Research Article

Hybrid Polymer-Immobilized Nanosized Pd Catalysts for Hydrogenation Reaction Obtained via Frontal Polymerization

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A new approach to the synthesis of mixed-type immobilized catalysts by frontal polymerization of metal-containing monomer in the presence of highly dispersed mineral support has been developed. Synthesis of the acrylamide Pd(II) nitrate complex, Pd(CH$_2$=CHCONH)$_2$ (NO$_3$)$_2$ (PdAAm), on the SiO$_2$ (Al$_2$O$_3$, C) surface and its consequent frontal polymerization and reduction lead to the formation of organic-inorganic composites with polymer-stabilized Pd nanoparticles. The immobilized metal complexes and palladium nanoparticles were characterized by various physical and chemical methods. The synthesized hybrid nanocomposites are efficient and selective catalysts for hydrogenation of cyclohexene, alkene, and acetylenic alcohols, as well as di- and trinitrotoluene. Catalyst intermediates separated by nondestructive testing method have been described and changing in the palladium charge during the catalytic process has been identified.

1. Introduction

In recent years materials containing metal nanoparticles were intensively studied specially as catalysts due to their unique physical and chemical properties [1], high ratio of surface atoms to the total number of atoms in a particle, and possibility to vary catalytic properties by controlling the size of particles [2–4]. Zero-valent palladium complexes and nanoparticles are well known as efficient and selective catalysts for many organic reactions such as alkene arylation [5, 6], cross-coupling [7], hydrogenation of dienes, olefins [8, 9], and unsaturated alcohols [10]. Liquid phase catalytic hydrogenation of aromatic nitro compounds is widely used to produce corresponding amino derivatives, which are intermediates in the production of plastics, pharmaceuticals, and so forth. Hydrogenation of trinitrotoluene (TNT) in recent years becomes a reaction of practical importance for utilization of nitroaromatic explosives to useful chemicals (dyes, amino compounds, etc.) [11, 12]. Platinum metals catalyze selective reduction of nitroaromatic compounds. Particular attention is paid to developing effective and selective palladium catalysts based on complexes and nanoparticles [13–16]. Aggregation and agglomerometry of nanoparticles limits their use as catalysts, so they are fixed on supports (metal oxides, zeolites, carbon, etc.) or stabilized with different types of ligands, including polymers. One of the promising methods to obtain metal polymers is a polymer-mediated synthesis based on in situ poly- and copolymerization of metal-containing monomers with subsequent controlled thermolysis of the resulting products. This approach allows one to combine the formation of metal nanoparticles and stabilizing polymer shells in one stage [17, 18].

The aim of this paper is to demonstrate a new approach to the design of catalysts by the frontal polymerization of acrylamide Pd(II) nitrate complex on inorganic supports and to characterize the features of their catalytic properties in reactions of hydrogenation of various unsaturated compounds (cyclohexene, olefinic and acetylenic alcohols and selective reduction of di- and trinitrotoluene).
**Figure 1:** Photomontage of polymerization front propagation of metal nitrate acrylamide complex.

**Figure 2:** XPS spectra of (a) acrylamide complex monomer with Pd(NO\textsubscript{3})\textsubscript{2}, (b) PdAAm after polymerization, and (c) the same after cyclohexene hydrogenation.
2. Experimental

2.1. Reactants. Benzene and diethyl ether (chemically pure grade) were purified by standard methods. Methanol, PdCl₂·4H₂O, acrylamide (AAm) (Fluke), and toluene were used without additional purification. Allyl alcohol (99%, Reanal Budapest) was distilled at atmospheric pressure and the main fraction was collected at bp. 96 °C. 3,7,11,15-Tetramethylhexadecine-1-ol-3 (C₂₀ acetylenic alcohol) was purified by double distillation and the purity was checked chromatographically. Concentrated HNO₃ (p = 1.18 g/cm³) was distilled at atmospheric pressure; the main fraction was collected at bp. 110 °C. Silica gel 60 (220–240 mesh, specific area Sₚₑᶜₑ = 240 m²/g, Lancaster), carbon black (Sₚₑᶜₑ = 850 m²/g), and Al₂O₃ (Sₚₑᶜₑ = 123 m²/g) were used as inorganic supports. The supports were preactivated (calcination and evacuation at 450 °C) and cooled in an inert atmosphere.

2.2. Synthesis of Pd(NO₃)₂·2H₂O. Pd(II) nitrate was synthesized by the interaction of freshly distilled HNO₃ and freshly precipitated palladium hydroxide (2.6 g, 1.84·10⁻² mol) obtained by the treatment of Na₂PdCl₄ complex salt (5.5 g, 1.84·10⁻² mol) with sodium hydroxide. Found (%): N, 10.2; H, 1.4; Pd, 40.4. Calculated (%): N, 10.5; H, 1.5; Pd, 39.9. IR spectrum (tablets with KBr), ν/cm⁻¹: 850, 1386 (NO₃), 1650. XPS, eV: Pd3d₅/₂ = 338.8, N1s = 407.2, O1s = 532.8.

2.3. Synthesis of Pd(CH₂=CHCONH)₂(NO₃)₂ (PdAAm). PdAAm metal monomer was synthesized by a modified method for preparation of acrylamide complexes of transition metal nitrates [19]. Pd(II) nitrate and acrylamide were mixed in a molar ratio of 1:5 in an inert atmosphere and ground into paste-like consistency, then washed with dry ether and dried in vacuum to constant weight. Found (%): C, 20.1; N, 15.1; H, 3.5; Pd, 29.4. Calculated (%): C, 19.4; N, 15.0; H, 2.7; Pd, 28.6. IR spectrum (tablets with KBr), ν/cm⁻¹: 3190 (νₕNH), 3428 (νₕNH), 1665 (C=O), 1384 (NO₃).

2.4. Synthesis of PdAAm in the Presence of an Inorganic Support. PdAAm in the presence of SiO₂ or Al₂O₃ or C was synthesized by the method mentioned above. Calculated content of Pd is 5–10 wt.%/g in the mixed type catalyst (polymer + inorganic support). In a typical procedure a mixture of calculated amounts of Pd(II) nitrate, acrylamide, and SiO₂ (Al₂O₃, or C) were ground into paste-like state in an agate mortar inside a box with an inert atmosphere, then washed with benzene, ether, and dried in a vacuum during 12 hours at 30 °C. The content of Pd (wt%) was 5.2 (PdAAm/SiO₂), 8.9 (PdAAm/Al₂O₃), and 10.2 (PdAAm/C).

2.5. Preparation of Pd/C. Standard Pd/C catalyst (for comparison) was synthesized by impregnation of activated carbon with a calculated amount of aqueous solution of Na₂PdCl₄ prepared by boiling a mixture of PdCl₂, water, and concentrated HCl during 2 hours, then was washed and reduced by NaBH₄ at 40 °C and additionally heated for 15 minutes at 80 °C. The resulting catalyst was filtered and washed with distilled H₂O, then dried at 110 °C during 3–5 hour. The content of Pd was 5 wt.%.

2.6. Frontal Polymerization of PdAAm and PdAAm/SiO₂ (Al₂O₃, C). To carry out frontal polymerization (FP) the sample of prepared PdAAm or PdAAm/SiO₂ (Al₂O₃, C) was prepressed into tablets with 0.5–0.8 cm diameter, 1.2–1.5 cm height, and density of 1.45±0.02 g/cm³ and placed into a glass ampoule. To initiate polymerization, the bottom part of the ampoule with the sample was immersed at a depth of 0.2 cm
### Table 3: Specific surface areas and pore sizes for polymer hybrid nanocomposites based on PdAAm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{sp}$, m$^2$/g</th>
<th>Pore volume, cm$^3$/g</th>
<th>Average pore radius, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly-PdAAm</td>
<td>18.2</td>
<td>0.10</td>
<td>113.2</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>238.7</td>
<td>0.41</td>
<td>34.3</td>
</tr>
<tr>
<td>poly-PdAAm/SiO$_2$</td>
<td>146.8</td>
<td>0.28</td>
<td>37.8</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>123.6</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>poly-PdAAm/Al$_2$O$_3$</td>
<td>60.2</td>
<td>0.17</td>
<td>55.0</td>
</tr>
</tbody>
</table>

### Table 4: Initial rates of cyclohexene hydrogenation ($w_0$) in the presence of hybrid polymer-immobilized Pd nanoparticles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation conditions</th>
<th>$w_0$, (mol H$_2$) (mol Pd)$^{-1}$ min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cycle 1</td>
<td>cycle 2</td>
</tr>
<tr>
<td>Poly-PdAAm/SiO$_2$</td>
<td>FP</td>
<td>76.5</td>
</tr>
<tr>
<td></td>
<td>FP, 100°C</td>
<td>36.0</td>
</tr>
<tr>
<td></td>
<td>FP, 120°C</td>
<td>44.5</td>
</tr>
<tr>
<td></td>
<td>FP, 150°C</td>
<td>3.5</td>
</tr>
<tr>
<td>Poly-PdAAm/Al$_2$O$_3$</td>
<td>FP</td>
<td>111.2</td>
</tr>
<tr>
<td></td>
<td>FP, 100°C</td>
<td>37.8</td>
</tr>
<tr>
<td></td>
<td>FP, 140°C</td>
<td>8.2</td>
</tr>
<tr>
<td>Poly-PdAAm/C</td>
<td>FP</td>
<td>37.8</td>
</tr>
<tr>
<td>Pd/C</td>
<td>FP</td>
<td>38.7</td>
</tr>
</tbody>
</table>

In a bath with a heat carrier (Wood's alloy) at 80–100°C for 10–15 seconds (Figure 1). The rate of reaction was evaluated from the migration of the front of a colored zone. Powdered polymer and hybrid nanocomposite were washed with methanol and ether, and dried in vacuum at room temperature to constant weight.

2.7. Hydrogenation Reactions. Hydrogenation reaction was carried out in a non-flow glass reactor under a constant atmospheric hydrogen pressure with vigorous stirring (300–400 rocking min$^{-1}$). Hydrogen was fed into the reactor from a calibrated receiver with a water lock. The reaction rate was calculated graphically from the initial part of kinetic curves of hydrogen consumption over time. Discrepancies in parallel experiments did not exceed 5%.

2.7.1. Cyclohexene Hydrogenation. The reaction was carried out at 20°C in isopropyl alcohol with substrate concentration of $(4.72–14.5) \times 10^{-3}$ mol/L. Catalyst amount was 0.06–0.12 g. Before introducing cyclohexene, the catalyst was treated with hydrogen for 15 min immediately in the reactor with stirring.

2.7.2. Hydrogenation of Allylic and Acetylenic Alcohols. The reactions were carried out at 40°C in ethanol (20 mL) with substrate concentration of $2.2 \times 10^{-3}$ mol/L. Catalyst amount was 0.03 g. Catalyst was pretreated by hydrogen for 30 minutes before injection of the substrate into reactor. Catalyst selectivity was evaluated as the mass fraction of the desired product in the total content of the reaction products.

2.7.3. Hydrogenation of Di- and Trinitrotoluene. The reaction was carried out in methanol with concentration of substrate of $(4.72–14.5) \times 10^{-3}$ mol/L at 36°C. Catalyst was pretreated by hydrogen for 15 minutes before injection of the substrate into reactor.

2.8. Characterization. The specific surface area ($S_{spec}$) and pore size of inorganic supports and polymer hybrid nanocomposites were determined by static volumetric method for N$_2$ adsorption at 77 K (AUTOSORB-1, Quantachrome, USA).

Analysis of the products of allyl alcohol hydrogenation and isomerization was carried out on “Crystal-2000M” chromatograph (Russia) with a flame ionization detector under isothermal conditions. The universal capillary column for organic compounds of 50 m length and 0.20 mm inner diameter was used. Helium was carrier gas.

Elemental analysis was carried out by organic microanalysis and flameless atomic absorption method using spectrometer AAS3, Germany.

XPS analysis of the powders was studied by X-ray diffraction “DRON UM-2” and “Philips PW 1050” using Cu-K$\alpha$ radiation ($\lambda = 1, 54184$ Å).

IR absorption spectra were recorded on a Specord 75 IR using the KBr disc method.

Electron microscopic studies were performed using JEM-3010 transmission electron microscope with an accelerating voltage of 100 kV. The samples were prepared by dispersing the diluted catalyst suspension in heptane onto copper grids.

XPS spectra were recorded on an ES-2401 spectrometer with a magnesium anode. X-ray tube power was 200 watts; a vacuum in the analyzer chamber was $10^{-6}$ Pa. The analyzer energy was 50 eV. The Au4f7/2 line (84 eV) was used to calibrate the spectrometer. The binding energy of C1s line of
Table 5: Initial rates and selectivities of the hydrogenation of allyl alcohol and 3,7,11,15-tetramethylhexadec-1-yn-3-ol on Pd hybrid polymer-immobilized catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Allyl alcohol $w \times 10^5$, mol L$^{-1}$ s$^{-1}$</th>
<th>selectivity (%)</th>
<th>C20 acetylene alcohol $w \times 10^5$, mol L$^{-1}$ s$^{-1}$ (after 10 min)</th>
<th>selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-PdAAm/Al$_2$O$_3$</td>
<td>4.98</td>
<td>97.2</td>
<td>1.4</td>
<td>70</td>
</tr>
<tr>
<td>Poly-PdAAm/SiO$_2$</td>
<td>56.7</td>
<td>95.6</td>
<td>2.8</td>
<td>49.9</td>
</tr>
</tbody>
</table>

Note: reaction conditions: alcohol concentration: 0.225 mol/L; catalyst sample weight: 0.03 g (1.41 $\times 10^{-5}$ g-at. of Pd/g); temperature: 40°C; pressure: 0.1 MPa; solvent: 20 mL of ethanol.

3. Results and Discussion

3.1. Synthesis of Pd(CH$_2$=CHCONH$_2$)(NO$_3$)$_2$ (PdAAm).

Acrylamide complex of Pd(II) nitrate was synthesized by substitution of crystallization water in crystalline hydrate of metal nitrate by acrylamide molecules (AAm). Elemental analysis and some spectral characteristics of the complex are given in Table 1.

The infrared spectroscopy data indicated coordination of metal atom with the oxygen atoms of carbonyl group of electrons in alkyl group was taken as 285.0 eV. The accuracy of identification of the line positions in the scale of binding energies was 0.1–0.2 eV. Standard samples in the XPS analysis were PdCl$_2$·4H$_2$O ($E_{\text{bond}}$(Pd3d$_{5/2}$) = 337.5 eV) and palladium black ($E_{\text{bond}}$(Pd3d$_{5/2}$) = 335.5 eV).

Intermediates, products of the hydrogenation reaction, and catalysts were identified in nondestructive testing by NMR $^1$H in acetone-$d_6$ using NMR spectrometer Bruker AC-200P (1H 200 MRC), as well as X-ray diffraction of powders and by XPS method.
AAm-ligand. Bands νCO (1665 cm\(^{-1}\)) are shifted into long-wave region as it was shown previously for similar complexes of transition metals [20]. The valence vibration bands of anion-nitrate at 1384 cm\(^{-1}\) (νNO\(_3\)) were also observed in the spectra of the complexes. In XPS spectra the shifts of lines 8 C1s (bond energy \(E_{\text{bond}} = 288.3\) eV), N1s (\(E_{\text{bond}} = 399.8\) eV) and O1s (\(E_{\text{bond}} = 531.6\) eV) by 0.5, 0.7, and 0.5 eV to high-energy region correspondingly were observed. The appearance of a low-intensity line with \(E_{\text{bond}} = 337.2\) eV in Pd3d\textsubscript{5/2} spectrum and the increase in the intensity of the line with \(E_{\text{bond}} = 285.7\) eV could be explained by additional
π-coordination of metal atom with the double bond of the ligand. Such examples for Pd-alkene complexes are known [21]. For the surface layer the ratio of Pd/N atoms is equal to 0.11 and O/N = 1.4 (Table 1).

The line in the N1s spectrum with $E_{\text{bond}} = 407.2 \text{ eV}$ is 10% of the integral spectral intensity, correlating with the line intensity in the Pd3d5/2 spectrum with $E_{\text{bond}} = 338.8 \text{ eV}$ and indicating that the Pd atoms are shielded by the AAm groups. The results of elemental analysis and study by physical and chemical methods confirm the formation of a palladium complex of the following composition: $\text{Pd(CH}_2=\text{CHCONH}_2)_2(\text{NO}_3)_2(\text{PdAAm})$.

3.2. PdAAm Frontal Polymerization with and without Inorganic Support. As shown earlier [20, 22], the acrylamide complexes of metal nitrates in the condensed state can efficiently be polymerized in the frontal mode, that is, 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. 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, that is, 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 of the system with the inorganic support. The appearance and propagation of the melt zone (phase transition of the first order) (Figure 1) 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. Kinetic studies showed the high rate of frontal polymerization of Pd(II) acrylamide complex ($w = 0.038 \text{ cm/s}$) for which the "ignition" temperature (80–100°C) was much lower than for AAM complexes with Co(II), Ni(II) nitrates and other metal ions (170–180°C) [20].

At higher ignition temperatures (150–170°C), we observed the release of the reaction mass from a glass tube and the combustion mode (!), that probably were caused by the formation of fine particles of pyrophoric palladium. According to XPS data, the basic line in Pd3d5/2-spectrum of polymerization product (Figure 2) is characterized by $E_{\text{bond}} = 336.5 \text{ eV}$, which is higher than $E_{\text{bond}}$ in Pd0 (336.0 eV) because of formation of fine particles of Pd0 and $\text{Pd}^{2+}$ [9, 23].

Increase in $E_{\text{bond}}$ of basic line in the N1s spectrum from 399.8 to 401.7 eV is probably caused by the reaction of cyclization of polymer chains and formation of imide groups [24] (see Scheme 1).

Previously developed approach to obtaining nanocomposite materials by the frontal polymerization [25] is of interest for the design of polymer-immobilized catalysts of mixed (hybrid) type: metal nanoparticles-polymer-inorganic support. Indeed, synthesis of Pd(II) acrylamide complex on the surface of the mineral support and its subsequent polymerization lead to formation of polymer-inorganic composite (e.g., poly-PdAAm/SiO2) (see Scheme 2).

According to electron microscopy data, the resulting composite includes Pd nanoparticles with a diameter of 10–20 nm, stabilized with a polymer matrix (Figure 3).
As expected, the stabilizing effect of the fillers-SiO$_2$ (Al$_2$O$_3$, C) on autowave mode of polymerization ($w = 0.024$ cm/s) shows that the polymerization front becomes space-time stable: thermophysical properties of the system are such that frontal mode is carried out with a high (75 wt.%) degree of filling. Wide diffraction peaks at $2\Theta = 36–85$ degrees corresponding to crystal Pd$^0$ were registered on X-ray diagram for synthesized composites (Figure 4).

The diffuse diffraction maxima and line broadening indicate that the sample contains small particles (Table 2). The prepared nanocomposites are characterized by a microporous structure with pore sizes from several nm to 20 nm and uniform size distribution (Figure 5). It should be noted that the specific surface of the mixed-type supports decreases after PdAAm frontal polymerization on their surface, although its value is higher than $S_{sp}$ of PdAAm polymerization product prepared without inorganic support (Table 3). Thus, the synthesized hybrid nanocomposites have sufficiently developed surface and a porous structure that provides access of reactants to active sites of the catalyst and their high activity in the studied catalytic reactions.

3.3. Catalytic Properties of PdAAm/SiO$_2$ (Al$_2$O$_3$, C) in the Reaction of Cyclohexene Hydrogenation. The analyzed systems showed sufficiently high activity in the model reaction of cyclohexene hydrogenation. Thus, under comparable conditions, the initial reaction rate in the presence of poly-PdAAm/Al$_2$O$_3$ catalyst nearly 2-times higher than that for the standard Pd/C (Table 4, Figure 6).

It is important that the studied nanocomposites keep high catalytic activity in the recycle, and the immobilized form is easily separated from the reaction medium and can be reused. Even more importantly, it provides an opportunity to explore catalytic intermediates by various physical and chemical methods of nondestructive testing. In some cases, there is increased activity with repeated use, so-called “developing”
3.4. Catalytic Properties of Poly-PdAAm/SiO₂ (Al₂O₃) Nanocomposites in the Hydrogenation of Allyl Alcohol. It is known that hydrogenation of allyl alcohol is often accompanied by undesirable side reaction of substrate isomerization, which sometimes may even prevail over the main process. Therefore minimization of isomerization is essential for increasing the yield of the target hydrogenation products. For example, catalysts based on Pd nanoparticles encapsulated in polyelectrolyte multilayers [27] or dendrimers [28] were used for this purpose.

Conditions for formation of Pd nanoparticles also effect the catalytic properties of the composites, for example, different modes of frontal polymerization in an inert environment or afterheat treatment at 100–150°C in a reduction atmosphere (H₂) (Figure 7). Thus, the rate of hydrogenation on the nanocomposites obtained by this method decreases with increasing temperature of their reduction.

Similar effect is observed for catalysts with both SiO₂ and Al₂O₃ (Table 4). Probable reason for the decreasing reaction rate is agglomeration of Pd particles at higher temperatures of treatment in the process of nanocomposite preparation.

After hydrogenation the basic part of Pd (90%) in poly-PdAAm is in zero valence state (the line of Pd₃d₅/₂ spectrum with $E_{\text{bond}} = 335.9$ eV) (see Figure 2) and its shielding by the polymer matrix is decreased, as it is evidenced by increasing Pd content in the surface layer (from 1.5 at.% in the initial polymer complex to 4.3 at.%). Polymer matrix is also changed, which is confirmed by the broadening of N1s spectrum.

Thus, the hybrid polymer-immobilized Pd nanoparticles show high stable activity in the hydrogenation of cyclohexene. The catalysts preserve their activity in repeated cycles. The catalytic properties depend on the conditions of nanocomposite synthesis, which is probably associated with the formation of Pd nanoparticles of different sizes.

of the catalysts, which is typical for many of immobilized systems. The phenomenon recently was demonstrated for polymer rhodium clusters [26].

Figure 12: X-ray photoelectron spectra of poly-PdAAm/SiO₂: after the hydrogenation of p-nitrotoluene (a) and 2,4-dinitrotoluene (b).

\[ \text{H}_2\text{N} \quad \text{N} \quad \text{H} \quad \text{O} \]
\[ \text{H}_2\text{N} \quad - \quad \text{O} \quad + \quad \text{NH}_3 \]

\textbf{Scheme 1}

\[ \text{Pd}^{II}\text{-monomer} \quad \text{Pd}^{II}\text{-polymer} \]
\[ \text{SiO}_2, \text{Al}_2\text{O}_3, \text{C} \]

\textbf{Scheme 2}

i. Frontal polymerization
The synthesized Poly-PdAAm/SiO$_2$(Al$_2$O$_3$) catalysts show different activity and high selectivity in the hydrogenation of allyl alcohol (Table 5). The main product of allyl alcohol hydrogenation is propanol-1, propionaldehyde—a product of the allyl alcohol isomerization is identified in small amount (up to 2% on poly-PdAAm/Al$_2$O$_3$, 5%—in the presence of poly-PdAAm/SiO$_2$). No other products were detected. Higher reaction rate over PdAAm/SiO$_2$ catalyst is apparently explained by more developed surface area of the catalyst and the specific adsorption of the substrate molecule on the surface of catalysts (see Table 3).

The stability of the catalysts was evaluated in hydrogenation of successive portions of allyl alcohol on the same catalyst loading (Figure 8). Poly-PdAAm/SiO$_2$ catalyst shows high activity in repeated cycles; the rate has decreased only after 11 reaction runs. Interrupting the process for several hours (portions 7 and 10) apparently leads to the increasing of the reaction rate due to equalization of the concentrations of all process components (solvent, products, and substrate) near the active centers.

3.5. Catalytic Properties of PdAAm/SiO$_2$ (Al$_2$O$_3$) Nanocomposites in the Hydrogenation of 3,7,11,15-Tetramethylhexadecine-1-ol-3 (C20). A steric effect on the selectivity of the catalytic reaction is conveniently demonstrated by hydrogenation of hindered long chain acetylene alcohol. While the overall trend in activity and selectivity of the studied catalysts are similar, the rate of hydrogenation to compare with one overall trend in activity and selectivity of the studied catalysts generates from hindered long chain acetylene alcohol. While the catalytic reaction is conveniently demonstrated by hydrogenation of hindered long chain acetylene alcohol. The main product of allyl alcohol hydrogenation is propanol-1, propionaldehyde—a product of the allyl alcohol isomerization is identified in small amount (up to 2% on poly-PdAAm/Al$_2$O$_3$, 5%—in the presence of poly-PdAAm/SiO$_2$). No other products were detected. Higher reaction rate over PdAAm/SiO$_2$ catalyst is apparently explained by more developed surface area of the catalyst and the specific adsorption of the substrate molecule on the surface of catalysts (see Table 3).

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According to chromatographic analysis (Figure 10) the triple bond of C$_{20}$ acetylene alcohol is reduced with high rate to a double one. The reaction rate reaches a maximum at the 10th minute (see Figure 9) and then drastically decreases to (0.05–0.1) $\times$ 10$^{-5}$ mol/L. During this time, 100% conversion of acetylene alcohol to reaction products is achieved on poly-PdAAm/SiO$_2$ catalyst. However, the process is not selective. Hydrogenation of the triple bond of acetylene alcohol occurs simultaneously with the reduction of forming double bond: both saturated 3,7,11,15-tetramethylhexadecane-1-ol-3 and olefinic alcohol are detected in the reaction products.

Somewhat different results were obtained for the hydrogenation of C$_{20}$ acetylenic alcohol in the presence of the poly-PdAAm/Al$_2$O$_3$. Initially, acetylene alcohol is mainly converted to olefinic one. And only after 20 minutes when the content of the initial substrate in the reaction mixture is about 10%, 3,7,11,15-tetramethylhexadecene-1-ol-3 formed is hydrogenated to aliphatic alcohol. Selectivity for olefin alcohol is 70% (Table 5). Comparison of the data of chromatographic analysis and the reaction rates makes it possible to conclude that acetylene alcohol with high rate is converted to alkenol, but the formation of a saturated alcohol is 7–10-times slower ($w = 0.1 \times 10^{-5}$ mol/L). Currently, the mechanism of selective action of hybrid polymer-immobilized catalysts obtained is not completely clear and requires further study, as well as optimization of the catalytic process.

3.6. Catalytic Properties of PdAAm/SiO$_2$ in Hydrogenation of Nitro Derivatives of Toluene. Kinetics of hydrogenation of 2,4-dinitro-(DNT) and 2,4,6-trinitrotoluene (TNT) on poly-PdAAm/SiO$_2$ (curves 1) and usual Pd/C catalyst (curves 2) are compared in Figure 11. The reaction rates of 2,4-DNT and 2,4,6-TNT hydrogenation on poly-PdAAm/SiO$_2$ decrease by nearly ten times at conversion of 1/2 and 1/3, respectively. In case of Pd/C the rate of hydrogenation remains practically unchanged till complete conversion of 2,4-DNT. It is known that nitro groups of polynitrocompounds can be hydrogenated stepwise to the corresponding polyamines [29]. The kinetic curves indicate that the rate of formation of monoradical derivatives in the presence of the polymer-immobilized catalyst is significantly higher than for Pd/C. In addition, hydrogenation of the second and third (for TNT) nitro groups is carried out at lower rates than the first one.

To identify the main routes of nitro groups’ reduction in the studied processes, we have analyzed the composition of the reaction mixtures by $^1$H NMR. Indeed, the $^1$H NMR spectrum of reaction mixture recorded after $\sim$1/2 conversion of 2,4-dinitrotoluene indicates the presence of 4-amino-2-nitrotoluene (4A2NT) (4A2NT) ($^1$H NMR, δ: 2.70 (s, 3H, CH$_3$) (s-singlet, d-doublet, dd-doublet of doublets, bd-broadened); 6.89 (dd, 1H, H(1H); 7.11 (d, 1H); 7.23 (d, 1H); 7.54 (d, 1H, H(3)); 6.67, s, bd, 1H, NH$_2$), 2-(hydroxy)amino-4-nitrotoluene (2HA4NT) ($^1$H NMR, δ: 2.19 (s, 3H, CH$_3$); 7.10 (d, 1H, H(3)); 6.67 (s, bd, 1H, NH$_2$, or NHOH), 2-amino-4-nitrotoluene (2A4NT) ($^1$H NMR δ: 2.22 (s, 3H, CH$_3$); 7.11 (d, 1H, H(6)); 7.38 (dd, 1H, H(5)); 7.54 (d, 1H, H(3)); 6.67 (s, bd, 1H, NH$_2$, or NHOH). Some unidentified peaks in the spectrum probably refer to products of condensation and oxidation, which can be formed during the sampling at NMR analysis. These results confirm stepwise hydrogenation of 2,4-DNT in the presence of poly-PdAAm/SiO$_2$. According to the composition of the reaction mixture, the scheme of major transformations in the reaction system can be represented as follows shown in see Scheme 3.

The presence of 4A2NT among intermediate compounds indicates the possibility of parallel reaction routes that is consistent with references [29–31]. As the authors of the paper [29] have rightly noted the final mechanism of main conversions of toluene nitroderivatives has not been yet elucidated. Probably, the use of the considered hybrid nanocomposite catalysts will help to solve this problem. On the one hand, the steric factors, including those caused
by the presence of the polymer matrix, can lead to strong
differentiation in coordination of substrate nitro groups. Consequently, the adsorption of the second and third nitro
group will be much weaker. On the other hand, this type of
contacts [2] allows to use methods of nondestructive
testing for intermediate aromatic nitroamine; their different
reactivity is demonstrated in many systems [30–32].

Thus, due to the immobilized form of the studied cata-
lysts, it was possible to separate catalytic intermediate after
reduction of the first nitro group of 2,4-DNT and analyze
it by XPS, as well as to compare the resulting spectrum with the Pd3d5/2 spectrum of the catalyst, separated after
complete hydrogenation of 2,4-dinitrotoluene (Figure 12).
The analysis showed that the intermediate contains, along
with Pd⁰ (335.5 eV), palladium atoms with partially posi-
tively charged Pd⁰⁺ (337.0 eV), promoting coordination of
substrate molecules that affect the activity of the catalyst
and, probably, a preferential hydrogenation of one nitro

4. Conclusions

Effective approach to obtain mixed-type catalysts based
on polymer-immobilized Pd nanoparticles on the support
surface has been developed for selective hydrogenation of
unsaturated compounds. In the case of unsaturated alco-

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