Reactivity of metal-containing monomers

66.* Hydrogenation of nitrotoluene derivatives in the presence of polymer-immobilized Pd nanoparticles

G. I. Dzhardimalieva,[a]★ V. G. Dorokhov,[a] N. D. Golubeva,[a] S. I. Pomogailo,[a] A. M. Lyakhovich,[b] V. I. Savchenko,[a] and A. D. Pomogailo[a]

[a] *Institute of Problems of Chemical Physics, Russian Academy of Sciences,*
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (496) 522 3507. E-mail: dzhardim@icp.ac.ru
[b] *Physical Technical Institute, Ural Branch of the Russian Academy of Sciences,*
132 ul. Kirova, 426000 Izhevsk, Russian Federation.
Fax: +7 (341 2) 72 2529

A new approach to the synthesis of immobilized catalysts of the mixed type was developed: frontal polymerization of metal-containing monomers in the presence of a highly dispersed inorganic support. The synthesis of the acrylamide complex of Pd^{II} nitrate on the SiO_2 surface followed by polymerization and reduction results in the formation of a polymer-inorganic composite with inclusions of Pd nanoparticles stabilized by the polymer matrix on the support surface. The study of the catalytic properties in the hydrogenation of nitrotoluene derivatives showed that the polymer-immobilized Pd nanoparticles on the inorganic support are efficient catalysts for the reduction of the nitrocompounds.

Key words: palladium acrylamide complexes, frontal polymerization, palladium nanoparticles, polymer-immobilized catalysts, nitrotoluene derivatives, hydrogenation.

The catalytic hydrogenation of aromatic nitrocompounds in the liquid phase are widely used for the synthesis of the corresponding amino derivatives, which are intermediate products in industrial processes aimed at producing plastics, pharmaceutical products, *etc.* The hydrogenation of trinitrotoluene (TNT) has recently gained practical significance due to the problem of utilization of nitroaromatic explosives to form useful products (dyes, polyurethane compositions, oligomers in the production of aminoplastics, *etc.*). Platinum group metals exhibit the high and selective ability to catalyze the reduction of nitroaromatic compounds, and special attention is paid to the development of efficient and selective catalysts based on the palladium complexes and nanoparticles.[2—6]

The materials containing nanosized metal particles are being intensely studied in recent years due to their unique physicochemical properties.[7] These systems are of special interest for catalysis because of a large fraction of surface metal atoms in a nanosized particle and a possibility to control the catalytic properties by varying the size of nanoparticles.[8—10] The zero-valence complexes and Pd nanoparticles are widely known as efficient and selective catalysts of many organic reactions, for example, arylation of alkenes[11,12] and hydrogenation of dienes, olefins,[13] and unsaturated alcohols.[14] The main problem arising when these active metal nanoparticles are used is their tendency to form agglomerates. Therefore, they are usually immobilized on the surface of supports (metal oxides, zeolites, carbon, *etc.*) or stabilized by ligands, particularly, various types of polymers.[7] One of promising methods for the preparation of metal-polymeric nanocomposites is the polymer-mediated synthesis based on the thermal poly- and copolymerization of metal-containing monomers followed by the controlled thermolysis of the products formed, which makes it possible to combine in one stage the formation of a metal nanoparticle and stabilizing polymer shell *in situ*.[15,16] The purpose of this study is the preparation of polymer-immobilized Pd nanoparticles on the inorganic support surface by the frontal polymerization of the acrylamide complex of Pd^{II} nitrate. In this work, we characterized a new approach to the construction of these catalysts and estimation of their catalytic properties in the hydrogenation of di- and trinitrotoluene derivatives.

Experimental

Benzene and diethyl ether (reagent grade) were purified according to standard procedures. Methanol (reagent grade),

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$PdCl_2 \cdot 4H_2O$ (reagent grade), acrylamide (AAm) (99.0%, Fluka), and nitro-, 2,4-dinitro-, and trinitrotoluene (NT, DNT, and TNT, respectively) (reagent grade) were used without additional purification. Concentrated HNO_3 (ρ = 1.18 g cm^{-3}) was distilled under atmospheric pressure, and the main fraction was taken at b.p. 110 °C. Inorganic supports were silica gels 60 (220—240 mesh, Lancaster) pre-activated (calcination with evacuation at 450 °C) and carbon black (specific surface area S_{sp} = 850 m^2 g^{-1}) and Al_2O_3 (S_{sp} = 123 m^2 g^{-1}).

Synthesis of $Pd(NO_3)_2 \cdot 2H_2O$. Pd^{II} nitrate was synthesized by the reaction of freshly distilled concentrated HNO_3 and freshly precipitated palladium hydroxide (2.6 g, $1.84 \cdot 10^{-2}$ mol), which was obtained by the treatment of the Na_2PdCl_4 complex salt (5.5 g, $1.84 \cdot 10^{-2}$ mol) with sodium hydroxide. Found (%): H, 1.4; N, 12.4; Pd, 40.4. Calculated (%): H, 1.5; N, 10.5; Pd, 39.9. IR (KBr pellet), ν/cm^{-1}: 850, 1386 (NO_3), 1650. XPS, E/eV: Pd3d$_{5/2}$, 338.8; N1s, 407.2; O1s, 532.8.

Synthesis of $Pd(H_2C{=}CHCONH_2)_2(NO_3)_2$ (hereinafter, PdAAm). The synthesis of PdAAm was carried out by the modified procedure for the preparation of acrylamide complexes of transition metal nitrates.[17] Palladium(II) nitrate and AAm were mixed in a mole ratio of 1 : 5 in inert atmosphere and triturated to a pasty state. Then the mixture was washed with anhydrous ether and dried *in vacuo* to a constant weight. Found (%): C, 20.8; H, 3.5; N, 15.1; Pd, 29.4. Calculated (%): C, 19.4; H, 2.7; N, 15.0; Pd, 28.6. IR (KBr pellet), ν/cm^{-1}: 3190 (ν_sNH), 3428 (ν_{as}NH), 1665 (C=O), 1384 (NO_3).

Preparation of PdAAm on the inorganic support surface. The synthesis of PdAAm in the presence of an inorganic support (SiO_2, Al_2O_3, C) was carried out according to the above described procedure from the assumption that the Pd content in the catalyst of the mixed type, namely, polymer + SiO_2(Al_2O_3, C), is 5—10 wt.% g^{-1}. In a typical experiment, a mixture of calculated amounts of Pd^{II} nitrate, AAm, and SiO_2 were triturated in an agate mortar in the box with an inert atmosphere to the pasty state, washed with benzene and ether, and dried *in vacuo* for at least 12 h at 30 °C. Pd content (wt.%): 5.2 (PdAAm/SiO_2), 8.9 (PdAAm/Al_2O_3), 10.2 (PdAAm/C).

Preparation of Pd/C. Palladium of carbon was obtained by the impregnation of activated carbon (AG-3M trade mark, S_{sp} = = 500 m^2 g^{-1}) with an aqueous solution of $PdCl_2$ followed by the reduction with $NaBH_4$ at 40 °C and additional heating at 80 °C for 15 min. The prepared catalyst was filtered off and washed with distilled H_2O and dried for 3—5 h at 110 °C. The content of Pd was 5 wt.%.

Frontal polymerization of PdAAm and PdAAm/SiO_2 (Al_2O_3, C). The PdAAm or PdAAm/SiO_2 (Al_2O_3, C) samples for frontal polymerization were pressed as pellets with the diameter d = 0.5—0.8 cm, height h = 1.2—1.5 cm, and density ρ = = 1.45±0.02 g cm^{-3} and placed in a glass ampule. To initiate polymerization, the bottom region of the ampule with the sample was immersed by 0.2 cm into the bath with the heat carrier (Wood alloy) for 10—15 s. The reaction rate was estimated from the migration of the front of the colored zone in time. The powdered polymeric and hybrid nanocomposite products were washed with methanol and ether and then dried *in vacuo* at room temperature to a constant weight.

Catalytic hydrogenation of di- and trinitrotoluenes. Experiments on the hydrogenation of nitroaromatic compounds was carried out in a non-flow glass reactor (so-called duck-reactor) in methanol with the substrate concentration $(4.72—14.5) \cdot 10^{-3}$ mol L^{-1} under a constant atmospheric hydrogen pressure at 36 °C with vigorous stirring (300—400 rocking min^{-1}). Hydrogen was fed to the reactor from a calibrated receiver with the water-gate valve. Before the introduction of the substrate into the reactor, the solvent and catalyst were treated with hydrogen for 15 min directly in the reactor with stirring. The reaction rate was calculated from the kinetic dependences of the hydrogen consumption in time. The discrepancies in parallel entries did not exceed 5%.

X-ray photoelectron spectra (XPS) were recorded on an ES-2401 spectrometer with the magnesium anode. The power of the X-ray tube was 200 W, the pressure in the analyzer chamber was 10^{-6} Pa, and the energy of the analyzer was 50 eV. The spectrometer was calibrated by the Au4f$_{7/2}$ line with E = 84 eV. The bond energy (E_b) of the line of the C1s electrons in the alkyl group was accepted to be 285.0 eV. The accuracy of determination of the line position by the scale of bond energies was 0.1—0.2 eV. The mathematical processing of the spectra was performed according to the earlier described procedure.[18] Standard samples in the XPS analysis were $PdCl_2 \cdot 4H_2O$ (E_b(Pd3d$_{5/2}$) = 337.5 eV) and palladium black (E_b(Pd3d$_{5/2}$) = = 335.5 eV).

Intermediate compounds and reaction products of hydrogenation were identified by ^{1}H NMR in acetone-d$_6$ on a Bruker AC-200P spectrometer (200 MHz). The XPS analysis of the powders was carried out on a DRON UM-2 spectrometer using Cu-Kα radiation. The microscopic studies were carried out with a JEM-3010 transmission electron microscope.

The specific surface area of the inorganic supports and polymer-hybrid nanocomposites and the pore size distribution were determined from N_2 adsorption at 77 K by the static volumetric method on an AUTOSORB-1 instrument (Quantachrome, USA).

Results and Discussion

Synthesis of $Pd(H_2C{=}CHCONH_2)(NO_3)_2$. The acrylamide complex Pd^{II} nitrate was synthesized by the substitution of water of crystallization in the crystalline hydrate of metal nitrate for AAm molecules. The elemental analysis and XPS data for the synthesized complex are given in Table 1.

The IR spectroscopic data indicate that the metal atom is coordinated to the oxygen atoms of the carbonyl group

Table 1. Elemental analysis data and the relative content of elements according to the XPS data (Y) for the acrylamide complexes of Pd^{II} nitrate

Complex	Found / Calculated (wt.%)				Y(at.%)			
	C	H	N	Pd	C	O	N	Pd
$Pd(NO_3)_2$	—	1.4	12.4	40.4	—	68	21	10.5
		1.5	10.5	39.9				
PdAAm	20.8	3.5	15.1	29.4	52	27	19	2
	19.4	2.7	15.0	28.6				
PdAAm/SiO_2	—	—	—	5.2	16	57	6	0.7
PdAAm/C	—	—	—	10.2	83	14	2.8	0.2

of the AAm ligand. The ν(CO) vibration bands (1665 cm^{-1}) are shifted to the long-wavelength region, which was observed earlier when analyzing analogous transition metal complexes.[19] This coordination is confirmed by the line shift in the XPS spectra: C1s (E_b = 288.3 eV), N1s (E_b = 399.8 eV), and O1s (E_b = 531.6 eV) are shifted by 0.5, 0.7, and 0.5 eV, respectively. The spectra of the complexes also contain stretching vibration bands of the nitrate anion at 1384 cm^{-1} (ν(NO_3)). The presence of the low-intensity band with E_b = 337.2 eV in the $Pd3d_{5/2}$ spectrum and the increase in the intensity of the line with E_b = 285.7 eV are related, possibly, to the additional π-coordination of the metal ion with the double bond of the ligand. Such examples are non-infrequent for the Pd alkene complexes.[20]. The atomic ratios Pd : N and O : N are 0.11 and 1.4, respectively (see Table 1). The line in the N1s spectrum with E_b = 407.2 eV is 10% of the integral spectral intensity, correlating with the line intensity in the $Pd3d_{5/2}$ spectrum with E_b = 338.8 eV (Fig. 1) and indicating that the Pd atoms are shielded by the AAm groups.

Frontal polymerization of PdAAm in the absence and presence of the inorganic support. As shown earlier, the acrylamide complexes of metal nitrates in the condensed state can efficiently be polymerized in the frontal mode, *i.e.*, under the conditions when the monomer is converted to the polymer in the localized reaction zone and is propagated by layers over the whole volume.[20,21] The reaction occurs under mildest conditions known for processes of this type: at atmospheric pressure and thermal initiation without chemical initiators and activators. In the mode of stationary propagation of the heat wave, polymerization occurs in a narrow temperature interval. The heat evolved in the reaction zone is transmitted to the heating zone, where the substance is heated due to heat conductivity and the temperature increases from the initial value to the temperature at which the reaction starts, *i.e.*, the polymerization front is propagated. The heat wave is initiated upon the short-term (~15 s) introduction of thermal perturbation into the terminal part of the PdAAm monomer sample molded as a cylinder or of the system with the inorganic support. The appearance and propagation of the melt zone (phase transition of the first order) and the color change (the reaction rate was monitored by the migration of the color boundary) from light brown to dark brown and black were visually observed. The kinetic studies showed high activity in the frontal polymerization of the Pd^{II} acrylamide complex (w = 0.038 cm s^{-1}), for which the ignition temperature (80—100 °C) is much lower than that for the AAm complexes with Co^{II}, Ni^{II}, and other metal nitrates (170—180 °C).[20,21] At higher ignition temperatures (150—170 °C) the reaction mass is rejected from the glass tube, and the combustion mode, possibly associ-

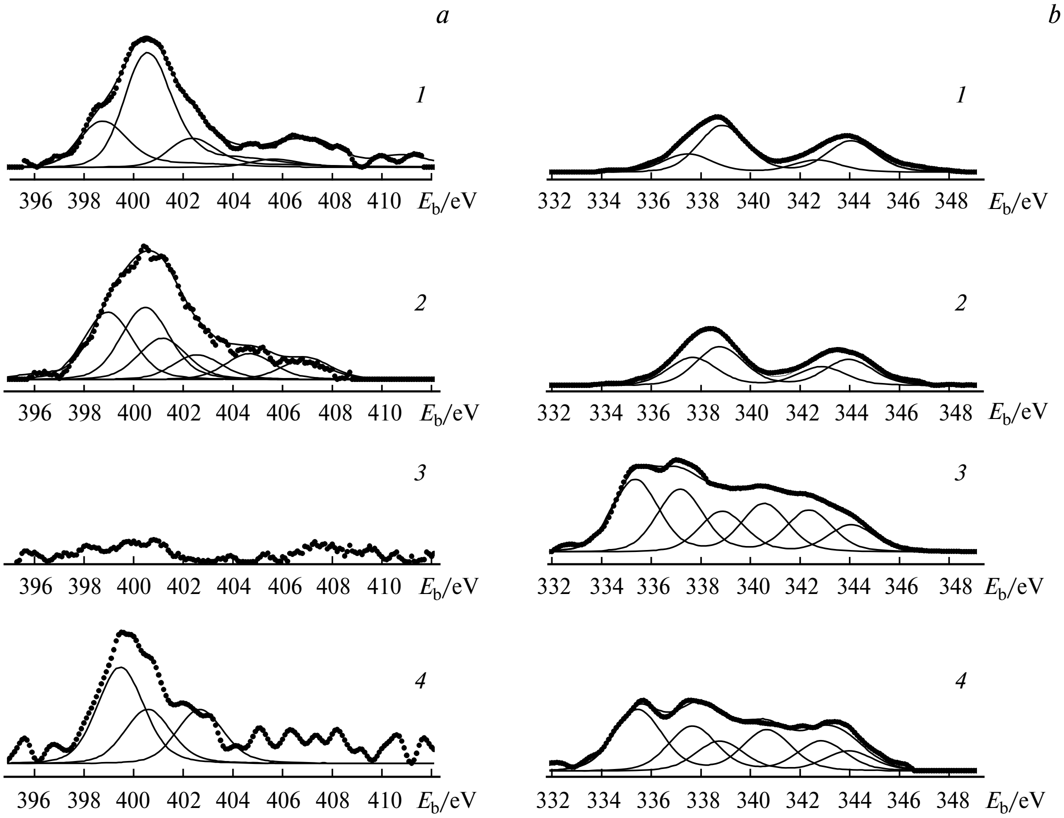
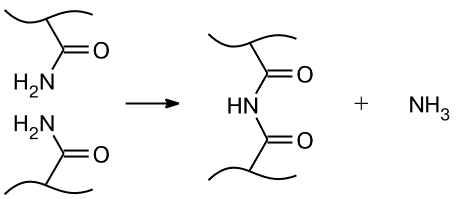


Fig. 1. X-ray photoelectron spectra (*a*, N1s; *b*, Pd3d) of the acrylamide complex of Pd^{II} nitrate for SiO_2 supporting: *1*, monomer; *2*, product after polymerization; *3* and *4*, after the hydrogenation of *p*-nitrotoluene (*3*) and 2,4-dinitrotoluene (*4*).

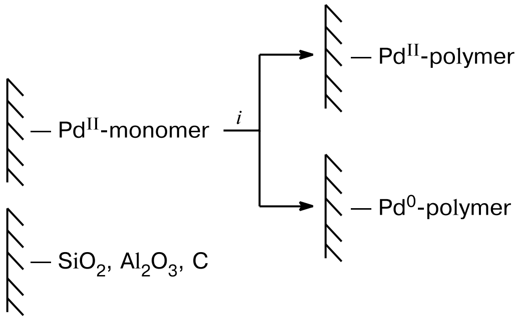
ated with the formation of highly dispersed pyrophoric palladium, is established. According to the XPS data, the main line (75%) in the $Pd3d_{5/2}$ spectrum of the polymerization products has E_b = 336.5 eV, which is higher than E_b in Pd^0 (<336.0 eV) and, most likely, indicates the formation of highly dispersed Pd^0 particles.[22] The increase in E_b of the main line in the N1s spectrum to 401.7 eV, most likely, is due to cyclization reactions of the polymer chain to form the imide groups[23] (Scheme 1).

Scheme 1



The earlier[19,24] developed approach to the synthesis of nanocomposite materials during frontal polymerization is interesting for the preparation of polymer-immobilized catalysts of the mixed (hybrid) type polymer—inorganic support. Indeed, the formation of the Pd^{II} acrylamide complex on the inorganic support surface followed by its polymerization (Scheme 2) results in the formation of a polymer-inorganic composite. According to the electron microscopic data, the latter included nanosized Pd particles (10—20 nm in diameter) stabilized by the polymer matrix (Fig. 2).

Scheme 2



i. Frontal polymerization.

As should be expected, the stabilizing effect of fillers on the autowave polymerization mode ($w = 0.024$ cm s^{-1}) is manifested as follows: the polymerization front gains properties of space—time stabilization.

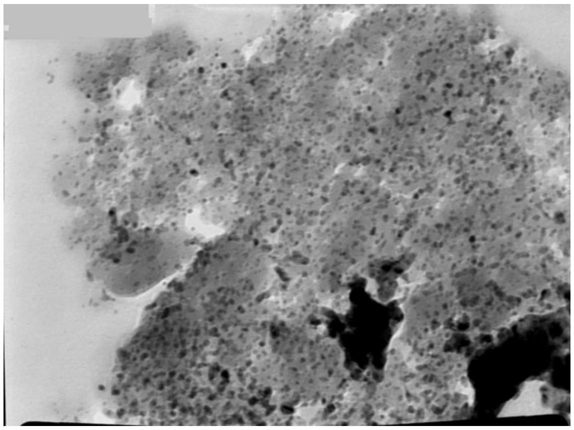


Fig. 2. Image of Pd^0-polymer AAm/SiO_2, ×125000.

The X-ray patterns of the obtained samples exhibit broad diffraction peaks corresponding to the phase of crystalline Pd^0 (Fig. 3). The diffuse diffraction maxima and line broadening indicate that the sample contains small particles. The nanocomposites prepared have the microporous structure with pores, whose size changes from several nanometers to 20 nm and they are uniformly distributed (Fig. 4). After the frontal polymerization of PdAAm on the surface of the mixed-type supports, the specific surface area decreases but remains higher than S_{sp} of the product of PdAAm polymerization obtained in the absence of a support (Table 2). Thus, the considered hybrid nanocomposites have well developed surface and porous structure providing the access of reactants to the catalyst sites and contributing to their high activity. However, the character of the bond of the polymer with the inorganic support requires further investigation.

Catalytic properties of $(PdAAm)_n/SiO_2$ in the hydrogenation of the nitrotoluene derivatives. The catalytic properties of the hybrid metal-polymer nanocomposite $(PdAAm)_n/SiO_2$ were studied in the hydrogenation reaction. The kinetic regularities of the hydrogenation of 2,4-DNT and 2,4,6-TNT in the presence of $(PdAAm)_n/SiO_2$ (curves *1*) and traditional catalyst Pd/C (curves *2*) are compared in Fig. 5. The reaction rate for the ~50% con-

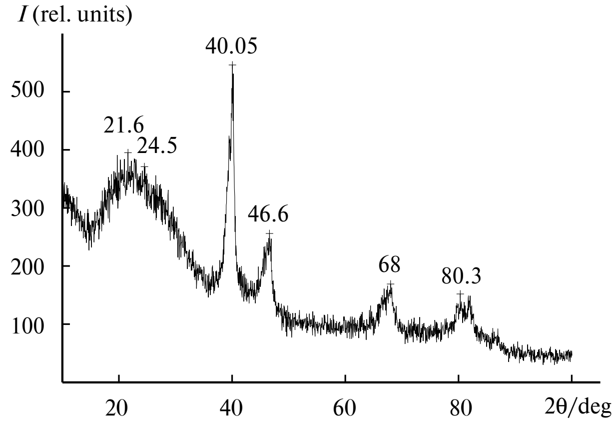


Fig. 3. XRD data for the $PdAAm/SiO_2$ nanocomposite obtained at 130 °C.

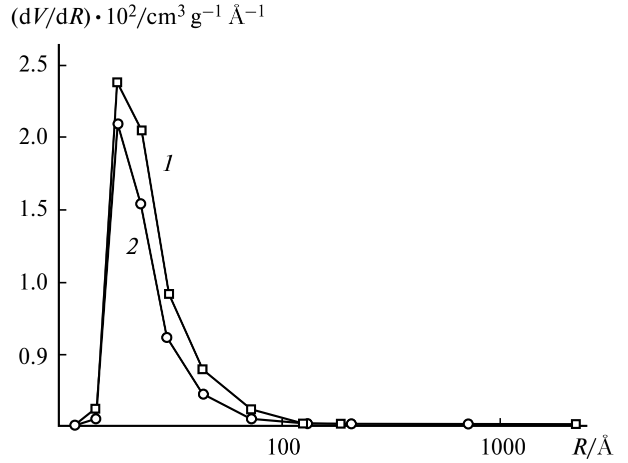


Fig. 4. Pore size distribution for the initial SiO_2 (*1*) and the PdAAm/SiO_2 nanocomposite (*2*).

version of 2,4-DNT or ~30% conversion of 2,4,6-TNT in the presence of the $(PdAAm)_n/SiO_2$ polymer decreases by almost an order of magnitude, whereas in the case of Pd/C the hydrogenation rate remains almost unchanged up to the complete conversion of 2,4-DNT. Since the main stages of hydrogenation of polynitrocompounds correspond to the stepwise reduction of the nitro groups to the corresponding polyamines,[6] the character of the kinetic curves indicates that the rate of formation of the monoamino derivatives in the presence of the polymer-immobilized catalyst is substantially higher than that for Pd/C. In addition, the hydrogenation rate of the second and third (for TNT) nitro groups is much lower than that in the case of the first nitro group.

We attempted to study the composition of the reaction mixtures by ^1H NMR in order to reveal the main routes of reduction in the analyzed systems. In fact, an analysis of the ^1H NMR spectrum shows that upon 2,4-DNT hydrogenation at the ~50% conversion the reaction mixture contains 4-amino-2-nitrotoluene (4A2NT, ^1H NMR, δ: 2.70 (s, 3 H, Me); 6.89 (dd, 1 H); 7.11 (d, 1 H); 7.23 (d, 1 H); 7.54 (d, 1 H, H(3)); 6.67 (br.s, 1 H, NH_2)), 2-hydroxyamino-4-nitrotoluene (2HA4NT, ^1H NMR, δ: 2.22 (s, 3 H, Me); 7.10 (d, 1 H, H(3)); 6.67 (br.s, 1 H, NH_2 or NHOH)), and 2-amino-4-nitrotoluene (^1H NMR, δ: 2.22 (s, 3 H, Me); 7.11 (d, 1 H, H(6)); 7.38 (dd, 1 H, H(5)); 7.54 (d, 1 H, H(3)); 6.67 (br.s, 1 H, NH_2 or NHOH)). Some unidentified peaks in the spectrum are assigned, probably, to the condensation and oxidation products

Table 2. Specific surface area, volume, and size of pores of the PdAAm-based polymer-hybrid nanocomposites

Sample	$S_{sp}/m^2 g^{-1}$	$V/cm^3 g^{-1}$	$\bar{r}$/Å
$(PdAAm)_n$	18.2	0.10	113.2
SiO_2	238.7	0.41	34.3
$(PdAAm)_n/SiO_2$	146.8	0.28	37.8
Al_2O_3	123.6	—	—
$(PdAAm)_n/Al_2O_3$	60.2	0.17	55.0

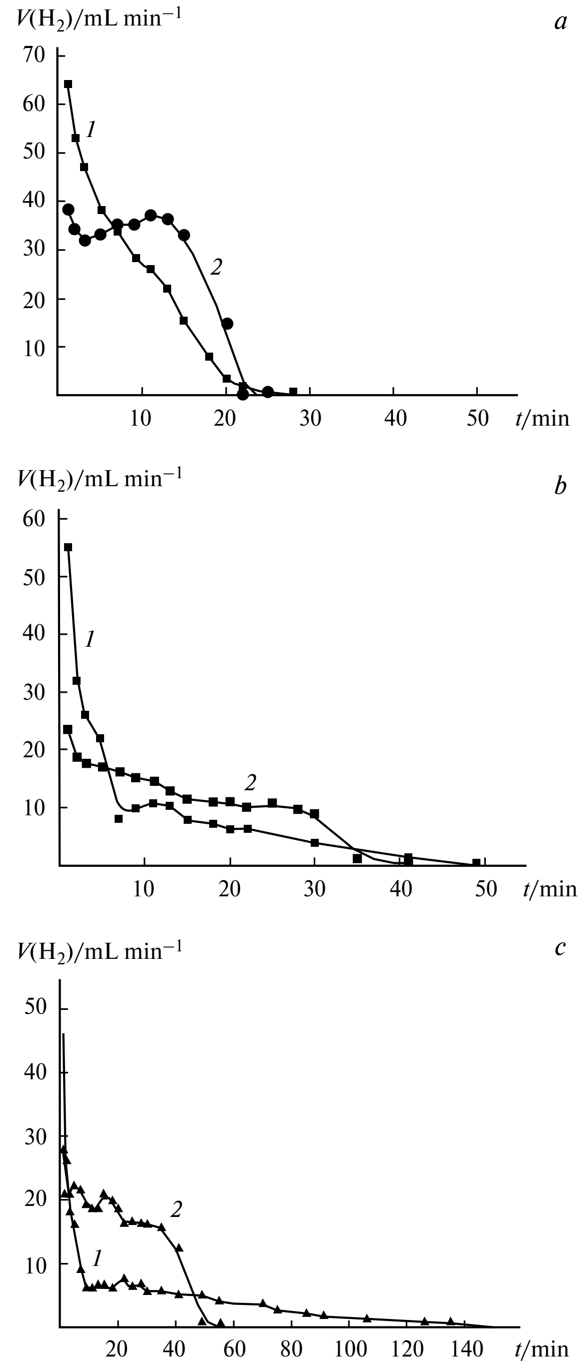
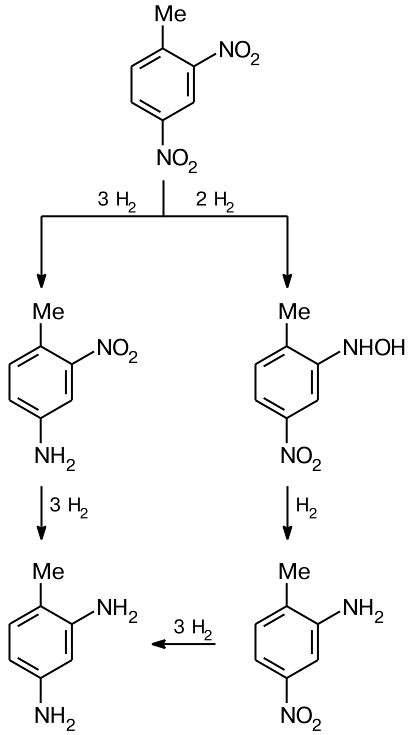


Fig. 5. Hydrogen absorption rate as a function of the duration of the hydrogenation of nitrotoluene (*a*), 2,4-dinitrotoluene (*b*), and 2,4,6-trinitrotoluene (*c*) in the presence of $(PdAAm)_n/SiO_2$ obtained by frontal polymerization (*1*) and Pd/C (*2*). Conditions: catalyst content $9.76 \cdot 10^{-5}$ (*a*), $8.58 \cdot 10^{-5}$ (*b*), and $1.1 \cdot 10^{-4}$ g-at. Pd g^{-1} (*c*); substrate content 7.29 (*a*), 2.36 (*b*), and 2.46 mmol (*c*); methanol (50 mL), temperature 36 °C, $P(H_2)$ = 1 atm.

formed during NMR sampling. These results can confirm the stepwise hydrogenation of 2,4-DNT in the presence of $(PdAAm)_n/SiO_2$. According to the composition of the reaction mixture, the main transformations in the reaction mixture can be presented by Scheme 3.

Scheme 3



The presence of 4A2NT among the intermediate compounds indicates parallel routes, which is consistent with the literature data.[6,25,26] The mechanism of the main transformations of the nitrotoluene derivatives remains unclear.[6] We hope that the use of the considered hybrid nanocomposite catalysts will contribute to the solution of this problem. On the one hand, steric factors, including those caused by the polymer matrix, can result in considerable differences in the coordination modes of various nitro groups of the substrate. Due to this, the adsorption of the second and third nitro groups on the catalyst surface is noticeably weaker than that of the first nitro group. On the other hand, contacts of this type[8] makes it possible to carry out methods of non-destructive control of the intermediates, *viz.*, intermediates aromatic nitroamines. The diverse character of their reactivity was demonstrated for many systems.[25—27]

For example, due to the immobilized form of the nanocomposite studied, we succeeded to isolate the catalytic intermediate after the hydrogenation of the first nitro group in 2,4-DNT, analyzed it by XPS, and compared the data with the $Pd3d_{5/2}$ spectrum of the catalyst isolated after the complete hydrogenation of 2,4-DNT (see Fig. 1). The analysis showed that the intermediate contains Pd^0 (335.5 eV) and Pd atoms with the partially positive charge, $Pd^{\delta+}$ (337.0 eV), which favor the formation of the coordination bond of the metal with the substrate molecules. This affects the activity of the catalyst and, probably, the preferred hydrogenation of one nitro group. The second stage the bond energy is shifted to the high-energy region (337.7 eV). The polymer matrix also undergoes substantial changes, which is indicated by the variations in the N1s spectrum.

Thus, the polymer-immobilized Pd nanoparticles on the inorganic support are efficient catalysts for the hydrogenation of the nitrotoluene derivatives. The further study will, in particular, reveal the size effects to establish the dependence of the reaction rate and selectivity on the size of palladium nanoparticles. This offers the way to carry out this catalytic reaction in the presence of nanocomposites based on other metals.

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