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# Structure and behavior of nanoparticulate catalysts based on ultrathin chitosan layers

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#### Abstract

This paper reports deposition of ultrathin poly(sodium-4-styrenesulfonate)/chitosan layers on a mesoporous alumina surface and the formation of catalytic Pd nanoparticles in mesopores covered by such layers. The structure of these nanoparticulate catalysts has been studied using scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, N<sub>2</sub> adsorption–desorption and CO chemisorption measurements. The Pd nanoparticles formed in the mesopores covered by ultrathin polymer layers do not exceed 2–3 nm, revealing that these layers can control nucleation and growth of nanoparticles. The catalytic behavior of these catalysts has been investigated in selective hydrogenation of dehydrolinalool to linalool. The catalytic properties were found to depend on the amounts of poly(sodium-4-styrenesulfonate) and chitosan deposited on alumina, determining the nanoparticle coverage and formation of catalytic centers either before hydrogenation or *in situ*: the latter occurred when chitosan coverage was insufficient. High stability, low cost and exceptionally high catalytic activity, makes these catalysts promising candidates for broad catalytic applications.

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### 1. Introduction

Metal nanoparticles (NPs) on solid supports have recently attracted considerable attention due to their superior catalytic properties as compared to conventional heterogeneous catalysts [1–3]. They are active and selective in many organic reactions due to a large metal surface area of nanoparticles and their surface modification [4–7]. Often the catalytic NPs are formed in stabilizing medium, but remain available for reactants. Recently, promising heterogeneous catalysts based on NPs formed in block copolymer micelles, dendrimers or poly-

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mer layers deposited on solid supports have been reported [8–14]. The majority of block copolymers or dendrimers are relatively expensive and difficult to synthesize. Therefore, we suggest herein inexpensive chitosan as a polymeric medium to form Pd NPs anchored to the surface of mesoporous alumina. Chitosan is an abundant biopolymer obtained by the alkaline deacetylation of chitin, a polymer containing acetylglucoseamine units [15]. The presence of amine groups in chitosan explains its cationic behavior in acidic solutions and affinity to metals ensuring a high sorption capacity [16,17].

Because of poor diffusion and weak mechanical properties, in many applications chitosan is deposited as a thin layer on the surface of other materials with high specific surface area in order to increase accessibility of the chitosan amino groups [18]. This

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Scheme 1. Reaction pathways of dehydrolinalool and linaool transformations.

is of particular importance when catalytic metals are stabilized by chitosan.

Silica beads have been used to immobilize chitosan for the preparation of advanced sorbents. This process consists of mixing wet beads with chitosan solution and neutralization at pH 8 to solidify and fix the coating layer. The final treatment consists in cross-linking chitosan with glutaraldehyde [19]. Chitosan can also be immobilized on amorphous silica particles after the metal-chitosan complex has formed [20]. An alternative procedure for the deposition of chitosan on the surface of silica or alumina consists of placing the mineral material into a chitosan solution (in acetic acid) then precipitating the polymer for example, by using acetone [21,22]. This, however, results in excessive polymer deposition. For a catalyst preparation, the next step is usually immobilization of a metal compound when precipitated chitosan is immersed in its solution. Examples of such catalysts include silica-supported chitosan-palladium catalysts used for hydrogenation of nitrobenzene to aniline, acrylic acid to propionic acid [21] and phenol to cyclohexanone [23]. Yin et al. used similar catalysts in the asymmetric hydrogenation of ketones (acetophenone, propiophenone, 3-methyl-2butanone and 4-methyl-2-pentanone) to corresponding alcohols ((R)-(+)-1-phenyl-1-ethanol, (R)-(+)-1-phenyl-1-propanol, (R)-(+)-1-phenyl-1-(+)-3-methyl-2-butanol, (R)-(+)-4-methyl-2-pentanol) [24]. The precipitation method was employed for manufacturing of Pd and Pt NPs in a chitosan layer deposited on TiO<sub>2</sub> [25]. These catalysts were studied in hydrogenation of octene and cyclooctene in methanol using hydrogen. All the above catalysts yielded close to 100% conversion of the target products; however, precipitation of chitosan on a solid support can hardly result in a thin polymer layer thus making some metal species poorly accessible for reactants.

Here we report an advanced method to deposit ultrathin layers of chitosan on alumina surface using pretreatment of an alumina surface with anionic polyelectrolyte (PE) and the formation of Pd NPs in such a support. These catalysts were tested in selective hydrogenation of dehydrolinalool (3,7-dimethyloctaen-6-yne-1-ol-3, DHL) to linalool (3,7-dimethyloctadiene-1,6-ol-3, LN). LN is a fragrance and an intermediate in the syntheses of Vitamins A and E [26,27], geraniol, citral [28] and exhibits antimicrobial activity [29]. The pathways of DHL and LN transformations are presented in Scheme 1.

For the DHL hydrogenation, a commercial Lindlar catalyst (palladium on CaCO<sub>3</sub> modified with lead diacetate) is usually applied [30] providing the selectivity of 95% at conversion of DHL close to 100%. Pd catalyst modification by pyridine and quinoline addition to the reaction mixture leads to the selectivity of 98.9% at  $\sim 100\%$  conversion [31], but in both cases the modifiers pollute the end products and have an unfavorable impact on the environment. We have reported selective and highly active catalysts for DHL hydrogenation based on NPs formed in amphiphilic block copolymer micelles [32,33]. Despite their excellent properties, the catalysts based on block copolymers are too expensive for applications. Herein we demonstrate high activity of the catalysts based on Pd NPs formed in the alumina mesopores and controlled by ultrathin chitosan layers deposited on the alumina surface. The catalysts were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), N2 adsorption-desorption, CO chemisorption, and X-ray photoelectron spectroscopy (XPS).

They are compared by activity to the reported catalytic systems based on the amphiphilic block copolymers but surpass the latter by their robustness, availability and facile preparation.

### 2. Experimental

## 2.1. Materials

Alumina (Al<sub>2</sub>O<sub>3</sub>,  $d < 60 \,\mu$ m, sieved) was obtained from Reachim (Russia) and used as received. Dichloroacetic acid (DCAA, Cl<sub>2</sub>CHCO<sub>2</sub>H, 99+%), hydrazine monohydrate (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, 98+%), Na<sub>2</sub>PdCl<sub>4</sub> × 6H<sub>2</sub>O, poly(sodium 4-styrenesulfonate) (PSS, MW 70,000), chitosan (viscosity 20–200 cP for 1% solution in 1% acetic acid, Brookfield, 75–85% deacetylation) were obtained from Sigma–Aldrich and used without purification. DHL (99% purity) was supplied by the pharmaceutical company OAO "Belgorodvitaminy" (Belgorod, Russia) and distilled under vacuum (40–45 °C at 50–60 kPa). Propan-2-ol (isopropanol) was obtained from Aldrich and distilled before use. KOH and hydrogen (KhimMedService, Tver, Russia) were used as received. Water was deionized with a Millipore purification system.

### 2.2. Preparation of catalysts

# 2.2.1. Preparation of a single-layer chitosan-coated alumina

First alumina was treated with NaOH to provide negatively charged surface and then cationic chitosan was deposited on the alumina surface. In a typical experiment, 2 mL of 2 M solution of NaOH was added to 50 mL of alumina suspension (10 g of alumina) in water and the suspension was stirred vigorously for 10 min. Then the suspension was filtered and the solid was dried in a vacuum oven at 60 °C for 24 h. Chitosan (0.05 g) was dissolved in 10 mL of a mixture of DCAA/water ([H<sup>+</sup>] = 0.25 g/L). One gram of the alumina pretreated with NaOH was suspended in a chitosan solution for 1 h. The product was filtered and washed with 10 mL of deionized water three times, then dried in a vacuum oven at 60 °C for 24 h. This sample was designated ACT-1. The elemental analysis data on C and H are presented in Table 2, while the data on N could not be obtained because of its low content.

#### 2.2.2. Preparation of a double-layer coated alumina

For preparation of a double-layer coated alumina, first anionic PSS was deposited on the alumina surface followed by deposition of cationic chitosan. The concentrations of PEs were varied as shown in Table 1.

In a typical experiment (PSC-1), 1 g alumina was added to 10 mL of the 5 g/L PSS solution and stirred for 1 h. The suspension was filtered and the solid was washed with 10 mL of deionized water three times and dried in a vacuum oven at  $60 \degree \text{C}$  for 24 h. The alumina-PSS sample was stirred with 10 mL of

the 5 g/L chitosan solution for 1 h. The product was filtered and washed with 10 mL of deionized water three times, then dried in a vacuum oven at  $60 \degree C$  for 24 h. The elemental analysis data on C and H for alumina-PSS and PSC-1 are presented in Table 3.

#### 2.2.3. Synthesis of Pd nanoparticles on bare alumina

One gram of alumina was stirred for 1 h with 3 mL of aqueous solution containing 0.05 g of Na<sub>2</sub>PdCl<sub>4</sub>·6H<sub>2</sub>O. Then this suspension was filtered and the solid was washed with 10 mL of deionized water three times. The light-brown solid was dried in a vacuum oven at 60 °C for 4 h. Reduction of Pd ions was carried out by addition of a fivefold excess of a freshly prepared N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O solution in water (3 mL/L) to the Pd-containing suspension. The suspension turned gray. After 1 h of stirring, the suspension was filtered and the solid was washed three times with 10 mL of deionized water and dried in a vacuum oven at 60 °C for 24 h.

#### 2.2.4. Synthesis of Pd nanoparticles on coated alumina

One gram of coated alumina was stirred for 1 h with 3 mL of aqueous solution containing 0.05 g of Na<sub>2</sub>PdCl<sub>4</sub>·6H<sub>2</sub>O. The suspension was filtered and the solid was washed with 10 mL of deionized water three times. The light-brown solid was dried in a vacuum oven at 60 °C for 24 h. Reduction of Pd ions was carried out by addition of a fivefold excess of a freshly prepared N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O solution in water (3 mL/L) to the Pd-containing suspension. The suspension turned gray. After 1 h of stirring, the suspension was filtered and the solid was washed three times with 10 mL of deionized water and dried in a vacuum oven at 60 °C for 24 h. By elemental analysis data (see Table 4), 1 h impregnation leads to 98–99% absorption of the Pd anions. The analogous samples were prepared and analyzed at least three times to assure reproducibility of the final products.

## 2.2.5. Synthesis of Pd nanoparticles for TEM studies

For transmission electron microscopy (TEM) characterization, PSS and chitosan layers were successively deposited on a carbon-coated copper grid followed by interaction with  $Na_2PdCl_4 \times 6H_2O$  and Pd reduction. The same concentrations of ingredients were employed as indicated in Table 1. The samples were prepared using alternating 5 min immersions in the

Table 1

The characteristics of coated alumina samples with different PSS and/or chitosan concentrations

<sup>a</sup> After 1 h stirring in water similar to the catalyst preparation.<sup>b</sup> The precursor of PSC-3.

Sample	Concentration of PSS (g/L)	Concentration of chitosan (g/L)	$S_{\rm BET}~({\rm m^2/g})$	Pore volume $(cm^3/g)$	The sizes of the major pores (nm)
Alumina <sup>a</sup>	_	-	163	0.270	4.0; 4.3; 4.7; 3.7
Chitosan	-	_	9	0.01	4.4; 4.8
ACT-1	-	5	85	0.238	7.2
PSS/Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	1	_	86	0.262	7.80
PSC-1	5	5	89	0.239	7.2; 7.8; 8.4
PSC-2	1	5	94	0.246	7.2
PSC-3	1	1	94	0.254	7.2; 7.8
PSC-4	0.5	5	54	0.251	7.8
PSC-5	0.5	0.5	86	0.253	7.2; 7.8

PSS and chitosan solutions with three water rinses (by immersion in fresh water) in between. This was followed by 30 s immersion in the Na<sub>2</sub>PdCl<sub>4</sub> ×  $6H_2O$  solution and three 1-min water rinses. The Pd NPs were obtained by 5 min immersion of the chitosan coated grids in the N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O solution with three 5-min water rinses after the reduction.

#### 2.3. Catalytic tests in DHL hydrogenation

The catalytic reactions were carried out in a glass batch isothermal reactor installed in a shaker (maximum 960 shakings min) and connected to a gasometric burette. The reactor was equipped with two inlets: for catalyst, solvent, and substrate loading and for hydrogen feeding. Isopropanol was used as a solvent. Before the substrate was charged into the reactor, the catalyst was pretreated with H<sub>2</sub> for 60 min at 70 °C. DHL concentration ( $C_0$ ), catalyst amount ( $C_c$ ), and hydrogenation temperature ( $T_h$ ) have been varied. The experiments were carried out at atmospheric pressure. Kinetic experiments have been carried out without diffusion limitations at 960 shaking/min [33].

Analysis of the reaction mixture was carried out by gas chromatography (GC) using a CHROM-5 chromatograph with FID and glass column 3 m/3 mm. The column has been filled with solid-phase Chromaton N (0.16–0.20 mm) saturated with 20 M carbowax (10% of liquid phase to support weight).

### 2.4. Catalyst characterization

TEM was carried out with a JEOL JEM1010 instrument at electron accelerating voltage of 80 kV. Samples were prepared by suspension in a mixture of water/acetone. A drop of the sample suspension was placed on a copper grid coated with a carbon film. The solvents were evaporated off at room temperature.

SEM was carried out with a JEOL 5800LV scanning electron microscope with available accelerating voltages of 0.3–30 kV. Samples were adhered to aluminum SEM stubs using double-sided carbon tape (Electron Microscopy Sciences, Inc., Cat. #77816). Stubs with samples were coated in a Polaron E5100 sputter coater using a gold/palladium target (Energy Beam Sciences, Inc. Cat. #SC510-314B). Digital images were acquired using a JEOL DSG digital scan generator connected to the 5800LV SEM.

Pd content was determined using X-ray fluorescence measurements performed with a Zeiss Jena VRA-30 spectrometer equipped with a Mo anode, a LiF crystal analyzer, and a SZ detector. Analyses were based on the Pd  $K_{\alpha}$  lines. A series of standards were prepared by mixing 1 g of polystyrene with 10-20 mg of standard compounds. The time of data acquisition was held constant at 10 s.

The specific surface area of Pd was measured by pulse adsorption of CO (3% CO in He) performed at 323 K via AutoChem 2910 (Micromeritics, USA). Before the measurements, samples were pretreated at 323 K first in the flow of He (10 mL/min, STP), then in H<sub>2</sub> flow (20 mL/min, STP). A stoichiometry of CO/Pd = 0.6 and a Pd surface density of  $1.2 \times 10^{19}$  atom/m<sup>2</sup> were used for calculations [34].

The BET specific surface area and pore size distribution of the support and the catalysts were determined using a Beckman Coulter<sup>TM</sup> SA  $3100^{TM}$  (Coulter Corporation, Miami, Florida) instrument via N<sub>2</sub> adsorption–desorption at 77 K.

The XPS was performed using Mg K $\alpha$  (hv = 1253.6 eV) monochromatized radiation with a modified ES-2403 Spectrometer (Saint-Petersburg, Russia). The electron energy analyser was operated at a pass-energy of 100 eV. All data were taken at an X-ray power-setting of 100 W in a vacuum of pressure  $10^{-8}$  Torr or less and with the step of 0.1 eV. The electron-flood gun accessory was used for our studies. The total emitted electron flux from the flood gun filament is adjustable in current, I, from I = 0-100 mA (optimal was found to be 70 mA, the electron energy of 2 eV). The binding-energy scale of the instrument was calibrated by setting S = 3 eV. Samples were allowed to outgas for 15–30 min before recording. They proved sufficiently stable under X-ray bombardment and showed no evidence of damage.

### 3. Results and discussion

# 3.1. Formation of the catalysts based on single- and double-layer coated alumina

For successful deposition of positively charged chitosan on the alumina surface, the latter should be negatively charged to provide electrostatic attraction [35], while normally the alumina bears a positive charge [36]. To recharge the alumina surface, it should be treated with alkaline solution at pH>11 [37]. After that, the alumina adsorbs chitosan very fast; this is typical for electrostatic interactions. The elemental analysis data presented in Table 2 demonstrate that the amount of chitosan on the alumina pretreated with NaOH does not exceed 4.0 wt.%. Considering that the surface area of ACT-1 is 85 m<sup>2</sup>/g (Table 1) and using the approximate polymer density of 1 g/cm<sup>3</sup>, one can calculate that only an ultrathin layer (~0.4 nm) can exist on the

Table 2

The composition and	l catalytic p	properties of ACT-1	and Pd-alumina

Sample	Elemental analysis of	lata (%)		Selectivity (conversion) (%)	Activity (mol LN mol Pd <sup>-1</sup> s <sup>-1</sup> )
	C (found/calc.) <sup>a</sup>	H (found/calc.)	Pd (found/calc.)		
Al <sub>2</sub> O <sub>3</sub>	Not found	Not found	_	_	_
Pd/Al <sub>2</sub> O <sub>3</sub>	Not found	Not found	0.35	96(84)	0.76
ACT-1	1.67/2.38	1.04/0.26	0.37/0.44 <sup>b</sup>	98 (100)	4.0

<sup>a</sup> Found/calc. indicates the amount of the element found from elemental analysis and calculated from the reaction loading.

<sup>b</sup> N:Pd = 5:1 mol.



Fig. 1. N<sub>2</sub> adsorption-desorption isotherms of ACT-1.

alumina surface if this surface is fully covered by a polymer. The indication of the full surface coverage can be obtained from nitrogen adsorption experiments.

The nitrogen adsorption experiments on ACT-1 show that porosity changes dramatically after the chitosan deposition. According to the IUPAC classification [38,39], the adsorption–desorption isotherms (Fig. 1) of ACT-1 as well as alumina, are typical for "IV + VI" type. The type IV is characteristic of mesoporous structure, while the type VI represents stepwise multilayer adsorption on a *uniform* surface, revealing that chitosan fully and homogeneously covers the alumina surface [40]. The shape of the hysteresis loop of ACT-1 is close to the H3 type, which does not exhibit any limiting adsorption at high Ps/Po and is normally observed with aggregates of plate-like particles giving rise to slit-shaped pores [41].

Comparison of the surface characteristics of bare alumina and ACT-1 shows that the BET surface area of ACT-1 decreases by half compared to that of alumina, while the pore volume decreases only by about 12%. Such a change is characteristic of blockage of small mesopores. A close look at the pore size distribution shows that the pores at 4.3 and 4.7 nm completely disappear while the fraction of the pores at 3.7 and 4.0 nm significantly decreases (by an order of magnitude) (Fig. 2). At the same time, the much larger mesopores at 7.2 nm appear in ACT-1. We



Fig. 2. Pore size distributions of bare alumina and single- and double-layer catalysts.

think that when chitosan is adsorbed, it intercalates into alumina pores (probably of 4.3 and 4.7 nm), leading to their expansion. The degree of expansion depends on the type, concentration and molecular weight of the adsorbing species; it is believed that the higher the concentration, the higher the degree of expansion [42,43]. It is worth noting that alumina used here represents aggregates of plate-like particles with slit-shaped pores so their expansion can be similar to that described for clay intercalation materials with poly(vinyl alcohol) [44–46]. On the other hand, the pores at 3.7 and 4.0 nm are too small and have too high curvature to accommodate the chitosan molecules and to allow the pore expansion. We believe that these pores are mainly blocked by the polymer but some fraction of them (about 10%) remains unchanged.

The catalytic properties, i.e., the selectivity, the DHL conversion, and the activity of ACT-1 and Pd/Al<sub>2</sub>O<sub>3</sub> (see Section 2) representing a commonly used industrial catalyst (control experiment), are shown in Table 2. It demonstrates that for ACT-1, the catalytic activity, selectivity and conversion are higher than those of the conventional Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. However, in the second use of ACT-1, the Pd content in the catalyst dropped from 0.37 to 0.12 wt.% accompanied by a significant loss of catalytic activity decreasing from 4.0 to 1.2 mol LN mol Pd<sup>-1</sup> s<sup>-1</sup>. This could be explained by peeling off the chitosan layer from the alumina surface.

To improve the adhesion of chitosan on alumina, we suggested using a strong anionic polyelectrolyte, PSS, to effectively negatively charge the alumina surface. The layer-by-layer deposition of PEs on flat and curved surfaces is a well-developed procedure [11,47-50]. When such layers contain catalytic particles, they can be used as catalysts [37]. However, if the particles are buried within multiple layers, this can jeopardize the access to the catalytic sites and consequently, the catalytic activity. To provide successful chitosan adsorption while keeping the minimal amount of layers for better access to catalytic sites, we chose to use only two layers: anionic PSS adsorbed on the positively charged alumina followed with adsorption of cationic chitosan. Table 3 presents the elemental analysis data for alumina treated with PSS (Table 1) and for PSC-1. These data demonstrate that the amount of PSS on the alumina does not exceed 2.0 wt.%, revealing that only an ultrathin PSS layer can exist on the alumina surface if polymer is evenly spread on alumina. Deposition of chitosan brings the polymer amount to about 4 wt.% also confirming a very thin chitosan layer on the alumina surface if we assume the full coverage. The recent study

Table 5							
Elemental	analysis	data o	of alumi	na-PSS	and	PSC-	-1 <sup>a</sup>

Sample	C (%)	H (%)	Pd (%)
	(found/calc.)	(found/calc.)	(found/calc.)
Al <sub>2</sub> O <sub>3</sub> -PSS	0.91/2.68	0.62/0.1	-
PSC-1	1.83/5.01	0.55/0.25 <sup>b</sup>	0.23/0.23

Found/calc. indicates the amount of the element found from elemental analysis and calculated from the reaction loading.

<sup>a</sup> N:Pd = 5:1 mol.

Table 2

<sup>b</sup> Higher than calculated amount of hydrogen is due to water adsorption.

revealed that the maximum amount of PSS of a similar molecular weight adsorbed on the positively charged alumina surface does not exceed 0.4 mg/m<sup>2</sup> matching the 0.4 nm thickness of the PSS layer [51] and corroborating our data. To clarify whether PSS and chitosan fully cover the alumina surface we carried out nitrogen adsorption measurements (see below).

# 3.2. Structural studies of double-layer coated catalysts with *Pd* nanoparticles

Fig. 3 shows the SEM images of the pristine alumina and the alumina samples after the corresponding treatment leading to the final Pd catalyst. One can see that the alumina beads are decreased in size after stirring for 1 h, but do not exhibit any other morphological changes after further treatments and do not change after the catalytic reaction.

The  $N_2$  adsorption-desorption isotherms of double-layer coated catalysts (Table 1) are similar to that of ACT-1. All the samples display adsorption-desorption isotherms of the type

"IV + VI" which represents stepwise multilayer adsorption on a *uniform* surface of mesopores, revealing that the PEs fully and homogeneously cover the alumina surface [40] with no free alumina surface exposed to the N<sub>2</sub> molecules. This suggests formation of ultrathin layers on the alumina surface. When two PEs are successively deposited on alumina, one can expect that only the first layer (here, PSS) intercalates and expands pores while deposition of the second PE (here, chitosan) leads to only a slight decrease of the pore size. The data presented in Table 1 show that for all the catalysts, the pore volumes and pore sizes (the latter are in the ca. 7–8 nm range) are similar. The values of BET surface areas are similar as well (in the range 86–94 m<sup>2</sup>/g) with one exception for the PSC-4 sample where the surface area is  $54 \text{ m}^2/\text{g}$  (see discussion below).

To further examine the structure of the catalysts prepared at different concentrations of PE, we carried out TEM studies (Fig. 4). Because the polymer layers are very thin and the electron contrast of the polymers compared to alumina is low, we cannot distinguish the polymer layers on the alumina from pure



Fig. 3. SEM images of (a) pristine alumina, (b) alumina after stirring for 1 h in water, (c) alumina-PSS, (d) alumina-PSS-chitosan, (e) PSC-5, and (g) PSC-5 after a catalytic reaction.



Fig. 4. TEM images of (a) pristine alumina after 1 h stirring in water, (b) PSC-1, (c) PSC-2, (d) PSC-3, (e) PSC-4, and (g) PSC-5. Black arrow show gray spots of free chitosan. White arrows indicate Pd NPs.

alumina (Fig. 4). On the other hand, one can clearly see that PSC-4 prepared at the much lower concentration of PSS compared to that of chitosan (Table 1) contains free chitosan appearing as gray matter between the alumina particles (shown by black arrow in Fig. 4e). Although the electron contrast of chitosan is low, still a large amount of the polymer is visible on the background due to different texture of the background and a polymer. The low BET surface area of PSC-4 (Table 1) corroborates this finding because the BET surface of free chitosan used in this work is only  $9 \text{ m}^2/\text{g}$  (Table 1). Thus the chitosan presence decreases the total BET surface area in PSC-4. Precipitation of free chitosan means that the PSS amount is insufficient to fully attach an ultrathin chitosan layer while rinsing conditions (with pure water) are not favorable to provide chitosan solubility and successful removal of the large amount of chitosan. The chitosan is well soluble in acidic medium [52,53] but poorly in pure deionized water. When

the PSS concentration is 1 g/L, while the chitosan concentration is 5 g/L (PSC-2), no free chitosan is observed suggesting that the higher amount of PSS deposited provides lower pH and better conditions for the removal of the chitosan excess. We also believe that the chitosan deposition efficiency depends on the amount of the deposited PSS, which in turn is dependent on its concentration in the solution. The TEM images reveal that for successful chitosan deposition, a sufficient amount of PSS should be deposited on the alumina surface.

From Fig. 4 one can see that, in the majority of the samples, the Pd NPs are hardly visible. A few exceptions are indicated by white arrows. These particles measure 2–3 nm in diameter. We believe that the Pd NPs are buried in the mesopores of the PE double-layer coated alumina and held therein by adhering PE layers, thus the high electron contrast of the alumina texture (Fig. 4) obscures the NPs. To estimate more accurately the size



Fig. 5. TEM images (left) of the double-layer nanocomposites PSC-1 (a), PSC-2 (b), PSC-3 (c), PSC-4 (d), and PSC-5 (e) formed on the carbon coated electron grid and the histograms (right) of the NPs shown in the TEM images. The mean particle diameters are presented in Table 4.

Catalyst	Pd content (wt.%)	Mean particle diameter (nm)	Selectivity (conversion) (%)	Activity <sup>b</sup> (mol LN mol Pd <sup>-1</sup> s <sup>-1</sup> )	Pd content (wt.% after the first use)	Selectivity (conversion) % in the second use	Activity (mol LN mol Pd <sup>-1</sup> s <sup>-1</sup> in the second use)	Pd content (wt.% after the second use)	Selectivity (conversion) % in the third use	Activity (mol LN mol Pd <sup>-1</sup> s <sup>-1</sup> in the third use)
PSC-1	0.23	$2.3 \pm 0.6$	95(100)	4.94	0.14	93 (100)	4.88	0.15	94(100)	4.78
PSC-2	0.30	$2.6\pm0.6$	94(98)	4.05	0.20	94 (98)	4.62	0.19	94(99)	4.64
PSC-3	0.30	$2.3 \pm 0.7$	94(99)	4.41	0.24	95 (99)	4.55	0.27	66) 26	4.65
PSC-4	0.25	$2.8\pm06$	95(98)	2.95	0.16	95 (99)	5.54	0.17	66(66)	5.48
PSC-5	0.22	$2.0\pm0.6$	94(100)	4.89	0.12	95 (100)	8.12	0.13	66(66)	8.03
Pd/Al <sub>2</sub> O <sub>3</sub>	0.35	$7.5\pm0.8$	96(84)	0.76	0.22	95 (88)	0.54	0.14	94(87)	0.25

Table

Activity is calculated as moles of LN formed per second per mole of Pd

of NPs, we carried out formation of the PSS-chitosan doublelayer nanocomposite with Pd NPs on a carbon-coated copper electron grid (similar to the method described elsewhere [54]), assuming that in this case, the PE double-layer is comparable to that formed on alumina. Analysis of the TEM micrographs presented in Fig. 5 shows that the mean Pd NP diameter is in the range 2.0–2.8 nm (Table 4) depending on the sample composition. The largest particles are obtained in the case of the lowest PSS/chitosan ratio in PSC-4, where free chitosan is observed, revealing that, in "bulk" chitosan, slightly larger particles are formed.

To determine the valence state of the Pd species we used XPS. The XPS Pd 3d data for all the catalysts before and after catalytic reaction show the presence of only the Pd(0) species with the Pd  $3d_{5/2}$  peak position in the range 335.6-335.8 eV [37,55]. We believe that the NP nucleation slowly occurs in the chitosan layer during reduction with hydrazine-hydrate (sluggish reducing agent). Despite the dimension of the chitosan layer being much smaller than the NP diameter, we think that in the majority of cases the NPs are formed in the alumina mesopores either at the interface of the PSS and chitosan layers or extended beyond the PSS layer towards alumina, thus the NP is covered with a chitosan layer (see discussion below on catalytic properties of NPs).

# 3.3. Catalytic properties of the double-layer based catalysts with Pd nanoparticles

The catalysts listed in Table 1 were studied in catalytic hydrogenation of DHL to LN. This reaction was carried out in isopropanol at atmospheric pressure varying the temperature and concentration of the catalyst and substrate. Effective stirring (960 shakings/min) allowed elimination of the external diffusion effect. Usually sufficiently small heterogeneous catalyst grain [56] allows excluding the internal diffusion as well. Although these catalysts contain polymer, which might be responsible for transport limitations [57], the thinness of the polymer layers ensures that at the above stirring rate the DHL hydrogenation is free of transport limitations. It is worth noting that the reaction medium, isopropanol, is a non-solvent for chitosan so we do not expect the swelling of the chitosan layer during the reaction.

Table 4 displays catalytic properties of these PE double-layer catalysts. The reaction conditions were varied to find those (see the footnote to Table 4) allowing maximum selectivity of the reaction at the highest conversion. From the data presented one can see that selectivity of all the catalysts is about 94–95% at the DHL conversion of 98–100%. As was discussed in our preceding papers, the selectivity of a nanoparticulate catalyst is mainly determined by the chemical modification of a NP surface with polymer functional groups [7,32,33,58]. The presence of pyridine units leads to selectivity of about 99%, while the chitosan amine group provides lower selectivity. This can be caused by the unfavorable influence of lower basicity of the chitosan amino group on selectivity [59–61].

Most active in the DHL hydrogenation are the catalysts prepared at equal concentrations of PSS and chitosan (Table 4), revealing that these conditions promote formation of the PE

	1	· · · ·				
Catalyst	Pd content (%)	Amount of catalyst (g)	Metal dispersion (%) <sup>a</sup>	Pd surface are		$TOF (mol LN mol Pd_{sur}^{-1}s^{-1})$
				m <sup>2</sup> /g of catalyst	m <sup>2</sup> /g of metal	
PCS-1	0.23	0.1188	5	0.05	21	108.7
PSC-3	0.30	0.3234	5	0.07	23	68.2
PSC-5	0.22	0.2401	32	0.32	144	15.2
Pd/Al <sub>2</sub> O <sub>3</sub>	0.35	0.1235	43	0.29	123	3.8

Table 5 The CO adsorption characteristics for PSC-1, PSC-3, and PSC-5

<sup>a</sup> Metal dispersion is defined as the ratio of surface atoms to the total Pd atoms.

double-layer with optimal structure. We assume that the "optimal" PE double-layer provides a suitable access of reactants to NPs and proper modification of the NP surface. The lowest activity was observed for PSC-4 where free chitosan presence was confirmed by  $N_2$  adsorption measurements and TEM. We believe that in this case, the Pd species are partially buried within the bulk chitosan so access to these species is limited.

Comparison of the catalysts studied in this work with a control system (analog of a commercial catalyst) shows that the double-layer based catalysts containing Pd NPs demonstrate higher activity than that of the commercial catalyst (Table 4). In the first place, this could be explained by the smaller size of the Pd NPs formed in the presence of chitosan compared to the Pd/Al<sub>2</sub>O<sub>3</sub> sample. However, the differences observed between the chitosan-based catalysts whose NP sizes are rather similar, show that there are more factors (than the particle size only) influencing the catalytic activity.

After the reaction, the Pd content in all the samples is somehow decreased suggesting partial leaching of Pd, but after the second use it remains practically the same, suggesting formation of structurally stable catalysts. Upon the second use of the same catalysts, the selectivity stays unaffected, while the catalytic activity changes depending on the catalyst composition. The activity of the catalysts PSC-1 and PSC-3 (prepared at 5 and 1 g/L, respectively of both PE solutions) remains unchanged, revealing that the NP environment does not change. For PSC-2, the activity only slightly increases suggesting that after the first reaction more optimal PE double-layer was formed. For the other two catalysts the activity nearly doubles. We think that in the PSC-4 catalyst free chitosan, with Pd species having lower activity in hydrogenation than ultrathin chitosan layers (because of steric hindrances), is removed during the first use. Indeed, the TEM examination of these catalysts after catalytic reaction reveals the absence of free chitosan. Thus, the remaining Pd species are located in ultrathin chitosan layers with higher catalytic activity. PSC-5 also displays a significant increase of activity after the first catalytic reaction although it does not contain free chitosan. We think that, in this catalyst, PSS and chitosan form especially thin layers (the sample is prepared at the lowest PE concentrations, Table 1), and the Pd NPs are not fully covered with chitosan. As a result, the NPs are better exposed to reactants during catalytic reaction and the new active centers form due to interaction with DHL or LN. These new catalytic centers should be responsible for higher activity.

To verify this hypothesis, we carried out the CO adsorption experiments for PSC-1, PSC-3, PSC-5, and Pd/Al<sub>2</sub>O<sub>3</sub>. Unlike

nitrogen adsorbing non-specifically on any surface, CO adsorbs preferentially on Pd (or other metals) due to complexation, so the surface area obtained from these experiments reflects the Pd surface available for reactive species. Table 5 shows that for PSC-1 and PSC-3, the available Pd surface areas are low and nearly the same, suggesting that Pd NPs are covered with a chitosan layer. On the contrary, PSC-5 has a much higher available Pd surface area, revealing that chitosan does not fully cover the NPs, thus making Pd species more accessible for CO. The turnover frequency values (TOF) calculated from the catalyst activity per accessible Pd atoms shows the remarkably high TOF for PSC-1 and PSC-3. For comparison, the TOF of Pd/Al<sub>2</sub>O<sub>3</sub> (0.35% Pd) used in this work is lower by more than the order of magnitude (Table 5).

It is noteworthy that after the third use (Table 4) both Pd content and catalytic activity in all the catalysts remain unchanged, suggesting that all modifications to the catalysts occurred during the first use and the catalysts remain stable after that. At the same time, control experiments with  $Pd/Al_2O_3$  (Table 4) show that both the Pd content and activity deteriorate after the each consecutive reaction.

# 3.4. Kinetics of LN formation with double-layer coated catalysts

To study the kinetics of selective LN formation, we chose two catalysts: PSC-3 and PSC-5, i.e., with poorer or better accessible Pd active centers. For better understanding of the differences between the two catalysts we compared these catalytic studies with those of Pd/Al<sub>2</sub>O<sub>3</sub> [62] where Pd species are not modified with organic groups before catalytic reaction.

# 3.4.1. Influence of the catalyst amount $(C_c)$ and the initial DHL concentration $(C_0)$ on hydrogenation

To evaluate the dependence of the DHL conversion on time at different  $C_0$  and  $C_c$ , we used the substrate-to-catalyst ratio  $q = C_0/C_c$  (mol/mol). The dependencies of LN formation versus the reaction time at different q values for PSC-3 and PSC-5 are presented in Figs. 6–7. In both cases the higher the q, the slower the reaction: this is typical for the majority of catalytic reactions. It is noteworthy that for PSC-3, the LN formation increases monotonically in time, while for PSC-5, there is an induction period, when catalytic reaction occurs much slower or not at all. This is normally due to formation of catalytic species *in situ* at the beginning of the reaction. Here the induction period is 7 min while in some cases it can reach 100 min [63]. We believe



Fig. 6. Dependences of LN formation on reaction time for different q values for PSC-3 (a) and PSC-5 (b).

that in PSC-3 all catalytic NPs are located in the chitosan layer and the catalytic centers are already formed before the reaction starts, thus no induction period is observed. Oppositely, in PSC-5, the NPs are only partially covered with chitosan, so some active centers form *in situ* during interaction with DHL or LN.

The data presented in Fig. 6, show that for PSC-3, the optimal q is 10,500 mol/mol, while for PSC-5, this value is 12,506 mol/mol. These q values provide sufficiently high selectivity towards the reaction product (LN) at the maximal catalytic activity.

As a result of experimental data processing, the 50% DHL conversion time ( $\tau_{0.5}$ ) has been determined. The value of  $\tau_{0.5}$  was found to depend on the  $q^n$ 

$$\tau_{0.5} \sim q^n \tag{1}$$

where *n* is the formal parameter characterizing a slope of the  $\ln \tau_{0.5}$  dependence on  $\ln C_0/C_c$ . The linear dependence of  $\ln \tau_{0.5}$  on  $\ln q$  was found. For both catalysts, n = 1.

#### 3.4.2. Influence of reaction temperature on hydrogenation

To choose the optimal temperature, i.e., the temperature leading to sufficiently high selectivity towards LN at the maximal catalytic activity, the temperature of the DHL hydrogenation was varied in the range 40–75 °C. The highest possible temperature was limited by the isopropanol boiling point (82.4 °C).



Fig. 7. Dependences of LN formation on reaction time at different temperatures for PSC-3 (a) PSC-5 (b).

Dependences of LN formation on reaction time at different temperatures for PSC-3 and PSC-5 are presented in Fig. 7.

It is worth noting that for PSC-3, the optimal temperature of the DHL hydrogenation is  $60 \,^{\circ}$ C (Fig. 7a), while for PSC-5, at  $70 \,^{\circ}$ C the higher selectivity is achieved.

#### 3.4.3. Kinetics models

Based on kinetic studies, the mathematical kinetic models were computed. The GC analysis showed that along with LN (the target product), DiHL (Scheme 1) forms as well. Thus the following reaction pathway could be assumed:

$$DHL \xrightarrow{k_1}_{+H_2} LN \xrightarrow{k_2}_{+H_2} DiHL$$

where  $k_1$  and  $k_2$  are the hydrogenation rate constants.

The linear dependence of  $\ln \tau_{0.5}$  on  $\ln (C_0/C_c)$  allows us to introduce an independent variable, relative time  $\Theta$ 

$$\Theta = \frac{\tau}{q^n} \tag{2}$$

where  $\tau$  is the current reaction time.

For both PSC-3 and PCS-5, n is equal to 1 (see above). In doing so, the experimental data, presented in Fig. 6, have been brought together into a family of curves (Fig. 8) in the coordinates LN formation versus  $\Theta$ .



Fig. 8. Dependences of LN formation on  $\Theta$  for PSC-3 (a) and PSC-5 (b).

For the computation of the kinetic model parameters  $k_1$  and  $k_2$  and mathematical description of the reaction, in the present paper the integral method has been used [64]. Cubic spline serves as interpolating functions in this method, while the integral efficiency function has been minimized by the combined gradient method of Levenberg–Marquardt [65,66].

Based on this computation, for both catalysts, the kinetic models have been chosen which describe well the hydrogenation kinetics (see Table 6, Fig. 8). These models are a formal description of the DHL hydrogenation kinetics. The kinetic model of the DHL hydrogenation with the commercial Pd/Al<sub>2</sub>O<sub>3</sub> [62] is also presented in Table 6. Unlike the chitosan-based catalysts, the

Table 6 Kinetic models of DHL hydrogenation with PSC-3 and PSC-5

Parameters of the Arrhenius equations for PSC-3 and PSC-5

Catalyst	$E_{\rm a}$ (kJ/mol)	$K_0$
PSC-3	17	2,215
PSC-5	25	44,802
Pd-alumina	56	9,615

reaction rate with Pd/Al<sub>2</sub>O<sub>3</sub> is not proportional to the substrate concentration,  $X_1$ , revealing differences in the mechanisms of hydrogenation.

One can see that for all the catalysts, the models are described by three equations (Table 6) and in each of them the adsorption parameter, Q, is present, however, its values are very different. The low Q values of PSC-3 and PSC-5 suggest that adsorption of LN only slightly influences the behavior of the PE doublelayer catalysts. (It is worth mentioning that in the case of PSC-5, the mathematical model describes the experimental data excluding the induction period, see Fig. 8b, which would require a more complicated equation.) At the same time, the Q value of Pd/Al<sub>2</sub>O<sub>3</sub> is close to unity, indicating that adsorptions of LN and DHL are the same. We believe that different adsorptivity is caused by different structures of the catalytic active centers.

Based upon the mathematical model and experimental data at various temperatures the parameters of Arrhenius equation (3) for each catalyst were determined (Q is constant and does not depend on the temperature [67]). From the Arrhenius dependence in the coordinates  $\ln K - 1/T$ , the frequency factor  $K_0$  which characterizes the amount of active centers [68] and apparent activation energy  $E_a$  were calculated (Table 7)

$$K = K_0 \,\mathrm{e}^{-E/RT} \tag{3}$$

The  $E_a$  of PSC-5 is higher than that of PSC-3, but lower than  $E_a$  of Pd/Al<sub>2</sub>O<sub>3</sub> studied in this work. These values suggest that reactive centers formed in PSC-3 (higher amount of chitosan) have a more favorable environment than that of the reactive centers in PSC-5 or in Pd/Al<sub>2</sub>O<sub>3</sub>.

The higher activation energy of PSC-5 compared to that of PSC-3 can be due to lesser degree of modification of Pd NPs with chitosan. On the other hand, the higher activity of PSC-5 compared to PSC-3 can be explained by a larger amount of active centers as follows from the values of frequency factors. These results corroborate the data obtained from the CO adsorption measurements.

Catalyst	Model <sup>a</sup>	$k_1^{\rm b} ({\rm mol/mol})^n {\rm s}^{-1}$	$k_2^{\rm b}  ({\rm mol/mol})^n  {\rm s}^{-1}$	$Q^{c}$	$\sigma \times 10^{2\rm d}$
PSC-3 PSC-5	$W_1 = -k_1 X_1 / (X_1 + QX_2), W_2 = (k_1 - k_2) X_1 / (X_1 + QX_2), W_3 = k_2 X_1 / (X_1 + QX_2)$	$4.99 \pm 0.06$ $7.21 \pm 0.10$	$0.55 \pm 0.03 \\ 0.32 \pm 0.04$	$\begin{array}{c} 0.04 \pm 0.01 \\ 0.05 \pm 0.01 \end{array}$	1.36 1.89
Pd-alumina	$W_1 = -k_1 X_1 / (X_1 + QX_2), W_2 = (k_1 - k_2) / (X_1 + QX_2), W_3 = k_2 / (X_1 + QX_2)$	$1.32\pm0.001$	$1.79\pm0.003$	$0.99\pm0.018$	2.78

<sup>a</sup>  $W_i$  is the rate of chemical reaction,  $X_i$  is the relative concentration,  $X_i = C_i/C_0$ , where i = 1, 2 for DHL and LN, respectively, and  $C_i$  is the current substrate or product concentration.

<sup>b</sup>  $k_1$  and  $k_2$  are the kinetic parameters.

<sup>c</sup>  $Q = K_2/K_1$  is the adsorption parameter which is accountable for the adsorption of the product ( $K_2$ ) and substrate ( $K_1$ ) with the catalyst.

<sup>d</sup>  $\sigma$  is the root-mean-square deviation.

Thus, despite a slightly lower selectivity of the chitosan based catalysts (94–95%) compared to some other catalytic systems (98–99%) studied by us earlier [32,33,58], the selectivity of double-layer catalysts remains unchanged after a catalytic reaction. The combination of high stability, low cost and exceptionally high catalytic activity, makes these catalysts promising candidates for future industrial applications.

## 4. Conclusions

Successful deposition of an ultrathin chitosan layer on alumina requires a negatively charged alumina surface. This was achieved by deposition of a strong anionic polyelectrolyte, PSS, on mesoporous alumina, while merely pretreatment of alumina surface with sodium hydroxide is not efficient in providing a stable chitosan layer. Moreover, if the concentration of the chitosan solution strongly exceeds the concentration of the PSS solution, part of the chitosan is not deposited as a thin layer but precipitates as free chitosan. Pd NPs formed in mesopores of the alumina covered by ultrathin PE layers do not exceed 2.5 nm, revealing that these layers can control nucleation and growth of NPs. The PE double-layer nanocomposites containing Pd NPs are efficient catalysts of selective hydrogenation of DHL to LN. In so doing, the catalytic properties strongly depend on the amounts of PSS and chitosan deposited on alumina. For all the catalysts except PSC-5, chitosan covers Pd NPs, thus forming the catalytic centers on the NP surface. In PSC-5, Pd NPs are not fully covered with chitosan thus catalytically active centers are formed in situ during the DHL hydrogenation. The presence of chitosan around catalytic centers significantly lowers the activation barrier compared to Pd deposited on alumina, while lower amounts of deposited PEs allow incomplete NP coverage with chitosan and better exposure of Pd NPs to reacting molecules.

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