Mesoporous organic Pd-containing catalysts for the selective hydrogenation of conjugated hydrocarbons

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Palladium catalysts supported on ordered organic mesoporous polymers were synthesized. The catalysts are characterized by the narrow size distribution of palladium nanoparticles with an average particle size of 2.2–5.2 nm. They demonstrate high catalytic activity and selectivity in phenylacetylene hydrogenation (896–2590 min⁻¹, selectivity 89–98%). High activity and selectivity for alkenes are observed in the hydrogenation of conjugated dienes (for isoprene, TOF = 1850–5000 min⁻¹, selectivity 99%; for 2,5-dimethyl-2,4-hexadiene, TOF = 1294–2400 min⁻¹, selectivity 100%; for 1,4-diphenyl-1,3-butadiene, TOF = 14–22 min⁻¹, selectivity on the nature of the support and substrate was found for the hydrogenation of 1,4-diphenyl-1,3-butadiene.

Key words: organic mesoporous supports, palladium nanoparticles, selective hydrogenation, phenylacetylene, conjugated dienes.

Development of catalysts for selective hydrogenation is one of the most important problems of petrochemical synthesis. Olefins obtained by pyrolysis or dehydrogenation contain acetylene and diene hydrocarbons that poison the catalysts in the course of subsequent olefin polymerization. Therefore, one of the main stages of olefin preparation to polymerization is the selective hydrogenation of acetylene and diene hydrocarbons to alkenes. When styrene is produced by catalytic dehydrogenation, phenylacetylene is formed, whose content, according to GOST 10003-90, should be decreased to 0.01% (for styrene of the superior quality). According to GOST 25043-87, the volume fraction of hydrocarbons (propadiene and butadiene) in propylene of the superior quality should be $\leq 0.01\%$.

Since selective hydrogenation is structure-sensitive process in which activity and selectivity of the catalyst depend on the particle size of the active component, it is necessary to develop methods for the production of catalysts with the rigidly controlled particle sizes.¹ Modern methods for direct supporting of metals, for example, laser ablation, can form catalysts with a narrow size distribution of metallic particles.² However, the main problem appeared when using metal nanoparticles in catalytic processes is their aggregation leading to a decrease in the catalytic activity during operation. Such supports as mesoporous aluminosilicates or crosslinked dendrimeric matrices are used, for example, for the stabilization of nanoparticles.³

Methods for synthesis of mesoporous organic supports are being actively developed recently.^{4–7} The obtained materials seem to be very promising since they can easily be synthesized and the supports have regular structure, large surface area, variable pore dimensions, and surfaces amenable to chemical modification. This provides prerequisites for the synthesis of catalysts with a substrate selectivity.

The purpose of this work is to synthesize a series of Pd-containing catalysts using an organic mesoporous polymer as a support and to test the obtained catalysts in the hydrogenation of various unsaturated compounds.

Experimental

Supports were synthesized as described earlier⁸ using a procedure of solvent evaporation-induced self-assembly (EISA). The synthesis conditions are presented in Table 1. The role of the precursor was played by the low-molecular-weight soluble phenol resin (resol UPF) obtained by the polymerization of urea, phenol, and formaldehyde (Scheme 1). Triblock copolymer Pluronic F127 ($M_w = 12600$, PEO₁₀₆-PPO₇₀-PEO₁₀₆, Aldrich) was used as a template. The molar fraction urea : phenol : formaldehyde for all samples was 1 : 1 : 2.5.

Phenol (11.0 g) was placed in a glass reactor equipped with a magnetic stirrer and a reflux condenser and was melted at 45 °C.

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 Table 1. Synthesis conditions for the mesoporous polymer supports

Cata- lyst	Phenol : template	Annealing temperature/°C	Annealing time/h		
1	1:0.01	380	5		
2	1:0.01	380	10		
3	1:0.01	380	10		
		450	5		
4*	1:0.012	380	5		

* The sample was not evacuated.

Scheme 1



A 20% aqueous solution of NaOH (2.34 g) was added with stirring and stirred for 10 min more. Then, a 37% aqueous solution of formaldehyde (18.97%) was added dropwise at 50 °C, the mixture was stirred for 30 min at 70–75 °C, and then urea (7.02 g) and a 37% aqueous solution of formaldehyde (4.74 g) were added at once. The reaction mixture was stirred for 4 h at 65 °C and cooled to ~20 °C. The pH of the reaction mixture was brought to ~7.0 using 0.6 *M* HCl. After removal of water from the reaction mixture with a vacuum rotor evaporator at 50 °C, the final product was dissolved in ethanol, and a precipitate of sodium chloride was filtered.

Copolymer F127 (1.0 g) was placed in a round-bottom flask equipped with a magnetic stirrer and dissolved with stirring in ethanol (10.0 g). Then, resol precursor UPF (2.7 g) containing urea (0.40 g), phenol (0.62 g), and formaldehyde (0.50 g) was added to the solution. A homogeneous solution was obtained within 10 min of stirring. The solution was poured to the Petri

dish, where ethanol evaporated for 5–8 h at ~20 °C, after which the sample was placed in drying box and heated for 24 h at 100 °C. The product, being a semitransparent orange film, was powdered. The template in samples **1–3** was removed by annealing in a tubular furnace under evacuation, and that in sample **4** was removed by annealing the sample in a muffle furnace without evacuation. In all cases, the template was removed at a certain temperature in an inert atmosphere of nitrogen for a certain time (see Table 1). The heating rate was 1 °C min⁻¹, and the flow rate was 90 mL min⁻¹. The obtained product was a black powder.

Supports were studied using the methods of low-temperature nitrogen adsorption, solid-state NMR spectroscopy, and transmission electron microscopy (TEM). Nitrogen adsorption/desorption isotherms were studied at 77 K using a Gemini VII 2390 instrument. Prior to measurements, samples were degassed at 130 °C for 6 h. The adsorption data obtained in the range of relative pressures (P/P_0) 0.04–0.2 were used for the calculation of the surface area (S_{BET}). The pore volume and pore size distribution were determined from the adsorption branch of the isotherms using the Barrett–Joyner–Halenda (BJH) model. The total pore volume (V_t) was calculated taking into account the amount of nitrogen adsorbed at the relative pressure $P/P_0 = 0.995$.

An analysis by solid-state ¹³C NMR cross polarization magic angle spinning (CPMAS) spectroscopy was carried out on a Varian NMR Systems instrument at a working frequency of 125 MHz in the pulse mode at the rotation frequency 10 kHz.

TEM analysis was carried out with a LEO912 AB OMEGA microscope.

Synthesis of catalysts. Palladium was deposited on the synthesized supports by impregnation with a solution of $(AcO)_2Pd$ followed by the reduction of Pd^{II} to Pd^0 with sodium borohydride. The properties of the obtained catalysts are listed in Table 2.

A sample of mesoporous polymer (0.35 g) was pre-dried for 60 min using a vacuum rotor evaporator at 90 °C. The dried sample and palladium acetate (15.07 mg) were placed in a round-bottom 50-mL flask equipped with a magnetic stirrer and a reflux condenser, then CHCl₃ (3 mL) was poured, the mixture was stirred for 24 h, and CHCl₃ was removed from the mixture using a rotor evaporator at 30 °C. Then NaBH₄ (26 mg) was added to the dried mixture and CHCl₃ (3 mL) and methanol (1.5 mL) were poured. Palladium was reduced for 24 h. The obtained mixture was three times washed with distilled water and three times with methanol to remove borax, and the solid product was separated from the supernatant by centrifugation. The final product was a black powder.

The obtained catalysts **1**–**4** were studied by TEM and X-ray photoelectron spectroscopy (XPS). Palladium in the synthesized

Table 2. Properties of the Pd catalysts on the mesoporous polymer supports

Catalyst	Support	Pore volume $/\text{cm}^3 \text{g}^{-1}$	Si	Content	
	surface/m ² g ⁻¹		of pore	of particles	of Pd (%)
1	14	0.04	20.4	5.2±1.7	1.6
2	31	0.09	11.7	4.1±1.2	1.6
3	125	0.13	7.0	3.5±1.3	1.3
4	257	0.15	5.0	2.2 ± 1.0	1.9

samples were quantitatively determined on an ICP-AES 720-ES spectrometer (Agilent Technologies, USA).

The particle-size distribution and average particle size on the support surface were found using an analysis by the ImageJ program of TEM images of the samples containing 100–200 particles.

XPS studies were carried out on a LAS-3000 instrument equipped with an OPX-150 photoelectron analyzer with delaying potential. The X-ray radiation of the aluminum anode $(E(AI-K\alpha) = 1486.6 \text{ eV})$ at the voltage on the tube 12 kV and emission current 20 mA was applied for the excitation of photoelectrons. The C1s with a binding energy of 285 eV was used as a reference to calibrate binding energies.

Catalytic experiments were carried out in a steel temperature-controlled autoclave equipped with a magnetic stirrer and a glass tube-bush. The constant temperature in the reactor was maintained with a UTU-2/77 thermostat with an accuracy of ± 0.5 °C. The calculated weighed sample of the powdered catalyst, a magnetic stirrer, and calculated amounts of the substrate and solvent were placed in the glass bush. The amount of the substrate was calculated depending on the palladium content in the catalyst. Toluene served as a solvent. The bush was placed in the autoclave, and the autoclave was sealed, filled with hydrogen to a pressure of 10 atm, and connected to the thermostat. The experiments were carried out at 80 °C. After the end of the reaction, the autoclave was cooled and depressurized. The reaction mixture was analyzed by GLC.

A ChromPack CP9001 gas chromatograph with a flameionization detector, a capillary column (length 30 m, inner diameter 0.2 mm) with the SE-30 stationary phase was used for analysis of the substrates and reaction products. The substrate conversion was determined from a change in the relative surface area of peaks of the substrate and products (in %).

The commercially available catalyst Pd/AC, being palladium supported in active carbon, was used for comparison of the catalytic activity. The Pd content was 10 wt.%, and the average size of palladium particles in the Pd/AC catalyst was 2.2±0.7 nm.

The specific catalytic activity (turnover frequency on catalytic site per 1 min, TOF) was calculated using the following formula taking into account the surface palladium atoms

$$TOF = (Cv_{substr}/v_{cat})(1/D_M)$$

where C is conversion; v_{substr} and v_{cat} are the fractions of the substrate and catalyst, respectively; D_{M} is dispersity.

Dispersion defined as the ratio of the number of surface metal atoms to a total number present was calculated using the formula⁹ $D_{\rm M} = 0.885/d$, where *d* is the average diameter of particles (nm), and 0.885 is coefficient for palladium corresponding to the ratio of the atomic volume of the metallic phase $v_{\rm M}$ to the average effective surface area of atom $a_{\rm M}$ on the particle surface, which can be calculated by the formula

$$v_{\rm M}/a_{\rm M} = A_{\rm r}/(N_{\rm A}\rho a_{\rm M}),$$

where A_r is the relative atomic weight of the metal, N_A is Avogadro's number, and ρ is the density of the metal.

Results and Discussion

Results of studying the supports and catalysts. The TEM images indicate that the structure in the synthesized samples of the supports is ordered (Fig. 1).



Fig. 1. TEM image of sample 4.

The XPS analysis (Table 3) indicates that the spectra of samples 1-4 contain the characteristic peaks of the groups present in the structure of the phenol—urea—formaldehyde polymer. In sample 4, the ratio of groups NCON/ C—C is significantly higher than that for samples 1, 2, and 3. For samples 1 and 2, the ratio of surface areas of the characteristic peaks changes insignificantly with an increase in the annealing time, whereas an increase in the annealing temperature for sample 3 results in a considerable decrease in the intensity of signals from all groups, except for aromatic C—C and C—H bonds.

The ¹³C CPMAS spectrum of sample **4** exhibits signals at δ 125–130 (carbon atom of the aromatic ring) and 150–155 (carbon atoms of the aromatic ring linked with phenolic hydroxyl). An increase in the annealing temper-

 Table 3. Results of XPS analysis of the mesoporous polymer supports

Catalyst support	Bond energy C1s/eV	Surface area of peak (%)
1	284.3 (aromatic C–C, C–H)	51
	285.3 (aromatic C–OH)	12
	286.0 (aliphatic C–OH)	11
	286.5 (C=O, N-C=O)	5
	287.1 (NCON)	20
2	284.6 (aromatic C–C, C–H)	46
	285.6 (aromatic C–OH)	10
	286.4 (aliphatic C–OH)	11
	287.1 (C=O, N-C=O)	7
	287.7 (NCON)	25
3	284.7 (aromatic C–C, C–H)	83
	285.9 (aromatic C–OH)	6
	287.0 (aliphatic C–OH)	6
	288.0 (C=O, N-C=O)	1
	288.9 (NCON)	3
4	284.9 (aromatic C–C, C–H)	28
	286.0 (aromatic C–OH)	4
	286.9 (aliphatic C–OH)	5
	287.7 (C=O, N-C=O)	10
	289.1 (NCON)	53

Catalyst	Bond energy	Surface area		α* (%)				
	Pd3d _{5/2} /eV	of peak (%)	Pd	С	0	N		
1	335.2 (Pd ⁰)	19	22	42	23	13		
	337.8 (Pd ²⁺)	81						
2	335.8 (Pd ⁰)	54	14	60	16	10		
	337.3 (Pd ²⁺)	46						
3	336.7 (Pd ⁰)	16	11	60	17	12		
	337.5 (Pd ²⁺)	84						
4	337.4 (Pd ⁰)	59	10	46	29	15		
	339.1 (Pd ²⁺)	41						
Pd/AC	336.4 (Pd ⁰)	14	18	65	17	_		
•	337.4 (Pd ²⁺)	86						

 Table 4. Results of XPS analysis of the mesoporous organic

 Pd-containing catalysts and Pd/AC catalyst

* Weight fractions of elements on the surface.

ature of the template to 450 °C results in the formation of carbonaceous deposit on the sample, which is indicated by an increase in the surface area of the peak corresponding to the aromatic C–C and C–H bonds compared to the surface areas of other signals in the XPS spectrum of sample **3**. In addition, evacuation during annealing results in a significant decrease in the ratio of groups NCON/C–C in the samples (see Table 3).

According to the data of low-temperature nitrogen adsorption, sample **4** has a considerably larger surface area $(257 \text{ m}^2 \text{ g}^{-1})$ than samples **1**, **2**, and **3** (14, 31, and $125 \text{ m}^2 \text{ g}^{-1}$, respectively) (see Table 2). Sample **4** has a narrower pore size distribution than other samples. Template annealing under evacuation conditions destroys the mesoporous structure. The presence of coke on the sample also strengthens the porous structure and increases its resistance to mechanical stress, which is indicated by a larger size of the surface area of sample **3** than those for samples **1** and **2** (see Table 2).

The XPS results (Table 4) show that surface palladium exist on the catalyst as metallic nanoparticles (Pd^0) and

palladium oxide (PdO). The presence of palladium oxide is due to the fact that Pd^0 nanoparticles are readily oxidized by air oxygen. The palladium concentration on the surface on going from sample 1 to sample 4 decreases more than twofold (see Table 4). This is explained by a decrease in the palladium amount on the surface with an increase in the surface area and porosity of the samples, while the amount of palladium in pores increases.

As can be seen from Table 2, as the surface area of the support and pore volume increase, the pore and particle size increases and the fraction of particles with a broad size distribution increases (Fig. 2). This is related most likely to the fact that the palladium precursor penetrates deep inside the support and then forms smaller particles (2.2 nm) than other catalysts do. According to the XPS data, the palladium content on the support surface decreases regularly (see Table 4). At the same time, the palladium content on the surface of catalysts 1-3 increases and the particle size distribution becomes broader (see Fig. 2).

Activity and selectivity of the catalysts in hydrogenation. The synthesized catalysts were studied in the hydrogenation of phenylacetylene (A), isoprene (B), 2,5-dimethylhexa-2,4-diene (C), and 1,4-diphenyl-1,3-butadiene (D) (Scheme 2, Table 5).

Catalytic activity in the hydrogenation of phenylacetylene, isoprene, 2,5-dimethylhexa-2,4-diene increases with an increase in the size of metallic particles (Fig. 3), which is consistent with the published data on the hydrogenation of acetylene and diene hydrocarbons on the palladium nanoparticles.¹⁰ It should be mentioned that the conventional catalyst for hydrogenation Pd/AC exhibits somewhat higher activity than catalyst **4** (see Scheme 2), although the particle sizes of these catalysts are comparable. It is most likely that this is related to two factors. First, the porous structure of the Pd/AC catalyst is more developed and its catalytically active sites are more accessible for reactants. Second, the support of catalyst **4** con-

Catalyst	\mathbf{A}^{a}		\mathbf{B}^{b}		\mathbf{C}^{c}			\mathbf{D}^d				
	C ^e (%)	TOF/min ⁻¹	$S^{f}(\%)$	C ^e (%)	TOF/min ⁻¹	S(%)	C ^e (%)	TOF/min ⁻¹	S(%)	C ^e (%)	TOF/min ⁻	¹ S(%)
1	66	2593	98	63	5001	99	31	2398	100	6	21	12
2	48	1487	98	50	3082	99	32	1939	100	9	22	13
3	42	1367	98	60	3911	99	29	1863	100	5	14	7
4	64	896	89	66	1849	99	47	1294	100	16	19	16
Pd/AC	92	1219	85	94	2484	95	100	2652	99	14	16	15

Table 5. Results of the hydrogenation of substrates A–D on the mesoporous organic Pd-containing catalysts

^{*a*} Reaction conditions: Pd^0 /substrate = 1 : 8000 (mol.), 15 min, 80 °C, 10 atm H₂.

^b Reaction conditions: Pd^0 /substrate = 1 : 16000 (mol.), 15 min, 80 °C, 10 atm H₂.

^c Reaction conditions: Pd^0 /substrate = 1 : 16000 (mol.), 15 min, 80 °C, 10 atm H₂.

^{*d*} Reaction conditions: Pd^0 /substrate = 1 : 8000 (mol.), 3 h, 80 °C, 10 atm H₂.

^e Conversion.

^f In all cases, selectivity (S) based on alkene (in the case of phenylacetylene, based on styrene).



Fig. 2. TEM images (a-d) and histograms of the Pd particle distribution (e-h) for catalysts 1-4, respectively; N is the fraction of particles with the sized.



Sup is support.

tains oxygen-containing moieties, due to which the electron density on the metal increases, decreasing the specific catalytic activity.

According to the performed studies, palladium exists in two valent states on the support surface and exerts no effect on the catalytic activity in hydrogenation, because palladium oxide is rapidly reduced to Pd⁰ due to the interaction with gaseous hydrogen from the reaction mixture.²

For the hydrogenation of 1,4-diphenyl-1,3-butadiene, the activity of catalysts 1, 2, and 4 remains almost unchanged with a change in the palladium particle size (see Table 5). However, for catalyst 3 with an average particle size of 3.5 nm, catalytic activity decreases twofold and TOF is 14 min⁻¹. The surface area of the support and the average particle size exert, most likely, no effect on the catalytic activity (see Table 2, Fig. 3). A similar dependence can be due to the fact that in the case of catalysts 1 and 2 hydrogenation occurs on the external surface of the support and the dimensional effect of the palladium nanoparticles plays the decisive role. Catalyst 4 has a large surface and the substrate can penetrate deep inside the support. However, it can be assumed that the product do not immediately leave the support pores because of diffusional restrictions, resulting in a decrease in the TOF. It is most likely that the products of 1,4-diphenyl-1,3-butadiene hydrogenation can more easily be desorbed from the surface of catalyst 3 than from the surface of catalyst 4. In this case, the dimensional effect exerts a stronger effect than the geometry of the support. According to the published data, the number and the surface area of Pd(111) faces, which are the most active in hydrogenation, decrease with a decrease in the palladium particles,¹¹ while for adsorption of 1,4-diphenyl-1,3-butadiene a higher molecular area on the metal face is needed than for adsorption of other substrates. Correspondingly, catalytic activity decreases with a decrease in the size of palladium parti-



Fig. 3. Catalytic activity (TOF) in the hydrogenation of phenylacetylene (**A**), isoprene (**B**), 2,5-dimethylhexa-2,4-diene (**C**), and 1,4-diphenyl-1,3-butadiene (**D**) vs palladium particle size (*d*) on the support surface.

cles, 12,13 which is a reason for decreasing catalytic activity observed on going from catalysts 1 and 2 to catalyst 4.

In the case of 1,4-diphenyl-1,3-butadiene hydrogenation, the selectivity for alkenes was low (7-16%) (see Table 5). This can be explained by a stronger adsorption of 1,4-diphenyl-1,3-butadiene on the catalyst surface due to $\pi-\pi$ -stacking interactions with aromatic groups on the support surface. As a result, alkenes are poorly desorbed from the support surface and can undergo deeper hydrogenation to 1,4-diphenylbutane. The lowest selectivity (7%) corresponds to catalyst **3** that, according to the XPS data, contains the highest number of aromatic C-C bonds compared to other samples.

According to the performed studies, the synthesized catalysts turned out to be more active in hydrogenation than Pd/C. In all cases, the selectivity for olefins is higher with the catalysts described in this work (see Table 5) than that recorded in the presence of the Pd/C catalyst.

Thus, the palladium catalysts using mesoporous polymers as supports were synthesized. The catalysts were tested in the hydrogenation of isoprene (TOF = $1850-5000 \text{ min}^{-1}$), phenylacetylene (TOF = $900-2590 \text{ min}^{-1}$), 2,5-dimethyl-2,4-hexadiene (TOF = $1294-2400 \text{ min}^{-1}$), and 1,4-diphenyl-1,3-butadiene (TOF = $14-22 \text{ min}^{-1}$). The selectivity for alkenes in hydrogenation was 85-100%. The exception is the hydrogenation of 1,4-diphenyl-1,3-butadiene in which the selectivity is 7-16%. The decreased selectivity can be explained by a facile adsorption of 1,4-diphenyl-1,3-butadiene on the support surface due to $\pi-\pi$ -stacking interactions with aromatic groups of the support surface.

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