Dendrimer-based catalysts in Wacker-oxidation: Unexpected selectivity to terminal double bonds

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ABSTRACT

Catalytic systems based on palladium–copper complexes of PPI dendrimers with nitrile terminal groups formed *in situ* using dendrimer, palladium and copper salts as a catalytic precursor demonstrate high activity in the Wacker-oxidation of terminal alkenes along with good selectivity in respect to methylketone. The study of complexes in solution proved that the selectivity of the formation of methylketone as well as reactivity of alkenes is influenced by the steric parameters of dendrimer aggregates in solutions.

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1. Introduction

Anchoring of transition metal complexes on various soluble and insoluble supports has been a major challenge for a long time because such catalysts can combine all the advantages of homo- and hetero-geneous systems [1,2]. They should be easy to recycle and display high activity and selectivity. Studies of metal complexes immobilized on organic or inorganic supports allowed to expand knowledge on the development of effective catalysts with properties of both homo- and hetero-geneous systems. Numbers of effective catalysts were developed for different reactions, meanwhile, immobilization also resulted in dramatical changes of properties of neat metal complexes and some undesirable effects, e.g. decrease of reaction rate or selectivity changes [2–4].

The drawbacks mentioned above can be overcome partly by the use of such class of carriers as dendrimers (Fig. 1) [5–7]. Dendrimers are hyperbranched regular macromolecules with highly symmetrical structure. The features of the structure allow immobilization of metal ions in different regions of a dendrimer molecule (core, branches or periphery). The considerable interest in the design of dendrimer-based catalysts is explained by monodisperse polymeric structure of dendrimers and their solubility in different solvents, allowing to develop catalysts with high degree of surface density

and homogeneity. Such catalysts, both homo- and hetero-genous ones were applied to catalyze reactions of hydroformylation, hydrogenation, C—C coupling, Wacker-oxidation, metathesis, etc. [8–13].

Numerous examples of using such catalysts prove the occurrence of the so-called "negative" dendritic effect: activity of catalysts decreases with the increase of dendrimer generation, compared to lowmolecular analogue [14–16]. For instance, investigations of the Pd catalyzed Sonogashira-type carbon–carbon coupling reaction demonstrated that elevation of dendrimer generation in catalyst from 1 to 3 resulted in almost 2-fold decrease of the product yield almost two times [17]. The rate of asymmetric Rh-catalyzed hydrogenation of Z-methyl-α-acetamide of cinnamic acid decelerated several time with the increase of generation of dendrimers with BINAP groups [18].

It could assume that the "negative" dendritic effect in catalysis depends significantly on substrate properties, and only compounds with definite structure would interact with catalyst based on higher-generation dendrimer [19]. Thus, studies of dendrimers could favor the development of catalysts exhibiting substrate selectivity as catalysts based on macrocyclic receptor molecules [20–23]. In this paper we report the results of our investigation of Wacker-oxidation of unsaturated compounds catalyzed by bimetallic complexes of Pd and Cu with polypropelenimine (PPI) dendrimers with different cores (diaminobutane, diaminohexane) (Fig. 1) that actually demonstrate substrate selectivity to terminal double bonds.

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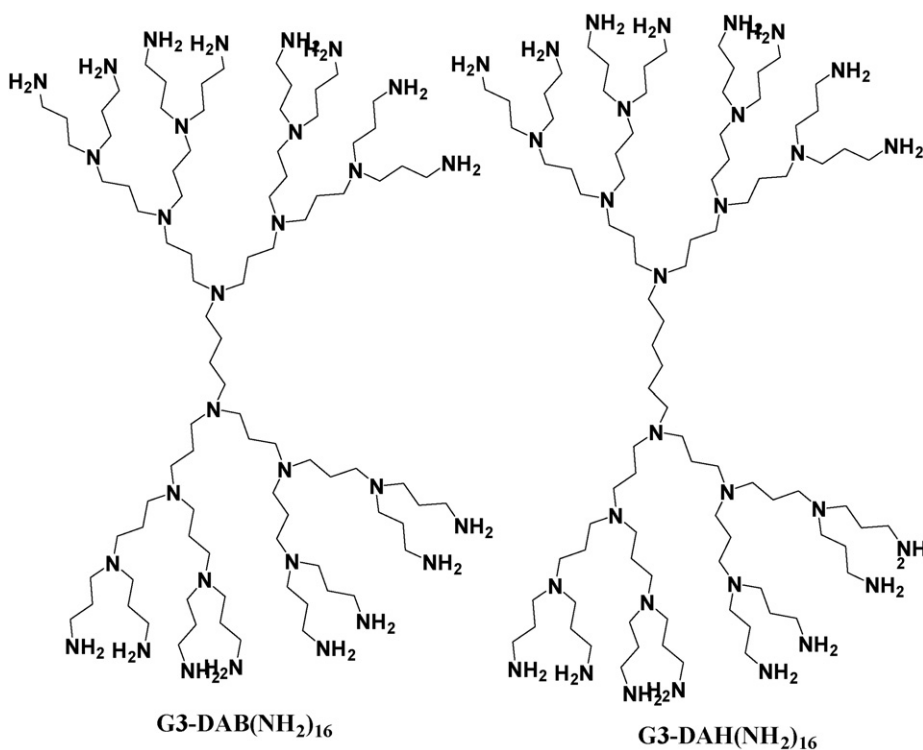*E-mail address:* kar@petrol.chem.msu.ru (E.A. Karakhanov).

Fig. 1. DAB and DAH dendrimers.

2. Experimental

2.1. General

Diaminobutane (DAB), diaminohexane (DAH), acrylonitrile, and olefins were purchased from AcrusOrganics, Reney 2700 Cobalt was a product of Aldrich. All solvents (ethanol, methanol, and water) were purified by standard methods. Palladium(II) sulfate dehydrate was a product of Fluka.

Dendrimers DAB-dendr used in this work were prepared from procedures given in [24].

At first stage acrylonitrile was added to a solution of diaminobutane in water. The reaction mixture was heated at 80 °C for 1 h to complete addition. Then excess of acrylonitrile was removed as a water aseotrope by vacuum distillation at 40 °C (16 mm).

At second stage the hydrogenation vessel filled with Renney 2700 Cobalt and water was added with $DAB(CN)_4$ and dissolved in methanol. Subsequently the mixture was hydrogenated at 40 atm of hydrogen pressure at 70 °C for 1 h. The cooled reaction mixture was then filtered and solvents were evaporated at reduced pressure. The residue was $DAB(NH_2)_4$.

By stepwise these iterations were prepared in next generation of dendrimers ($DAB(CN)_8$-G1.5, $DAB(NH2)_8$-G2.0, and $DAB(CN)_{16}$-G2.5). Dendrimers based on diaminohexane were prepared by the same method.

The purity of all ligands was established by ^1H NMR, ^{13}C NMR, IR-spectromertry and LS–MS.

2.2. Catalytic experiments

Wacker-oxidation of unsaturated compounds (C_6–C_{12} 1-alkenes, cyclohexene, allylbenzene, and 3-hexene) was carried out in 15 ml stainless autoclaves with glass insert in water–ethanol media (H_2O/EtOH 1:4 vol.) at 60–80 °C, oxygen pressure 5 MPa. Complexes of PPI dendrimers with Cu and Pd used as catalysts were formed *in situ.* Reagents and products of the reaction were extracted from water–ethanol media by diethylether and analysed by gas chromatography. Reaction products were confirmed using comparison to known compounds and further confirmed using GC–MS.

2.3. Instruments

The NMR spectra were recorded on Brucker Avance-400 instrument.

The electronic absorbtion spectra (UV–vis) were measured on Agilent 8453 spectrophotometer. LS–MS analysis was carried out on Agilent 1100 series liquid chromatograph/Ion-trap ESI SL detector.

TEM observations were carried out on a Leo 912AB under low-electron dose irradiation by focusing in an adjacent area to the selected specimen area at 100 kV by inserting the Omega filter.

The electronic state of Cu, Pd, N and Cl and their atomic ratios in the supported and unsupported complex was studied by XPS. Determinations were carried out on a LAS-300 (Riber) electron spectrometer coupled to a OPX-150 data system. For photoelectron excitation was used aluminium anode X-rays (Al Kα = 1 486.6 eV) under tube voltage 12 kV and emission current 20 mA. In order to correct possible deviations caused by electric charge on the samples, the C 1s line was taken as an internal standard at 285.0 eV. The superficial electronic state of palladium, nitrogen, and chlorine was studied following the position of the maximum of the Pd $3d_{5/2}$, N $1s_{1/2}$, Cu 2p and Cl 2p peaks. Determinations of the atomic Cu/Pd ratios were made by comparing the areas under the peaks after background subtraction and corrections due to differences in escape depths and in photoionization cross-sections.

FTIR spectra of complexion KBr were recorded using IR200 Thermo HicoLet single beam spectrometer.

Light-scattering spectroscopy was used for the determination of the particle size distribution in suspensions of the analysed sam-
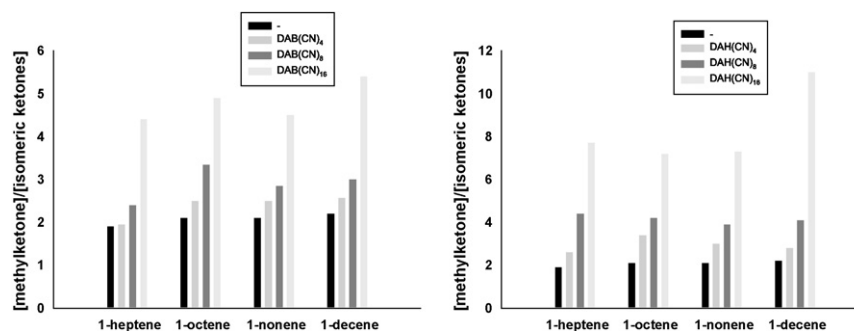
Fig. 2. Dependence of selectivity on methylketone on dendrimer generation for reaction of oxidation of 1-octene (Pd/CN/Cu/S = 1:2:10:200, 1 h, Pd = 7.3 mmol/l, water/EtOH/S = 0.8:0.2:0.2 by volume, T = 80 °C, and $P(O_2)$ = 0.5 MPa).

Table 1
Dependence of conversion and selectivity of the Waker-oxidation reaction on temperature.

Substrate	T (°C)	No ligand		DAB(CN)$_{16}$		DAH(CN)$_{16}$	
		Conversion to ketones (%)	Methylketone/ isomeric ketones	Conversion to ketones (%)	Methylketone/ isomeric ketones	Conversion to ketones (%)	Methylketone/ isomeric ketones
1-Hexene	60	45	3.1	27	4.7	24	6.0
1-Heptene		44	3.4	37	8.8	35	7.0
1-Octene		32	3.7	34	8.9	25	6.5
1-Nonene		30	3.9	27	8.7	23	7.2
1-Decene		29	4.7	23	9.0	22	11.0
1-Dodecene		13	7.7	12	25.0	10	14.0
1-Hexene	80	74	1.8	39	3.6	23	5.3
1-Heptene		71	2.0	40	4.4	29	7.0
1-Octene		64	2.1	44	4.5	33	7.2
1-Nonene		60	2.1	57	4.6	51	7.3
1-Decene		57	2.7	35	5.4	39	11.0
1-Dodecene		25	4.2	18	16.0	18	20.0

*Pd/CN/Cu/S = 1:2:10:200, 1 h, Pd = 7.3 mmol/l, water/EtOH/S = 0.8:0.2:0.2 by volume, $P(O_2)$ = 0.5 MPa.

ples. The Zetasizer IIc (Malvern, UK) equipped with a He–Ne-laser was used.

GC analyses of samples were performed on Chrompack CP 9001 FID/TCD gas chromatograph with 30 m capillary (S.E. −30, i.d. = 0.25 mm).

3. Results and discussion

Complexes of Pd(II) and Cu(II) with PPI were found to be active catalysts for Wacker-oxidation of 1-alkenes in alcohol–water conditions at 60–80 °C an 0.5 MPa O$_2$ (Table 1).

In general, methyl ketones are the favored products in the oxidation of 2-alkenes [22,25–27]. However, oxidation of 1-alkene in homogeneous media in the presence of alcohols results in rapid isomerization of the alkene, thus leading to the formation of several ketones in the reaction mixture [28–30]. It had been demonstrated that isomerization occurred quickly in the applied catalytical system: equilibrium mixture of alkenes was formed after 5 min [30–32].

Dendrimers did not have influence on the isomerization *and formation of isomeric alkene proceeds without changing of isomerization rate*. At the same time, the presence of the dendrimer ligand affected the rate of oxidation of olefins to ketones and the selectivity on the corresponding methylketone. When catalyst based on dendrimer DAB(CN)$_{16}$ was used, the ratio of methylketone/isomerised ketones was increased to 1.8–2.2-fold (80 °C) (Table 1). With dendrimer DAH(CN)$_{16}$ the ratio had grown to 3–4.5-fold at the same temperature. The effect was observed at lower temperatures also. Notably, the rate of reaction was slightly lower for dendrimer obtained from diaminohexane than for complexes of dendrimer with diaminobutane core.

The selectivity on methylkentone changes only slightly if another CN-based low molecular ligands, such as benzonitrile or acetonitrile, were used instead of dendrimer in water–ethanol mixtures (Table 2). Corresponding to literature data the high excess of low molecular nitrile-based ligand, such as acetonitrile does not suppress the formation of izomeric ketones. In solution of acetonitrile/water (7–1) when Pd–acetonitrile complexes were dominant the 2-decanone/isomeric decanons ratio was 3.7–5.6 at 60 °C [29]. For DAB(CN)$_{16}$ and DAH(CN)$_{16}$ corresponding ratios were 9 and 11, respectively at 60 °C in ethanol–water mixture (Table 1).

It should be stressed that the size of a dendrimer molecule has key influence on the selectivity of the process (Fig. 2). The latter increased with the elevation of the dendrimer generation independently from the structure of the core (positive dendritic selectivity effect). E.g. the ratio methylketone/isomeric ketones for octene-1 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)$_{16}$. For DAH dendrimers the effect was strongly

Table 2
Wacker-oxidation of octene-1 in water–ethanol mixture.

Ligand	Conversion, (%)	Methylketone yield (%)	Methylketone/ isomeric ketones
No	64	43	2.1
CH$_3$CN	45	30	2
PhCN	38	25	2
DAB(CN)$_4$	48	36	2.5
DAH(CN)$_4$	44	35	3.5
DAB(CN)$_{16}$	44	36	4.5
DAH(CN)$_{16}$	33	31	7.4

*Pd/CN/Cu/-octene = 1:2:10:200, 1 h, Pd = 7.3 mmol/l, water/EtOH/1-octene = 0.8:0.2:0.2 by volume, T = 80 °C, $P(O_2)$ = 0.5 MPa.
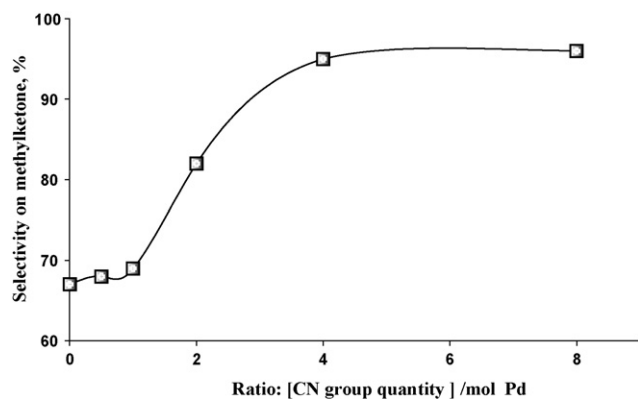
Fig. 3. Dependence of selectivity on methylketone on ratio CN group in dendrimer/Pd(II) for reaction of oxidation of 1-octene (Pd/Cu/S = 1:10:200, 1 h, Pd = 7.3 mmol/l, T = 90 °C, $P(O_2)$ = 0.5 MPa, and water/EtOH/S = 0.8:0.2:0.2).

pronounced and the ratio changes from 2.1 to 3.8 for DAH(CN)$_4$ and to 7.2 for DAH (CN)$_{16}$.

At the same time, the increase of the dendrimer size decreased the total yield of ketones (negative dendritic rate effect) e.g., at 80 °C the total yield of ketones was 44%, the yield of methylketone was 36% when DAB(CN)$_{16}$ dendrimer was used as a ligand. Without dendrimer, the yields reached 64% and 43%, correspondingly. At 90 °C the yield of methylketone actually did not change, while the yield of other ketones decreased from 18 to 8%. Just the same fall of the ketones' yield was observed when more dendrimer was taken. Growth of dendrimer/palladium ratio resulted in the decrease of the total conversion, the yield of methylketone was also falling slightly.

The role of the dendrimer in increasing the selectivity of the process was confirmed by the results obtained when the excess of the dendrimer ligand was used compared to Pd (Fig. 3). The ratio dendrimer/palladium could be considered as the quantity of terminal nitrile groups available for 1 ion of palladium. The considerable enhancement of selectivity was observed for the system where the ratio was equal to 2. When the ratio [CN]/[Pd(II)] was about 4 nitrile groups per 1 Pd(II) ion, the selectivity on methylketone reached 95% and remained constant with further increase of dendrimer concentration. Under these conditions with low molecular ligands electivity was not more than 80% [29].

Results of the kinetic experiments confirmed the conservation of the methylketone formation rate and the drastic decrease of isomeric ketones formation. Without the dendrimer ligand, the gradual increase of the conversion is observed along with considerable decrease of selectivity on methylketone. When dendrimer complex was used as catalyst, the rate of oxidation had decelerated dramatically after the reaction was carried out during 1 h at 80 °C. Meanwhile, the selectivity on methylketone changed very insignificantly. The essential fact was that the reaction of oxidation stopped after definite time. The resulting conversion depended on the ratio [substrate]/[Pd(II)]. When the latter was decreased, the conversion grew.

In oxidation of 3-heptene the addition of the dendrimer decreased significantly the total yield of ketones, especially of 3-heptanone and 4-heptanone. The rate of oxidation decreased with the increase of dendrimer concentration (Table 2). The similar effect was observed for Wacker-oxidation of cyclohexene with the ketone yield falling almost 5-fold. The prevailing product of allylbenzene oxidation was ethylphenylketone. The latter probably was formed from the propenylphenole, which was the result of allylphenole isomerization. When the dendrimer catalyst was used, the only product of oxidation was ethylphenylketone (Table 3).

The data obtained gave evidence proved that regioselectivity of converting alkene-1 to methylketone could be explained due to "negative" dendritic effect against alkenes with the internal double bond. The rate of their oxidation decelerated more rapid than of those with the terminal double bond.

A possible way to explain the effect was to consider the peculiarity of the catalyst structure and dendrimer aggregate formation in water–ethanol mixture.

To study the complexes in solution we have used a combination of UV–vis and electrospray mass spectrometry (ESI–MS). ESI–MS measurements for (DAB)CN$_4$/Pd/Cu complexes in methanol showed a spectrum with peaks corresponding to monomeric and dimeric dendrimer complexes.

UV–vis spectra of ligand DAB(CN)$_{16}$ solution in ethanol–water mixture changed after the addition of Pd(II)–Cu(II) solution ([Pd^{2+}]/[Cu^{2+}] = 1/3). The absorption spectra have got new peak at 620 nm that can be assigned to Cu(II)/Pd(II)/DAB(CN)$_{16}$ complex fomation. The absorption increased with increasing mol fraction of metal ions until the ratio Pd/CN-group of dendrimer was one (Fig. 5).

Under loading Pd/CN ratio 1.4–1.6 after 2–3 min the colloid system and precipitate of Pd/Cu-dendrimer complex is formed and the line at 620 nm are diminished that testify the aggregation of dendrimer during complex formation.

The size of aggregate was observed indirectly by a light-scattering particle size analyser and directly by a transmission electronic microscope (TEM). Aggregates for 10 mmol/l initial concentration of (DAB)CN$_{16}$ dendrimer solution in water–ethanol mixture have mainly diameter of 250–350 nm. No other specific peak of the diameter was observed in the region from 6 to 12,000 nm. The particle size distribution and particle average size were increased under increasing mol fraction of Pd(II)/Cu(II) ions (Fig. 4) Under reaction conditions (ratio Pd/CN = 0.5) the narrow size distribution were found from 320 to 850 nm (Fig. 5).

The formation of precipitate was occurred (size of aggregates of solution near 1 μm) when loading Pd(II)/CN ratio was more than 1.8 that correspond the UV–vis data.

Fig. 7 shows representative TEM images of formed dendrimer complex sample (DAB(CN)$_{16}$/Pd/Cu) formed as a precipitate. Black dots correspond to metal ion containing particles of dendrimers. The sample contained aggregates of dendrimers with size from 5 to 90 nm. EDAX analysis showed that both Pd and Cu were present in the aggregates, and metal mapping indicated that both ele-
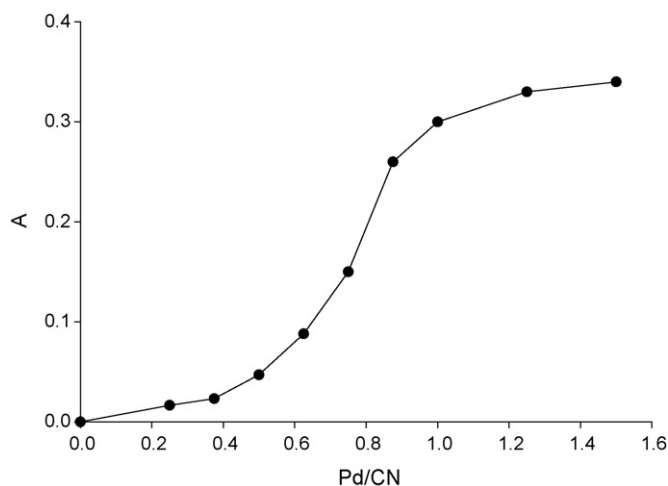

Fig. 4. Change of absorbance (620 nm) of DAB dendrimer ((DAB)CN$_{16}$) solution with the increase of Pd/CN-group ratio(ethanol–water = 4/1, [DAB(CN)$_{16}$] = 11.2 μmol/l, [PdSO$_4$] = 30 μmol/l, [CuSO$_4$] = 90 μmol/l).

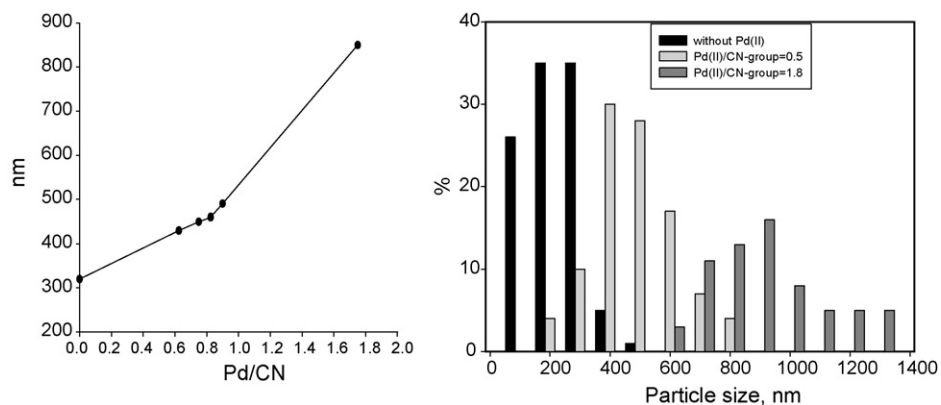**Fig. 5.** Particle average size (a) and particle size distribution (b) (ethanol–water = 4/1, [DAB(CN)$_{16}$] = 11.2 μmol/l, [PdSO$_4$] = 30 μmol/l, and [CuSO$_4$] = 90 μmol/l).

ments were reasonably evenly distributed throughout the material. The size of metal ion containing particles corresponds to size of DAB(CN)$_{16}$ dendrimers (1.6–2.0 Å) (Fig. 6). Results indicate that in ethanol–water solution the Pd/Cu/dendrimer complex formation and aggregation processes were progressed.

The complexes of dendrimers with Pd(II) and Cu(II) in solid state were studied by FTIR. XPS and EPR spectroscopy. IR spectra of the dendrimer complex ((DAB)CN$_{16}$, [Pd]/[CN$^-$] = 8) revealed only the band of adsorbtion corresponding to uncoordinated palladium ion. Increase of palladium concentration resulted in the occurrence
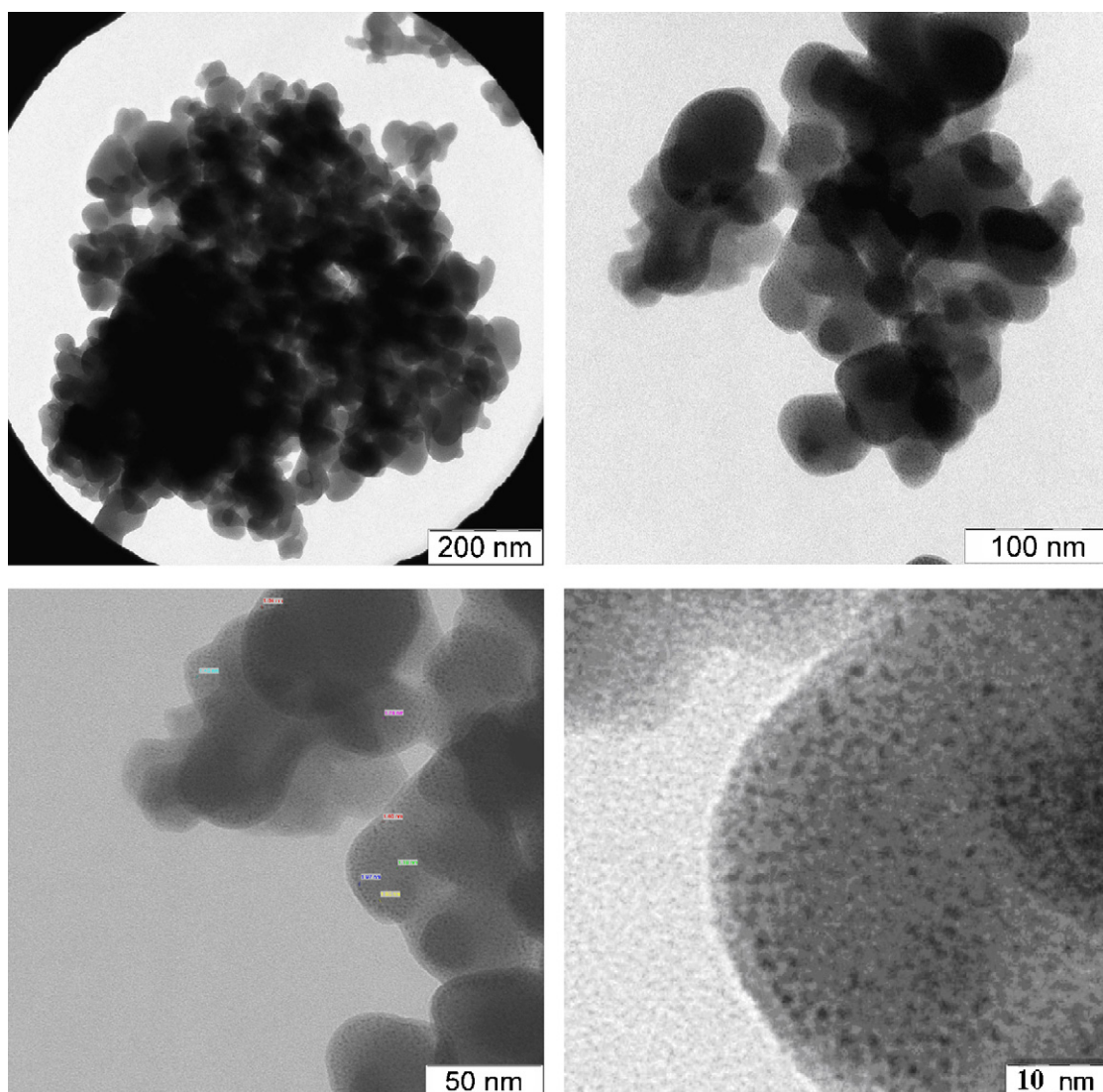

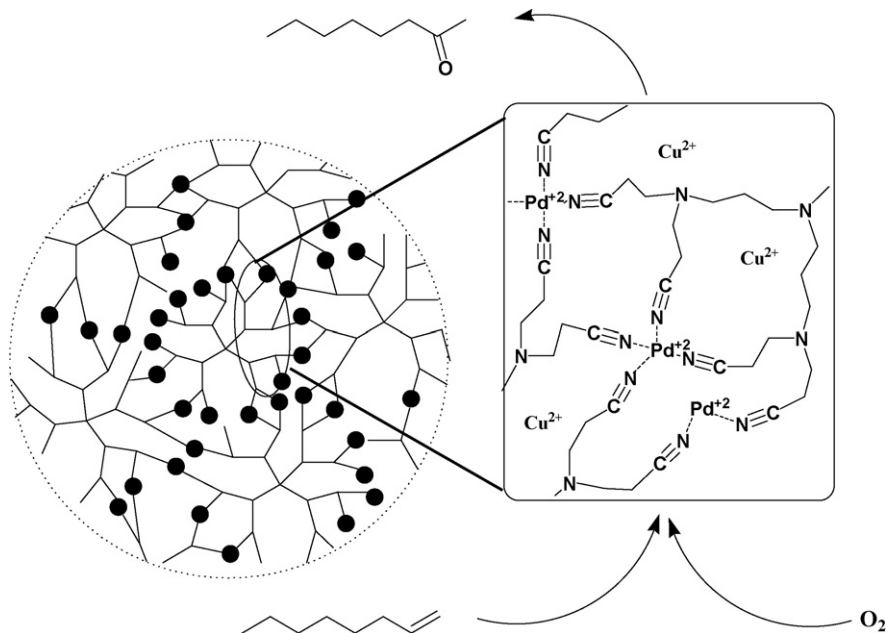**Fig. 6.** TEM images of dendrimer complex samples DAB(CN)$_{16}$/Pd/Cu.

Fig. 7. Schematic representation of Wacker-oxidation by dendrimer complexes based on PPI dendrimers.

of broad diffuse band at 2255–2306 cm^{-1}. Thus, we can assume that in monometallic ion complexes of copper interact with dendrimer branches at first, and only after that they could be bound by peripheral nitrile residues. As for bimetallic complexes containing both copper and palladium, even at low copper content, along with the absorption band of an unbound nitrile group, a new peak at 2304–2312 cm^{-1} emerges, which characterizes a nitrile group coordinated to palladium. The considerable intensity of absorption band at 2306 cm^{-1} corresponding to bound palladium ion was observed if there was sufficient quantity of copper ions. The intensity of the mentioned signal tended to increase with the growth of the ratio Cu(II)/Pd(II) The band which could be assigned to copper ion bound with nitrile group (2262–2265 cm^{-1}) appeared only when ratio Cu/dendrimer reached 16. Probably, with an increase in the concentration of copper(II) ions, which has a high affinity for amino groups, copper ions displace partly palladium from inner amino complexes and palladium coordinates with nitrile groups.

Table 3
Results of experiments on Waker-oxidation of 3-heptene, cyclohexene, propylene- and allylbenzene[a].

Substrate	CN/Pd	Product	Product yield (%)
3-heptene	–[b]	2-Heptanone	13
		Isomeric ketones	28
	2	2-Heptanone	6
		Isomeric ketones	5
	8	2-Heptanone	2
		Isomeric ketones	0.2
Cyclohexene	–[b]	Cyclohexanone	35
	2	Cyclohexanone	7
Allylbenzene	–[b]	Propenylbenzene	35
		Methylbenzylketone	10
		Ethylphenylketone	50
	2	Propenylbenzene	74
		Methylbenzylketone	8
		Ethylphenylketone	<1

[a] Pd/CN/Cu/S = 1:2:10:200, 1 h, Pd = 7.3 mmol/l, water/EtOH/S = 0.8:0.2:0.2 by volume, T = 80 °C, $P(O_2)$ = 0.5 MPa. Ligand DAB(CN)$_{16}$.
[b] No ligand.

In order to obtain further insight into the binding nature of the complex, the XPS spectra were recorded in the powder form at room temperature. The EB(Cu 2p) level are at 933.0 and 936.4 eV for complex with Pd/Cu/terminal–CN ratio 1/1/2. It indicates that the copper is present as copper(II) and copper(I) ions correspondently. In Cu(II) compounds Cu 2p energy is 934.0–935.5 eV; for Cu(I) it is 932.1–933.2 eV [33–36]. The Pd 3d5/2 spectrum is spin split into three peaks at 335.0, 337.1 and 338.1 eV that correspond to Pd(0) and Pd(II) ions complexated by nitrile groups and chloride [33,37–39]. Under higher Cu(II) concentration (Pd/Cu/terminal - CN ratio 1/10/2) the XPS spectra changes. The Cu 2p binding energy is 935.0 eV. Line shape indicates that the copper is present as two type of copper(II) ions that can be assigned to aqua and amino complexes. Wide peak at 337.5 eV is attributed to Pd 3d5/2 EB in nitrile polymers accordance with [34].

In addition, the XPS data from the copper–palladium atomic ratio illustrates that the surface composition of this complex is essentially different from that of the bulk material. After using ion gun (Ar$^+$) ratio Cu to Pd increased from 2 to 3 and the EB of Pd 3d$_{5/2}$ is 339.3 eV. These results also indicate that in interior of dendrimer some chemical bonds were formed between Pd(II) ions and the amino groups. Strong coordinated nitrogen atoms in the palladium(II) coordination sphere shift the Pd 3d$_{5/2}$ binding energy to higher values. This has been reported for, e.g. [Pd(pyridine)$_2$Cl$_2$] (BE Pd 3d$_{5/2}$ 1/4 338.2 eV) [40], [Pd(H$_2$NC$_2$H$_4$NH$_2$)$_2$] (BE Pd 3d$_{5/2}$ 1/4 339.0 eV) [41] The EPR spectra also indicate formation amine-Cu(II) coordination bond under high excess of Cu(II). The g value decreases with Cu(II) content increase that showed the formation of copper–amine complexes with PPI [42–44]. So the FTIR, XPS and EPR results indicate that copper ions were incorporated in the interior of dendrimer while Pd ions bind in periphery as well as in the interior of dendrimer.

From the analysis of spectra light-scattering, microscopic and spectroscopic data it seems reasonable to suggest that the oxidation proceed on the surface of dendrimer molecules in the interior of dendrimer network aggregates that formed by interaction of Pd(II) ions and CN-groups of dendrimer molecules (Fig. 7). The steric congestion in the aggregates prevents the coordination alkenes with

inner double bonds on Pd(II) ions that lead to negative dendritic effect and higher selectivity on methylketone.

4. Conclusion

The bimetallic complexes of Pd(II) and Cu(II) with PPI dendrimers demonstrate huge activity in Wacker-oxidation of terminal olefins bond in alcohol–water solutions. This soluble catalyst can be recovered and recycled effectively. The dendrimer fragment changes the selectivity in methylketone formation because of negative dendritic effect for substrate containing inner double bounds. The results suggest that the effect possibly being attributed to specific complex structure and dendrimer network aggregates formation under reaction conditions.

Acknowledgements

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