropyonitrile

PPI dendrimer DAB(NH$_2$)$_{16}$

Biscinchoninic acid based dendron (BQC-IPN)

Fig. 1 Dendrimers and synthesis of dendrimer-based megamers.

DENDRIMER-BASED CATALYSTS IN WACKER OXIDATION OF OLEFINES

PPI dendrimers were obtained as described [16], and the synthesis of biscinchoninic acid derivative was performed via amidation-suggested technique [17]. NMR and mass spectroscopy were applied to confirm the structure of the ligands.

Wacker oxidation of alkenes requires usage of a system, including both the complex of Pd to activate a substrate molecule and the Cu compound to reoxidize the Pd ion. Therefore, macrocomplex catalysts are supposed to have residues complexing both Pd(II) and Cu(II). The suggested ligands are expected to have exactly the required properties. Specifically, amino groups inside PPI dendrimers can bind Cu ions, and terminal cyano groups are able to form complexes effectively with Pd ions. Cu could also create a peculiar core in such branched structures when iminodipropionitrile or its biscinchoninic acid derivative is used (Fig. 2). Simultaneous coordination of cyano groups results in their association into regular "megamers".
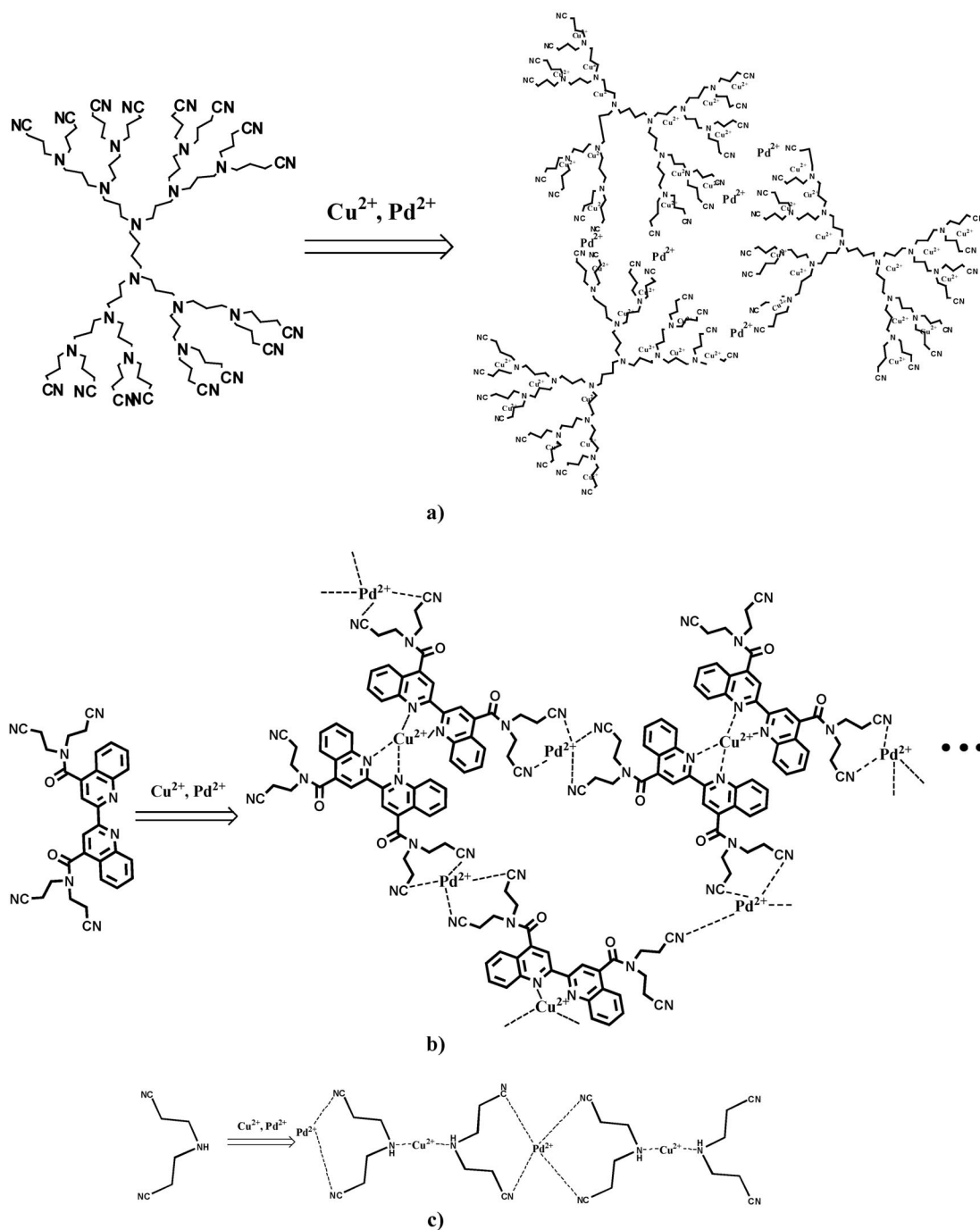
Fig. 2 Formation dendrimer-based macromolecular Pd(II)/Cu(II) complexes. (a) DAB(CN)$_{16}$; (b) 2,2'-biquinoline-4,4'-dicarboxylic acid *N,N*'-bis(3,3'-iminodipropionitrile)diamide; (c) 3,3'-iminodipropionitrile.

Formation of the network structures was confirmed by several methods of analysis. Thus, interaction between sulfate of Pd and Cu chloride with PPI dendrimers in aqueous-alcoholic medium generates changes detected by visible spectroscopy and an absorption band at 620 nm appears due to binding of Cu ions by dendrimer ligands. Light-scattering techniques prove formation of colloidal particles with the size 320–800 nm. When the concentration of dendrimer and metal salts was increased up to 10 mmol/l, it was possible to isolate the precipitate of the complex.

Quantitative analysis, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) techniques were applied to characterize the latter. Pd/CN ratio was 0.5, Pd/Cu ratio was 10. The size of precipitate particles varies from 10 to 90 nm, while minimum size of aggregates is 200 nm according to data obtained by electron microscope investigations (Fig. 3). The XPS spectrum has a wide peak at 337.5 eV, which could be assigned to $Pd3d_{5/2}$ electrons interacting with cyano groups [18], and a signal at 935.0 eV corresponds to the binding energy of Cu2p in complexes with amines. Analysis of FTIR spectra of the precipitated dendrimer complexes confirms that Cu interacts preferentially with amino groups of the dendrimer. The shift of C≡N absorbance band to 2304–2312 cm^{-1} demonstrates the complex formation with Pd.
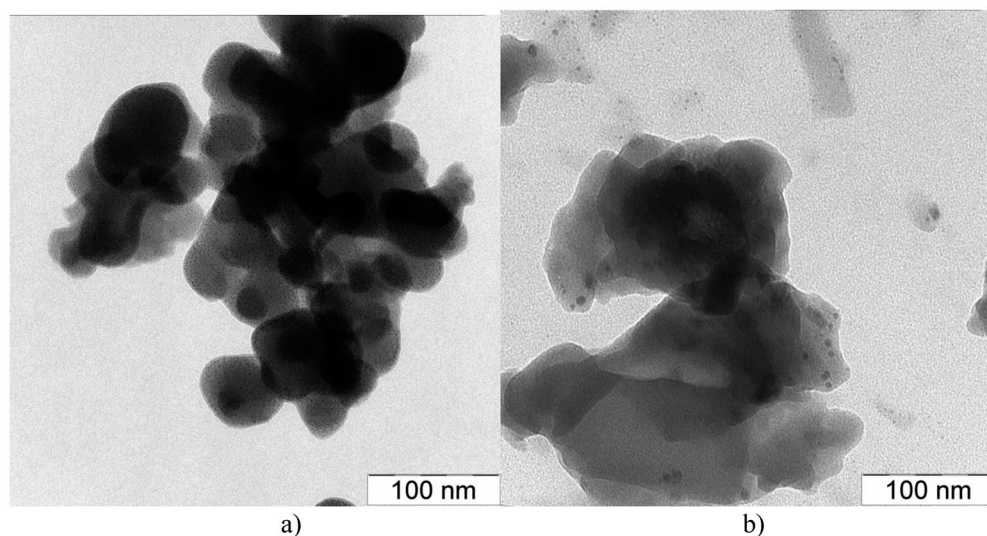

Fig. 3 Aggregates of PPI dendrimer complexes of Pd(II) and Cu(II) with $DAB(CN)_{16}$ (a) and BQC-IPN (b).

Formation of Pd and Cu complexes with ligands based on biscinchoninic acid and iminodipropionitrile was studied by mass spectrometry with ionization at atmospheric pressure. Results obtained confirmed the formation of particles in which complexes comprise both ligand and metal ions. Again, the complexes tend to aggregate in solutions as demonstrated by light-scattering techniques and electron microscopy. At low concentration of the reagents in solution, a colloidal system was formed with the size of particles varying from 20 to 100 nm. The increase of concentration resulted in forming precipitate as in the case of PPI dendrimers.

Wacker oxidation was carried out in water–ethanol mixture under an oxygen pressure 0.5 MPa. In all the experiments, complexes were formed in situ. Isomeric ketones were the main products of the oxidation in the case of the process being carried out without any ligand. Usage of metal complexes with dendritic ligands was shown to increase the selectivity of the process significantly, as exemplified by oxidation of 1-octene. The selectivity increased symbatically with the ratio of dendrimer/Pd (Fig. 4). Notably, the effect was observed both for systems based on PPI dendrimers, for iminodipropionitrile
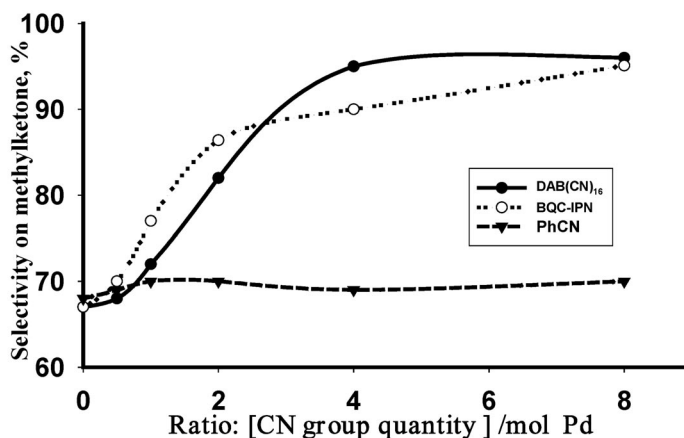
Fig. 4 Change of selectivity for methylketone on the ratio [CN group in dendrimer]/[Pd(II)] for reaction of oxidation of 1-octene ([Pd]/[Cu]/[S] = 1/10/200, 1 h, [Pd] = 7.3 mmol/l, T = 90 °C, P(O$_2$) = 0.5 Mpa, water/EtOH/S = 0.2:0.8:0.2).

[analogous to DAB(CN)$_4$ in the number of cyano groups], and for biscinchoninic acid derivative [analogous to DAB(CN)$_8$] (Table 1). It should be mentioned that when common ligands containing cyano groups were used, no significant changes of selectivity were noticed even at greater ligand excess.

Table 1 Oxidation of 1-octene. [Pd]/[Cu]/[S] = 1/10/200, 1 h, [Pd] = 7.3 mmol/l, EtOH/water/S = 0.8:0.2:0.2 by volume, P(O$_2$) = 0.5 MPa.

Ligand	CN/Pd	Yield of ketones, %	Selectivity for methylketone, %
–	–	64	69
PhCN	8	38	68
DAB(CN)$_4$	2	48	75
DAB(CN)$_8$	2	44	84
DAB(CN)$_{16}$	2	44	88
	4	37	94
HN(CH$_2$CH$_2$CN)$_2$	2	39	77
BQC-IPN	2	22	86
	4	29	90

A positive dendritic effect was observed. Selectivity for methylketone formation increased with elevation of the dendrimer generation independently from the structure of the core (positive dendritic selectivity effect). For example, the ratio methylketone/isomeric ketones for 1-octene oxidation changes from 2.1 to 2.5 with lower molecular ligand—dendrimer DAB(CN)$_4$—and increased to 4.6 for high molecular DAB(CN)$_{16}$. 2-Alkenes, 3-alkenes, and cyclohexene oxidized with low rate.

We suppose that high selectivity of dendritic systems can be explained by the oxidation of the alk-1-ene on the surface of dendrimer molecules in the interior of dendrimer network aggregates formed by interaction of Pd(II) ions and CN groups of dendrimer molecules. Steric congestion in the aggregates makes it difficult to transfer and coordinate alkenes on Pd(II) ions that would lead to higher selectivity on methylketone. Steric hindrances in the interior of the catalyst for substrate transfer and π-complex formation were insignificant for 1-alkenes and were high for alkenes with inner double bonds.

CROSS-LINKED DENDRIMER-BASED CATALYSTS FOR HYDROGENATION OF UNSATURATED COMPOUNDS

During the last years, much attention has been focused on the catalytic application of metal nanoparticles due to their unique physical and chemical properties, which are distinct both from the bulk phase and from isolated atoms. Metal nanoparticles are known to be one of the most effective hydrogenation catalysts. A drastic increase of the surface area and changes of the electron properties determine the significant increase of catalytic activity along with affecting the selectivity of the process. Immobilizing metal nanoparticles on organic or inorganic supports makes their usage as heterogeneous catalysts possible. Immobilization of nanoparticles provides the possibility to adjust the substrate- and regioselectivity by varying such properties of the carrier, as polarity, pore sizes, and interactions between carriers' functional groups and metal particles.

One of the important and challenging tasks in catalysis by nanoparticles is the synthesis of particles with narrow size distribution and homogeneous physicochemical properties. One of the most attractive hosts for catalytically active metal nanoparticles are dendrimers. The modified PAMAM and PPI dendrimers were demonstrated to be suitable for synthesis of 1–2 nm metal nanoparticles, the latter being active in hydrogenation and cross-coupling processes. Thus, nanoparticles of Pd were obtained using modified dendrimers and were active in homogeneous hydrogenation of some unsaturated compounds [20–23].

In the present study, new methodology was applied to the synthesis of Pd nanoparticles containing materials. Cross-linked megamers of dendrimers were used to synthesize heterogeneous immobilized catalysts based on Pd nanoparticles (Scheme 2).
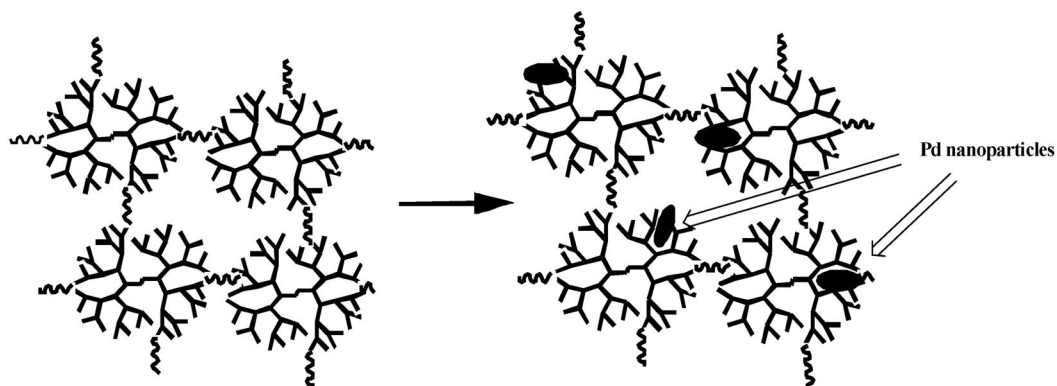
Scheme 2 Metal nanoparticle incapsulation in matrix of covalently cross-linked dendrimers.

2,4-Toluene diiosocyanate (TDI) or methylene(di-*p*-phenylene diiosocyanate) (MPDI) were applied as binding agents for the synthesis of cross-linked materials for PPI-DAB and PAMAM dendrimers (PPI-G*x*-MDI and PPI-G*x*-TDI, *x* = 1–3, PAMAM-G4-MPDI, PAMAM-G4-TDI). The insoluble reaction products were characterized by IR spectroscopy and TEM. Signals corresponding to carbonyl group of carbamate residues (1640–1650 cm^{-1}, 1597–1598 cm^{-1}) and aromatic fragments (2930–2950 cm^{-1}, stretch vibration of C–H and 1510–1550 cm^{-1}, backbone vibration of C–C bonds) were observed in IR spectra. The size of aggregate particles varied from 90 to 200 nm.

After addition of Pd salts in chloroform solution and further reduction of metal, a series of dendrimer-based catalysts was obtained (PPI-G*x*-MPDI-Pd and PPI-G*x*-TDI-Pd, *x* = 1–3). The same approach was used for synthesis of PAMAM (4th generation) based material (PAMAM-G4-MPDI-Pd, PAMAM-G4-TDI-Pd).

The megameric materials were investigated by XPS, atomic absorption spectroscopy (AAS) and TEM. TEM results confirmed that PPI-DAB-G*x*-Pd and PAMAM-G4-MPDI-Pd materials, linked with 2,4-TDI or MPDI included 0.5–3.0 nm metal nanoparticles (Fig. 5).
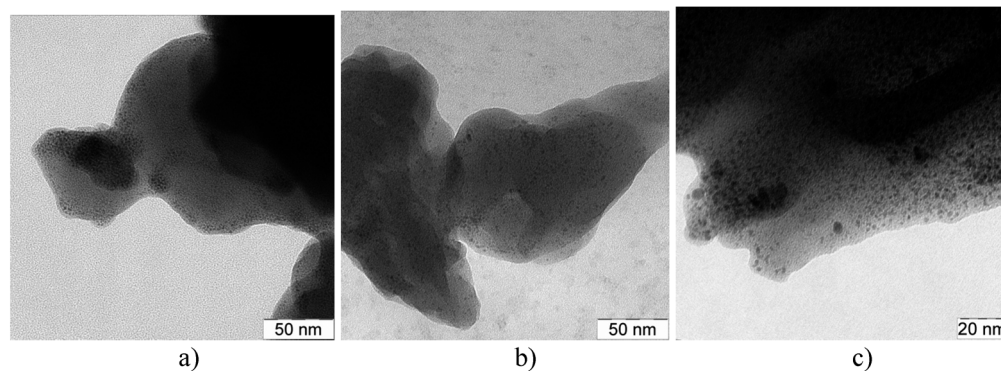

Fig. 5 TEM images of dendrimer Pd-containing samples: (a) PPI-G3-MPDI-Pd; (b) PPI-G3-TDI-Pd; (c) PAMAM-G4-MPDI-Pd.

Electron diffraction analysis gave evidence of the presence of amorphous Pd(0) in the samples investigated. The XPS spectra confirmed the presence of both Pd(0) similar to "nanoparticles", coordinated by amino groups (336.8–337 eV) and free metallic Pd (335–335.5 eV). The values of Pd content obtained (1.3–2 %) were in good agreement with the results obtained by AAS quantitative analysis.

Hydrogenation processes were carried out in an autoclave under hydrogen pressure 0.5 MPa, 80 °C. Pd nanoparticles, obtained in a matrix of the dendrimer linked with 2,4-TDI or MPDI, were used as catalyst. The activity of the catalysts depended significantly on the substrate type. Compounds with conjugated double bonds or with double bonds, activated by acceptor substituents, underwent quantitative hydrogenation easily in 60 min (Table 2). The turnover frequency (TOF) of the reaction (number of product formed per 1 Pd atom per minute) varied from 300 to 1000.

Table 2 Hydrogenation of unsaturated compounds using dendrimer-based catalysts. $T = 80$ °C, p (H$_2$) = 0.5 MPa, S/catalyst = 1000, 1 h.

Substrate	Catalyst			
	PPI-G1-MDI-Pd	PPI-G3-MDI-Pd	PPI-G1-TDI-Pd	PPI-G1-TDI-Pd
Styrene	86	100	79	100
1-Octene	15	11	9	7
1-Nonene	20	23	8	8
Cyclohexene	18	16	13	20
1,3-Cyclohexadiene	100	58	100	100
Allylbenzene	16	30	8	12
Propenylbenzene	76	80	79	83
Allylic alcohol	42	23	60	62
Methylacrylate	100	100	80	78

The difference of activity compared to common catalyst Pd/C (5 % of the metal) was tested on the reactions of 1-octene and styrene (Table 3). The dendrimer-based heterogeneous catalysts demonstrated a considerable increase of activity for reaction of styrene hydrogenation up to 4.5–15.5 times. Rate growth was not high for 1-octene hydrogenation. It did not exceed 3–4. Therefore, catalysts

demonstrated a significant increase of the substrate selectivity, the change of activity if styrene hydrogenation compared to 1-octene increased to 17–60 times. When joint hydrogenation of styrene and 1-octene was performed, conversion of styrene reached 85 % after 20 min of the reaction and 100 % in 1 h. For 1-octene, the values of conversion were 5 and 6 %, correspondingly.

Table 3 Hydrogenation of styrene and 1-octene. $T = 80$ °C, p (H$_2$) = 0.5 MPa, S/catalyst = 1000, 1 h.

Catalyst	TOF for styrene	TOF for 1-octene	TOF$_{st}$/TOF$_{octene}$
PPI-G1-MDI-Pd	506	21	24.0
PPI-G2-MDI-Pd	642	37	17.3
PPI-G3-MDI-Pd	503	13	38.0
PAMAM-G4-MDI-Pd	476	28	17
PPI-G1-MDI-Pd	312	8	36.7
PPI-G2-MDI-Pd	817	23	34.8
PPI-G3-MDI-Pd	1005	17	59.7
PAMAM-G4-MDI-Pd	950	41	23
Pd/C, 5 %	65	8	8.0

Studies of hydrogenation of cyclooctadiene, cyclohexadiene, allyl- and propenylbenzene were carried out to investigate the effect of conjugation with aromatic residues or with double bonds. When the reaction was carried out for 1 h, propenylbenzene had been converted completely, while allylbenzene conversion did not exceed 20–30 % depending on the generation of the cross-linked dendrimer. Under the reaction conditions, the process of isomerization was supposed to occur, which could lead to formation of propenylbenzene precursor. As for hydrogenation of conjugated cyclodiene substrates, the main products were monoenes (e.g., for 1,3-cyclohexadiene, cyclohexene was the main hydrogenation product). The selectivity for the main product exceeded 90 % at high conversion values for PPI- and PAMAM-based catalysts. The hydrogenation rate for 1,3-cyclohexadiene was 15 times greater than the rate for cyclohexene. A mixture of isomeric octenes was produced for the hydrogenation of 1,3-octadiene with selectivity for monoenes more than 95 % for 1 h.

The hydrogenation of methylacrylate, which presented another example of substrate with conjugation between double bond and accepting carbonyl group, also resulted in high product yields. The hydrogenation rate for allyl alcohol was significantly lower (this fact could be explained by the substrate's high polarity and low polarity of aromatic groups).

The effect of the distance between dendrimer units on reaction rates was analyzed by several examples. The substrate selectivity of catalysts depended on the size of binding agent: the reaction rates for bulk substrate were higher in the case of material, synthesized using longer linker–MPDI. For the catalyst based on PPI-G3-TDI-Pd, changing the substrate from *tert*-butylstyrene to phenylstyrene resulted in a drastic decrease in the hydrogenation rate, and 1,4-diphenyl-1,3-butadiene did not react at all (Fig. 6). The stilbene was hydrogenated quantitatively using PPI-G3-MPDI-Pd catalyst and with 35 % conversion for PAMAM-G4-MPDI-Pd catalyst. The yields of products with PPI-G3-TDI-Pd and PAMAM-G4-TDI-Pd were 5 and 10 %. Conducting the hydrogenation of 4-phenylstyrene on PPI-G3-MPDI-Pd and PPI-G3-TDI-Pd catalysts for 20 min at 80 °C led to conversion 24 and 2 %, respectively. Also, a significant increase of activity in hydrogenation of 1-nonene was observed for products based on MPDI. The yield of nonane was almost two-fold greater than for catalysts synthesized from 2,4-TDI.

Cross-linked denrimer catalysts are easy to separate from the reaction medium and could be reused without additional regeneration stage and without considerable decrease of catalytic activity.
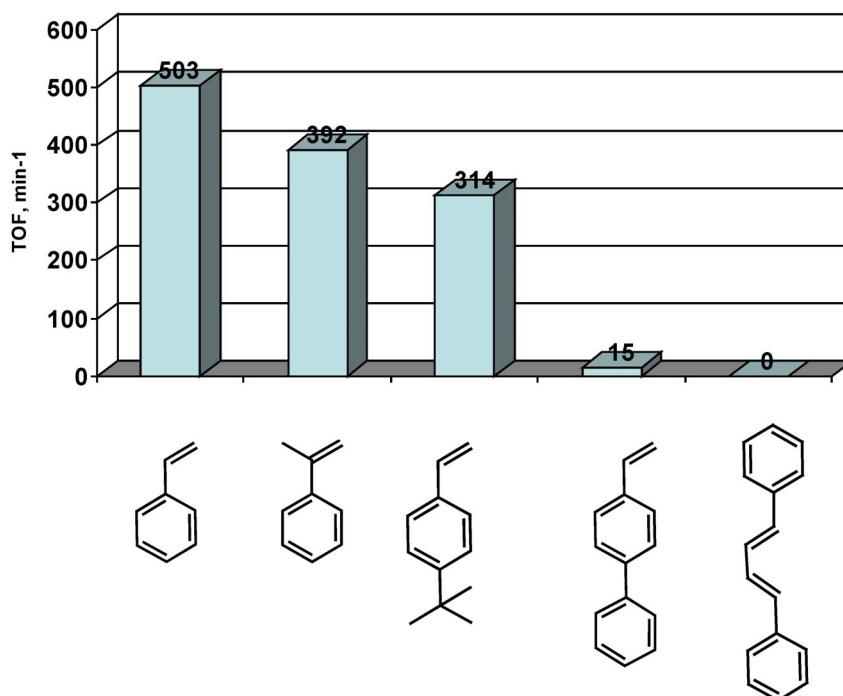
Fig. 6 Influence of substrate size on hydrogenation rate. Catalyst PPI-G3-TDI-Pd. Hydrogenation of styrene. $T = 80 \,°C$, p (H_2) = 0.5 MPa, S/catalyst = 1000, 1 h.

Uniting symmetrical spherical dendrimer molecules into the regular macromolecular "megamers" provides a novel approach for synthesis of molecular recognizing materials, capable of segregating various organic compounds.

ACKNOWLEDGMENTS

REFERENCES

1. E. Karakhanov, A. Maximov. In *Metal Complexes and Metals in Macromolecules*, D. Wohrle, A. Pomogajlo (Eds.), pp. 457–492, Wiley-VCH, Weinheim (2003).
2. E. Karakhanov, A. Maximov, Yu. Kardasheva, T. Buchneva, M. Gayevskiy, A. Zhuchkova, T. Filippova. *Polym. Adv. Technol.* **12**, 161 (2001).
3. A. L. Maksimov, T. S. Buchneva, E. A. Karakhanov. *J. Mol. Catal. A* **217**, 59 (2004).
4. E. A. Karakhanov, A. L. Maksimov, E. A. Runova. *Russ. Chem. Rev.* **74**, 97 (2005).
5. A. L. Maksimov, D. A. Sakharov, T. Yu. Filippova, A. Ya. Zhuchkova, E. A. Karakhanov. *Ind. Eng. Chem. Res.* **44**, 8644 (2005).
6. A. V. Ramaswamy. *Bull. Catal. Soc. India* **2**, 140 (2003).
7. G. R. Newkome, C. D. Shreiner. *Polymer* **49**, 1 (2008).
8. D. Méry, D. Astruc. *Coord. Chem. Rev.* **250**, 1965 (2006).
9. A. Dahan, M. Portnoy. *J. Polym. Sci., Part A: Polym. Chem.* **43**, 235 (2005).
10. A. S. H. King, L. J. Twyman. *J. Chem. Soc., Perkin Trans. 1* 2209 (2002).
11. D. Astruc, K. Heuzé, S. Gatard, D. Méry, S. Nlate, L. Plault. *Adv. Synth. Catal.* **347**, 329 (2005).

12. R. M. Crooks, B. I. Lemon, L. Sun, L. K. Yeung, M. Q. Zhao. *Top. Curr. Chem.* **212**, 81 (2001).
13. R. M. Crooks, M. Q. Zhao, L. Sun, V. Chechik, L. K. Yeung. *Acc. Chem. Res*. **34**, 181 (2001).
14. K. Esumi, R. Isono, T. Yoshimura. *Langmuir* **20**, 237 (2004).
15. X. Sun, S. Dong, E. Wang. *Macromolecules* **37**, 7105 (2004).
16. E. M. M. de Brabander-van den Berg, E. W. Meijer. *Angew. Chem., Int. Ed. Engl*. **32**, 1308 (1993).
17. A. L. Gershunz, A. A. Pavluk. *Ukr. Khim. Zh*. (Russian ed.) **30**, 955 (1964).
18. Sh. Deng, R. Bai, J. P. Chen. *J. Colloid Interface Sci*. **260**, 263 (2003).
19. L. K. Yeung, C. T. Lee Jr., K. P. Johnston, R. M. Crooks. *Chem. Commun*. 2290 (2001).
20. J. Lemo, K. Heuze, D. Astruc. *Inorg. Chim. Acta* **359**, 4909 (2006).
21. F. Bellina, A. Carpita, R. Rossi. *Synthesis* 2419 (2004).
22. L. K. Yeung, R. M. Crooks. *Nano Lett*. **1**, 14 (2001).
23. O. Masahiko, M. Makoto, M. Tomoo, E. Kohki, K. Kiyotomi. *Nano Lett.* **2**, 999 (2002).