Platinum and Palladium Nanoparticles in Modified Mesoporous Phenol—Formaldehyde Polymers as Hydrogenation Catalysts

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Abstract—Mesoporous polymeric supports modified with sulfo groups and PPI dendrimers have been prepared. Catalysts containing palladium and platinum nanoparticles have been synthesized on their basis. The resulting catalysts have been studied by transmission electron microscopy and X-ray photoelectron spectroscopy. It has been shown that the metal deposition procedure has an effect on the morphology of the resulting catalyst. Catalytic activity has been studied using the example of the hydrogenation of phenylacetylene and naphthalene at temperatures of 80 and 400°C, and pressures of 1.0 and 5.0 MPa, respectively.

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The use of polymeric supports with a regular structure for preparing metal-containing catalysts for various petrochemical processes is one of the most intensively developing fields of catalysis [1-3]. The composites formed via supporting metals contain particles of an active component with a narrow pore size distribution and can be used for the preparation of slurry catalyst systems, particularly as precursors of catalytically active nanoparticles. These supports include mesoporous phenol-formaldehyde polymers (with a pore size of 2-50 nm), which combine the qualities of both inorganic mesoporous materials (MCM-41 [4, 5], SBA-15 [6]) and hydrophobic organic supports (Cact, polystyrene) [7, 8]. It has been previously shown that Pd nanoparticles supported on mesoporous phenol-formaldehyde polymers exhibit activity in the hydrogenation of alkynes and dienes [9]. However, the size distribution of nanoparticles in the resulting catalysts is inhomogeneous and relatively broad; this feature is attributed to the fact that the metal ions are not immobilized within the pores of the support.

Immobilization of metal ions can be implemented by the surface modification of the polymer matrix with various functional groups (NH_2 , SO_3H , PPh_2) [10– 12]. The presence of these groups provides a further immobilization of the metal ions, stabilization of the nanoparticles, and a regular incorporation thereof into the pore space. In addition, the above groups act as modifying agents for the surface of nanoparticles of transition metals, in particular platinum and palladium, and can have a significant effect on the activity and selectivity of the catalyst [13-17].

Possible ligands for immobilization on the support surface are dendrimers, which are spherically symmetrical macromolecules with a regular branched structure. The use of dendrimers makes it possible to effectively retain metal nanoparticles within the pores of the support owing to a large number of functional groups; this feature prevents the elution of the metal during reaction; therefore, the catalyst can be used repeatedly [18–27].

Another practicable method of immobilizing particles on the support surface is the modification of the original polymer matrix with negatively charged sulfo groups $(-SO_3^-)$. An interaction between the metal cation and the sulfo group of the support is intended to provide the immobilization of the metal ions and the nanoparticles formed from these ions in the pores of the support [28].

In this study, a set of mesoporous phenol-formaldehyde polymers modified with third-generation polypropylenimine (PPI) dendrimers and sulfo groups was synthesized. The modified polymers were subsequently used as supports for synthesizing palladium and platinum catalysts for the hydrogenation of phenylacetylene and as precursors of catalysts for naphthalene hydrogenation under severe conditions.

EXPERIMENTAL

Materials

The reactants were phenylacetylene (98%, Aldrich); naphthalene (analytical grade, Reakhim); 1,4diaminobutane (Ferak); acrylonitrile (99+%, Acros Organics); triblock copolymer Pluronic F127 ($M_n =$ 12600, EO₁₀₆-PO₇₀-EO₁₀₆, Aldrich); phenol (highpurity grade, Reakhim); formaldehyde (37% aqueous solution, Sigma-Aldrich); sodium hydroxide (reagent grade, Irea 2000); hydrochloric acid (reagent grade, Irea 2000); chloromethyl methyl ether (technical grade, Sigma-Aldrich); aluminum chloride (99+%, Sigma-Aldrich); and chlorosulfonic acid ($\geq 98\%$, Fluka). The solvents were methanol (99+%, AcrosOrganics); ethanol (analytical grade, Irea 2000); chloroform (Purum, Ecos-1); and dimethylformamide (reagent grade, Khimmed). The solvents were purified by distillation over 4 Å molecular sieves. Dendrimer $DAB(NH_2)_{16}$ was synthesized under laboratory conditions as described in [29].

The source of the metal for the synthesis of Pd and Pt catalysts was palladium(II) acetate (99.9%, Aldrich) and tetraammineplatinum(II) chloride, respectively; the latter was prepared from $H_2[PtCl_6] \cdot 6H_2O$ as described in [30].

Equipment and Experimental Procedures

Low-temperature nitrogen adsorption. Nitrogen adsorption/desorption isotherms were recorded at a temperature of 77 K using a Gemini VII 2390 instrument. Prior to the measurements, the samples were degassed at 130°C for 6 h. The surface area (S_{BET}) was calculated by the Brunauer–Emmett–Teller (BET) method on the basis of adsorption data at relative pressures ((P/P_0) of 0.04–0.20. The pore volume and the 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 determined according to the amount of adsorbed nitrogen at $P/P_0 = 0.995$.

Transmission electron microscopy (TEM). TEM analysis was conducted employing a LEO912 AB OMEGA microscope. The processing of the micrographs and the calculation of the average particle size were conducted using the ImageJ software.

X-ray photoelectron spectroscopy (XPS). XPS studies were conducted on a Kratos Axis Ultra DLD electronic device. Photoelectrons were excited using the AlK α X-ray emission of an aluminum anode (1486.6 eV). Photoelectron peaks were calibrated against the carbon C 1s line at a binding energy of 284.8 eV. The pass energy of the energy analyzer was 160 eV (survey scans) and 40 eV (individual lines).

Solid-state NMR spectroscopy. Analysis by solid state (CPMAS) ¹³C NMR spectroscopy was conducted on a Varian NMR Systems instrument at an

operating frequency of 125 MHz in a pulsed mode at a speed of 10 kHz.

Atomic emission spectroscopy. The quantitative determination of palladium and platinum in the samples was conducted by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an IRIS Interpid II XPL instrument (Thermo Electron Corp., United States) in radial and axial viewing configurations at wavelengths of 310 and 95.5 nm.

Gas–liquid chromatography. The substrates and the reaction products were analyzed using a ChromPack CP9001 gas chromatograph equipped with a flame ionization detector and a 30 m \times 0.2 mm capillary column with the SE-30 grafted stationary phase.

Synthesis of Supports Based on Mesoporous Phenol– Formaldehyde Polymers

Synthesis of mesoporous phenol-formaldehyde polymer MPF. Mesoporous phenol-formaldehyde polymers were synthesized as described in [31]. PF resole, which is a soluble low-molecular-weight phenolic resin, was produced during the polymerization of phenol and formaldehyde in the presence of a base. The phenol/formaldehyde/NaOH molar ratio was 1 : 2 : 0.1.

In a typical procedure, 6.0 g of phenol (0.064 mol) was melted in a glass reactor equipped with a magnetic stirrer and a reflux condenser at 40-42°C. After that, 1.28 g (0.0064 mol) of a 20% aqueous solution of NaOH was added under stirring for 10 min. Next, 10.39 g (0.128 mol) of a 37% aqueous solution of formaldehyde was added dropwise to the resulting reaction mixture at 50° C; the reaction was run at 70– 75°C under stirring for 60 min; after that, the reaction mixture was cooled to room temperature. The pH of the reaction mixture was adjusted to a value of ~ 7.0 using a 0.6 M HCl solution. Water was removed using a rotary vacuum evaporator at 50°C. The final product was dissolved in ethanol (a grayish brown 20% ethanol solution); after that, the precipitate of sodium chloride was separated by filtration.

The MPF-1 and MPF-2 samples were synthesized using the procedure of solvent evaporation induced self-assembly. The carbon precursor was PF resole; block copolymer Pluronic F127 ($M_w \sim 12600$) was used as a template. For all the samples, the phenol/formaldehyde molar ratio was 1 : 2; the phenol/template (F127) ratio was 1 : 0.013. In a typical procedure, $10.0 \text{ g} (7.94 \times 10^{-4} \text{ mol})$ of F127 was placed in a round-bottom flask equipped with a magnetic stirrer and dissolved in 130 mL of ethanol at room temperature under stirring. After that, 46 g of the PF resole precursor containing 5.7 g (0.061 mol) of phenol and 3.7 g (0.122 mol) of formaldehyde was added. The mixture was stirred for 10 min to obtain a homogeneous solution, which was subsequently poured into a Petri dish. The ethanol contained in the reaction mixture was evaporated at room temperature for 5-8 h; after that, the Petri dish was placed in a desiccator and held at 100°C for 24 h. The product, which was a semitransparent grayish brown film, was ground to a powder.

The template was removed via calcining the sample in a muffle furnace at a temperature of 350° C in an inert atmosphere of argon for 150 min. The heating rate was 1°C/min; the volumetric flow rate was 90 mL/min. The resulting product was a black powder. The yield of the MPF-1 and MPF-2 samples was 6.5 and 6.1 g, respectively. ¹³C NMR (ppm): 29 (CH₂), 132 (CH_{Ar}), 153 (C_{ArOH}) for sample 1 and 27 (CH₂), 128.5 (CH_{Ar}), 154.5 (C_{ArOH}) for sample 2.

Synthesis of mesoporous chloromethylated phenolformaldehyde polymer MPF-CH₂Cl-(1). Modification with chloromethyl groups was conducted as described in [11]. Two grams of mesoporous polymer MPF-1 and 20 mL (0.26 mmol) of chloromethyl methyl ether were placed in a round-bottom flask equipped with a magnetic stirrer and a reflux condenser. The resulting suspension was admixed with 8.0 g (1.5×10^{-3} mol) of AlCl₃; after that, the reaction was run under stirring for 10 h. After reaction, the suspension was filtered off; the remaining black residue was washed three times with water and three times with acetone. The resulting modified MPF-CH₂Cl polymer was a black powder. The product yield was $2.2 \text{ g}^{-13}\text{C}$ (ppm): 27 (CH₂), 128.5 (CH_{Ar}), 154.5 $(C_{ArOH}).$

Synthesis of sulfonated mesoporous phenol-formaldehyde polymer (MPF-SO₃H). In a typical procedure, a mesoporous phenol-formaldehyde polymer powder was placed in a three-necked flask equipped with a magnetic stirrer and a reflux condenser and dispersed in anhydrous CH₂Cl₂; after that, chlorosulfonic acid was added dropwise [32]. The reaction was run at 0°C in an argon atmosphere under stirring for 24 h. Three materials with different amounts of deposited sulfo groups were prepared. The ratio between the weight of the polymer (g) and the amount of acid (mL)was 0.55, 2.3, and 3.3 for the MPF–SO₃H-a, MPF– SO₃H-b, and MPF–SO₃H-c materials, respectively. The yield of the MPF–SO₃H-a, MPF–SO₃H-b, and MPF-SO₃H-c samples was 1.80, 1.35, and 1.25 g, respectively.

Synthesis of DAB(NH₂)₁₆ dendrimer-functionalized mesoporous phenol-formaldehyde polymer MPF-PPI-G3. One gram of chloromethylated polymer MPF-CH₂Cl and 1.0 g (0.59 mmol) of DAB(NH₂)₁₆, which was predissolved in a mixture of 5 mL of water and DMF in a ratio of 1 : 1, were placed in a round-bottom flask equipped with a magnetic stirrer and a reflux condenser. The reaction was run at a temperature of 80°C under stirring for 24 h. An effective occurrence of the reaction was evidenced by a gradual discoloration of the solution above the precipitate. After reaction, the resulting solid precipitate was separated by centrifugation and washed three times with water and three times with methanol. The yield of the MPF–PPI-G3-(1) product, which was a black powder, was 1.35 g. 13 C (ppm): 35.2 (CH₂), 132.3(CH_{Ar}), 150.3 (C_{ArOH}).

Synthesis of Pd and Pt Catalysts Based on Phenol– Formaldehyde Polymers

Synthesis of catalyst MPF-PPI-G3-Pd. Palladium catalysts based on dendrimer-modified mesoporous phenol-formaldehyde polymers were synthesized by the impregnation of the original supports with a $Pd(OAc)_2$ solution and the subsequent reduction of NaBH₄. In a typical procedure, 1.0 g of mesoporous polymer MP-PPI-G3 was preliminarily dried in a rotary vacuum evaporator at a temperature of 60°C for 60 min. The dried sample was placed in a round-bottom flask equipped with a magnetic stirrer and a reflux condenser; after that, 420 mg (1.87 mmol) of palladium acetate and 20 mL of CHCl₃ were added. The reaction was run at room temperature under stirring for 12 h. After this period, CHCl₃ was separated by centrifugation. The resulting catalyst precursor was suspended in 30 mL of CHCl₃ and 20 mL of methanol; 720 mg (18.95 mmol) of sodium borohydride was added portionwise. Reduction was conducted at 70°C for 24 h. To remove the borax formed as a byproduct, the resulting mixture was washed three times with water and three times with methanol. The remaining solid product was dried in air. The resulting sample was a black powder with a weight of 1.16 g.

XPS, eV: 400.1 (N 1s, N–C, 3.9%); 335.6 (Pd° $3d_{5/2}$, 6.3%), 338.4 (PdO $3d_{5/2}$, 0.2%); 285.0 (C 1s, C–C, 41.9%), 286.4 (C 1s, C–O, N–C, 20.2%), 287.7 (C 1s, C=O, 6.5%), 289.1 (C 1s, O–C=O, 3.6%); 532.5 (O 1s, 17.3%). ICP-AES: 10.0 wt %.

Synthesis of catalyst MPF–SO₃H–Pd-b. Synthesis was conducted similar to the above procedure. The precursors were 620 mg of the sulfonated mesoporous MPF–SO₃H-b polymer and 65 mg (0.29 mmol) of palladium acetate in 6 mL of CHCl₃. The reaction was run at room temperature with stirring for 8 h. Chloroform was removed in a rotary vacuum evaporator at 30° C.

Reduction was conducted via suspending the resulting catalyst precursor in 6 mL of $CHCl_3$ and 3 mL of methanol; 100 mg (2.7 mmol) of sodium borohydride was added portionwise to the suspension. The resulting sample was a black powder with a weight of 550 mg.

XPS, eV: 167.9 (S $2p_{3/2}$, 0.1%); 335.3 (Pd° $3d_{5/2}$, 1.7%), 337.9 (Pd²⁺ $3d_{5/2}$, 0.3%); 284.8 (C 1s, C–C, 52.6%), 286.3 (C 1s, C–O, 14.5%), 287.4 (C 1s, C=O, 5.3%), 288.8 (C 1s, O–C=O, 14.5%); 532.5 (O 1s, 21.7%). ICP-AES: 2.24 wt %.

Synthesis of catalyst MPF–SO₃H–Pd-c. Synthesis was conducted similar to the above procedure, yet with some differences. The precursors were 815 mg of sulfonated mesoporous phenol–formaldehyde poly-



Fig. 1. Micrographs of polymers (a) MPF-1 and (b) MPF-2.

mer MPF–SO₃H-(c)-c predried in a rotary evaporator at 50°C and 86 mg (0.38 mmol) of palladium acetate in 6 mL of CHCl₃. The reaction was run for 24 h; after that, CHCl₃ was separated by centrifugation. Pd(II) was reduced to Pd(0) using 162 mg (4.38 mmol) of NaBH₄ in 5 mL of CHCl₃ and 3 mL of CH₃OH. The mass of the resulting product, which was a black powder, was 770 mg.

XPS, eV: 167.9 (S $2p_{3/2}$, 0.65%), 169.7 (C $2p_{3/2}$, R– SO₃H, 0.35%); 335.6 (Pd⁰ $3d_{5/2}$, 1.2%), 337.9 (Pd²⁺ $3d_{5/2}$, 0.1%); 284.8 (C 1s, C–C, 53.2%), 286.3 (C 1s, C–O, 13.3%), 287.3 (C 1s, C=O, 3.7%), 288.9 (C 1s, O–C=O, 3.7%); 533 (O 1s, 23.8%). ICP-AES: 3.2 wt %.

Synthesis of catalyst MPF–SO₃H–Pt-a. Platinum catalysts based on sulfonated mesoporous phenol–formaldehyde polymers were synthesized by a similar procedure by impregnating the polymers with a $[Pt(NH_3)_4]Cl_2$ solution and subsequently reducing with NaBH₄. The precursors were 1.0 g of the mesoporous polymer predried in a rotary vacuum evaporator at 60°C for 60 min and 3 mL of an aqueous solution of $[Pt(NH_3)_4]Cl_2$ (85 mg, 0.25 mmol). After the reaction, water was removed in a rotary vacuum evaporator at 55°C.

To reduce Pt(II) to Pt(0), the resulting catalyst precursor was suspended in 2 mL of water; 48.5 mg (1.3 mmol) of NaBH₄ was added portionwise to the suspension. The reaction was run at room temperature under stirring for 1 h. The resulting product was a black powder with a weight of 900 mg.

XPS, eV: 71.4 (Pt⁰ $4f_{7/2}$, 0.1%), 73.4 (Pt²⁺ $4f_{7/2}$, 0.2%); 167.6 (S $2p_{3/2}$, R–SO₃⁻, 0.5%), 168.4 (C $2p_{3/2}$, R–SO³H, 0.5%); 284.8 (C 1*s*, C–C, 53.7%), 286.4 (C 1*s*, C–O, 16.3%), 288.2 (C 1*s*, O–C=O, 4.82%); 532.5 (O 1s, 23.7%). ICP-AES: 2.6 wt %.

Synthesis of catalyst MPF–SO₃H–Pt-b. Synthesis was conducted by a procedure similar to the previous one. The precursors were 490 mg of the mesoporous polymer predried in a rotary vacuum evaporator at 60°C for 60 min, 41 mg (0.123 mmol) of Pt(NH₃)₄Cl₂ in 8 mL of distilled water. The reaction was run at room temperature under stirring for 24 h; after that, the solvent was removed by centrifugation.

To reduce Pt(II) to Pt(0), the resulting catalyst precursor was suspended in 5 mL of water; 51 mg (1.37 mmol) of sodium borohydride was added portionwise to the suspension. The product was a black powder with a weight of 380 mg.

XPS, eV: 71.2 (Pt° $4f_{7/2}$, 0.082%), 73.5 (Pt²⁺ $4f_{7/2}$, 0.096%), 75.6 (Pt⁴⁺ $4f_{7/2}$, 0.022%); 168.1 (S $2p_{3/2}$, R–SO₃H, 0.1%); 284.8 (C 1s, C–C, 56.2%), 286.5 (C 1s, C–O, 15.2%), 288.4 (C 1s, O–C=O, 4.6%); 532.5 (O 1s, 23.8%). ICP-AES: 1.5 wt %.

Catalyst Testing Procedure

Calculated amounts of the catalyst and the substrate were placed in a thermostatically controlled steel autoclave equipped with an insertable glass tube and a magnetic stirrer. The autoclave was hermetically sealed, filled with hydrogen to a pressure of 1.0 or 5.0 MPa and held at 80°C for 1 h or 15 min or at 400°C for 5 h. After reaction, the autoclave was cooled below room temperature and unsealed. The reaction mixture was analyzed by gas—liquid chromatography.

The catalyst activity for each reaction was calculated according to [33] as the amount of the substrate reacted per mole of the metal on the particle surface.

RESULTS AND DISCUSSION

Support Synthesis and Modification

Mesoporous organic polymers based on phenol– formaldehyde resins were synthesized as initial supports. The first stage of the synthesis consisted in the formation of a phenol–formaldehyde precursor, which was subsequently structured around the Pluronic F127 template by self-assembly. The resulting intermediate product was subjected to thermal polymerization at 100°C for strengthening the structure and then to calcination in an inert atmosphere at a temperature of 350°C for 3 h to remove the template.

Characteristics of the resulting materials are shown in Table 1 and Figs. 1 and 2.

According to low-temperature nitrogen adsorption, the samples exhibit a high specific surface area of 383 and 579 m²/g, respectively, and are characterized by type IV curves with a hysteresis loop in a relative pressure range of 0.4-0.6, which indicate the presence of micropores in the structure of the material.

The TEM micrographs (Fig. 1) show clearly evident channels and hexagonal cells with a diameter of ~ 10 nm characteristic of SBA-15 mesoporous materials [34]. Thus, the low-temperature nitrogen adsorption/desorption and TEM data suggest that all the samples have an ordered porous structure.

The ${}^{13}C$ NMR spectra of the samples (Fig. 2) exhibit signals in a region of 110-150 ppm corresponding to the C atoms of aromatic moieties; the signals in a range of 150-170 ppm are attributed

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Sample	$S_{ m sp.},$ m²/g	Pore volume, cm ³ /g	Pore size, nm	Polymer mass (g)/amount of acid (mL)	S, %	Cl, %	N, %
MPF-1	579	0.50	4.5	_	_	_	_
MPF-2	383	0.44	4.2	_	_	_	_
MPF-CH ₂ Cl	541	0.46	4.6	_	_	1.9	_
MPF-PPI-G3	170	0.21	3.7	_	_	_	2.9
MPF-SO ₃ H-a	75	0.10	5.2	0.55	2.1	—	_
MPF-SO ₃ H-b	149	0.12	3.7	2.3	1.38	_	_
MPF-SO ₃ H-c	275	0.22	3.3	3.3	<1	_	_

Table 1. Physicochemical characteristics of the mesoporous polymers before and after modification

to the phenol atoms carbon (ArOH); the signals at 10–50 ppm correspond to methylene bridges and formaldehyde residues [31].

Support Modification with PPI Dendrimers

The prepared mesoporous supports were subjected to functionalization for the subsequent immobiliza-

tion of PPI dendrimers and sulfo groups on the supports. The surface modification of the MPF-1 material was conducted in two steps: (1) activation with chloromethyl methyl ether in the presence of $AlCl_3$ and the subsequent introduction of CH_2Cl groups and (2) reaction of the activated polymer with PPI dendrimer DAB(NH₂)₁₆ (see Scheme 1).



Scheme 1. Stages of the synthesis of the mesoporous MPF-PPI-G3 support.

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The chloromethylation of the mesoporous carbon polymers occurred by the mechanism of electrophilic aromatic substitution in the *ortho* and *para* positions relative to the hydroxyl groups of the aromatic moieties. The $ClCH_2^+$ particles were capable of attacking both the unoccupied and occupied positions (*ipso* attack); the last-mentioned process led to the partial destruction of the surface layer of the support and a decrease in the specific surface area thereof, as con-firmed by low-temperature nitrogen adsorption—desorption (Table 2). The chlorine content in the MPF—

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Fig. 2. CPMAS ¹³C NMR spectra of the MPF-1, MPF-2, MPF-PPI-G3, and MPF-SO₃H-a samples.

CH₂Cl sample was determined by mercurimetric titration.

Functionalization with PPI dendrimers was conducted in a methanol–DMF mixture. The choice of this solvent was based on the low solubility of amineterminated dendrimers in most organic solvents (including DMF), except for water and lower alcohols (ethanol, methanol), whereas it was DMF that contributed to the occurrence of the reaction by the $S_N 2$ mechanism. The grafting of the dendrimers to the inner walls of the pores of the mesoporous carbon polymers contributed to a significant decrease in the specific surface area owing to steric hindrances generated by the dendrimers (Table 2). However, both samples preserved a regular porous structure, as evidenced by low-temperature nitrogen adsorption—desorption.

The NMR spectra of the MPF–PPI-G3 material preserved signals at 150–170, 110–150, and 10–50 ppm, which are characteristic of the aryl and phenol moieties and methylene bridges (Fig. 2). The signals of the α -methylene groups at the nitrogen atoms (40–55 ppm) are weak because they overlap with the methylene groups of the initial support. However, it is evident that the peak maximum is shifted to the region of 50–60 ppm corresponding to the α -methylene groups at the tertiary amino groups of the dendrimers (50–54 ppm) and the $-N-CH_2-N-$ moieties formed during the crosslinking of the dendrimers with each other.

Sulfonation of the Mesoporous Support

Surface modification with sulfo groups was conducted using chlorosulfonic acid (Scheme 2, reaction (a)). Three sulfonated mesoporous polymers with different amounts of chlorosulfonic acid added during the synthesis and, as a consequence, with different sulfur content on the surface of the material were synthesized.

The data in Table 1 show that an increase in the amount of chlorosulfonic acid used to modify the polymers leads to an increase in the sulfur content in the final product and a simultaneous decrease in the surface area of the material; the decrease can be attributed to the occurrence of *ipso* substitution in the aromatic moieties (Scheme 2, reaction (b)). This process partially destroys the polymer structure and thus causes a decrease in the specific surface area and an increase in the pore size.

		XPS, %										
No. Catalyst	Catalyst							Pd 3d _{5/2} , % (eV)		Pt 4f _{7/2} , % (eV)		
	0	C	S	Ν	Pd	Pt	Pd ⁰ , % (eV)	PdO,% (eV)	Pt ⁰ , % (eV)	Pt ⁺² , % (eV)	Pt ⁺⁴ , % (eV)	
1	MPF-PPI-G3-Pd	17.3	72.3	_	3.9	6.5	_	97 (335.6)	3 (338.4)	_	_	_
2	MPF-SO ₃ H-Pd-c	21.7	76.2	0.1	_	2.0	_	85 (335.3)	15 (337.9)	_	_	_
3	MPF-SO ₃ H-Pd-b	23.8	73.9	1.0	_	1.3	_	92 (335.6)	8 (337.9)	_	_	_
4	MPF-SO ₃ H-Pt-a	23.7	74.9	1.0	_	_	0.3	_	_	26 (71.4)	74 (73.4)	_
5	MPF-SO ₃ H-Pt-c	23.8	75.9	0.1	_	_	0.2	_	_	41 (71.2)	48 (73.5)	11 (75.6)

Table 2. Relative contributions of components of the XPS spectra and the corresponding chemical states of the elements



Scheme 2. Sulfonation of the mesoporous support:(a) sulfonation of the mesoporous phenol-formaldehyde polymer;(b) *ipso* attack of the aromatic ring during the sulfonation of the polymer.

An additional peak with a maximum at 168-170 ppm corresponding to the carbon atoms of the aromatic ring that are directly bound to the introduced sulfo groups is observed in the ¹³C NMR spectrum of the sulfonated sample (Fig. 2). A shift to the region of weaker fields is also observed for the carbon atoms corresponding to the bridging CH₂ groups; it can be attributed to the appearance of CH₂Cl- or CH₂OHgroups, which result from the ipso attack of the aromatic ring, in the polymer structure. The ¹³C NMR spectrum of the sulfonated sample exhibits a peak in the region of 168 ppm; it can be assigned to the carboxyl groups bound to the benzene ring. The appearance of these groups suggests that, during synthesis, the surface of the mesoporous polymer undergoes partial oxidation.

The above data show that, despite the partial degradation of the structure of the material during sulfonation, all the samples preserve regular porosity and exhibit the adsorption isotherm characteristic of a mesoporous material.

Synthesis of Catalysts

The resulting mesoporous materials modified with sulfo groups or polymers were used as supports for catalysts based on platinum and palladium. The metal was supported by two different methods. In the first case, after the impregnation of the material with a respective metal salt, the solvent was removed using a rotary vacuum evaporator (the MPF–SO₃H–Pt-a and MPF–SO₃H–Pd-c samples); after that, the metal was reduced with sodium borohydride. The MPF–PPI- G3, MPF–SO₃H–Pd-b, and MPF–SO₃H–Pt-c samples were synthesized by the second method, in which, after impregnation, the solvent was removed by centrifugation. The resulting catalysts were characterized by TEM and XPS.

The highest metal content is observed in the MPF-PPI-G3–Pd sample, which was synthesized using a support modified with dendrimers which are polydentate ligands and therefore capable of retaining a significantly larger amount of the metal than SO₃H- and OH groups. It has been found that the method of supporting of palladium has a considerable effect on the morphology of particles in the resulting catalyst. In the first approach, the metal particles are located both within the pores and on the surface of the polymer and have a larger average size and a broader size distribution. The use of the second approach (centrifugation) provides the formation of catalysts in which the particles are mostly located within the pores of the support. During evaporation, the entire deposited metal, including the unadsorbed metal, remains on the sample surface; as a consequence, large particles are formed outside the pores of the support (Figs. 3a, 3b).

According to XPS, in the palladium catalysts, the metal is mostly zero-valent and the fraction of oxide does not exceed 15% (Table 2). At the same time, the fraction of the zero-valent metal in the platinum catalysts is significantly lower; in the MPF–SO₃H–Pt-a catalyst, platinum is mostly in a divalent state (74%); in the MPF–SO₃H–Pt-c catalyst, it is in the form of both Pt²⁺ (48%) and Pt⁴⁺ (11%).



Fig. 3. Micrographs and particle size distribution of (a) MPF-PPI-G3-Pd, (b) MPF-SO₃H-Pd-b, (c) MPF-SO₃H-Pd-c, (d) MPF-SO₃H-Pt-a, and (e) MPF-SO₃H-Pt-c.

The assignment of signals of carbon in the XPS spectra was conducted in accordance with [35]. On the surface of the synthesized catalysts, the spectrum is represented mostly by aromatic moieties (284.8 eV) corresponding to the structure of the original mesoporous phenol–formaldehyde polymer and aliphatic chains (285.1 eV) corresponding to the bridging CH_2 groups within both the support and the grafted dendrimers (in the case of the MPF–PPI-G3–Pd sample). The presence of the C=O and O–C=O moieties

(287.1–289.4 eV), the fraction of which is $\sim 10\%$, is apparently attributed to the partial oxidation of the support during the calcination of the template.

In should be noted that the platinum-containing samples do not exhibit a peak corresponding to the C=O group. Apparently, the reduction of Pt(II) in an aqueous medium is accompanied by the simultaneous reduction of the C=O group to the C-OH group. In addition, the absence of a peak corresponding to the C=O bonds in the XPS spectra of the Pt catalysts, in

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Fig. 3. Contd.

conjunction with the partial reduction of the metal, can indicate that the C=O and COOH groups formed during the calcination of the template are mostly reduced precisely at the expense of Pt(0) or Pt(II).

The N 1s spectrum (for the dendrimer-containing MPF–PPI-G3–Pd sample) exhibits the most intense signal which, according to [36], corresponds to the tertiary amino groups of the dendrimer NR₃ (399.9 eV) and the signal of NR₄⁺ (401 5 eV), which can indicate the electron density transfer from the amino groups of the dendrimer to the palladium nanoparticles the surface of which has a partial positive charge.

The signals at 167.6 (sulfones [37]), 167.9–168.4 (sulfo groups according to [32, 38, 39]), and 169.7 eV (unionized sulfo groups according to [40]) correspond to sulfur on the surface of the sulfonated catalysts. In the case of the MPF–SO₃H–Pt-c and MPF–SO₃H–Pd-b samples, sulfur is present only in the form of a sulfo group. The MPF–SO₃H–Pd-c sample, along with ions of sulfo groups, contains unionized sulfo groups; this feature can be attributed to the adsorption of chlorosulfonic acid. In the MPF–SO₃H–Pt-a cat-

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alyst with the highest sulfur content, sulfur is present in the form of both sulfo groups and sulfones.

Catalytic Experiments

The resulting mesoporous hybrid catalysts were tested in the hydrogenation of phenylacetylene and naphthalene (Tables 3, 4). The phenylacetylene hydrogenation products were styrene and ethylbenzene. The catalyst activity in the phenylacetylene hydrogenation increased in the following order: MPF–SO₃H–Pt-a < MPF–SO₃H–Pt-c < MPF– PPI-G3–Pd < MPF–SO₃H–Pd-b < MPF–SO₃H– Pd-c; it was 102, 930, 1032, 2619, and 2809 min⁻¹, respectively (Table 3).

In the case of dendrimer-containing catalyst 1, the styrene selectivity was 92%. In this case, this feature can be attributed to the donor effect of the polydentate N-containing ligand, which increases the electron density on the palladium surface and thus hinders the readsorption of the alkene [41–43]. An increase in the reaction time to 1 h had hardly any effect on the selectivity.

Conditions: 80°C, 15 min, 1.0 MPa H_2									
No.	Catalyst	conversion, %	styrene, %	ethylbenzene, %	substrate/ catalyst	TOF _S , min ⁻¹			
1	MPF-PPI-G3-Pd	37	92	8	9300	1032			
1	MPF-PPI-G3-Pd*	98	92	8	9300	_			
2	MPF-SO ₃ H-Pd (b)	95	88	12	8000	2619			
2	MPF-SO ₃ H-Pd (b)*	100	35	65	8000	—			
3	MPF-SO ₃ H-Pd (c)	87	86	14	9900	2809			
4	MPF-SO ₃ H-Pt (a)	4.3	96	4	8000	102			
5	MPF-SO ₃ H-Pt (c)	43	89	11	8000	930			

 Table 3. Phenylacetylene hydrogenation

* 2 h.

Table 4. Naphthalene hydrogenation

Conditions: 400°C, 5 h, 5.0 MPa H ₂ , 10 wt % naphthalene in hexane									
No.	catalyst	conversion, %	hydrogenation	n products, %	substrate/	$\mathrm{TOF}_\mathrm{S}, \mathrm{h}^{-1}$			
	Catalyst		tetralin	decalin	catalyst				
1	MPF-PPI-G3-Pd	90	19	81	67	222			
2	MPF-SO ₃ H-Pd (b)	20	5	95	82	82			
3	MPF-SO ₃ H-Pt (c)	30	9	91	99	103			

Pd-containing catalysts 2 and 3 modified with sulfo groups exhibited higher activity than platinum catalysts 4 and 5 did. Thus, in the 15-min reaction over the Pd-containing catalysts, the styrene selectivity was fairly high (86–88%) at a high conversion of phenylacetylene (87–95%). With an increase in the reaction time to 1 h, the main product became ethylbenzene. These data are consistent with the electronic effect of sulfo groups, which contribute to the formation of a positive charge on the surface of the metal nanoparticles. It is assumed that the metal and the hydroxyl oxy-



Fig. 4. Assumed scheme of interaction between the metal and the sulfo group.

gen of the sulfo group undergo a Coulomb interaction, which results in the electron transfer from the metal to the oxygen (Fig. 4) [28]. As a consequence, the resulting styrene much more readily undergoes readsorption and hydrogenation on the electron-depleted Pd surface. Thus, it was shown [44] that the hydrogenation of 1,3-butadiene over a palladium catalyst supported on sulfo group-modified carbon nanofibers gives exceptionally *n*-butane.

The platinum catalysts, conversely, exhibited an anomalously high styrene selectivity; in the 1-h reaction, the proportion of styrene was 75-90% at a conversion of 45-100%. At the same time, it is known that Pt catalysts typically higher activity and lower selectivity compared with Pd catalysts [45].

Catalyst 4 exhibited a significantly lower activity than that of catalyst 5 (conversion of 4.3 and 43%, respectively). The low activity of catalyst 4 is apparently due to a considerably lower specific surface area of this sample; as a consequence, the metal particles are distributed nonuniformly and undergo agglomeration, which leads to a decrease in the number of accessible adsorption sites and in the specific catalytic activity. It should also be noted that the concentration of sulfo groups on the surface of catalyst 4 is higher. More active catalyst 5, conversely, is characterized by a lower content of sulfo groups on the surface and, at

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the same time, a lower Pt content; platinum occurs both in the form of Pt⁰, the proportion of which is 1.5 times that in catalyst 4, and in the forms of Pt²⁺ and Pt⁴⁺. Apparently, in the case of sulfonated Pt catalysts, a special synergetic effect occurs between Pt⁰, Pt⁴⁺, and SO₃⁻⁻ groups; it is responsible for activity and selectivity. It should be noted that the average particle size did not have a significant effect on the activity and selectivity of both the Pt and Pd catalysts in the phenylacetylene hydrogenation.

Naphthalene hydrogenation. It was of interest to use the prepared nanocomposites as precursors of catalysts for the hydrogenation and hydrocracking of aromatic hydrocarbons. Under severe conditions (400° C, 5.0 MPa H₂), the prepared materials can provide the formation of metal nanoparticles in a hydrocarbon medium owing to the hydrocracking of the polymer support. Naphthalene was selected as a substrate. The hydrogenation products were tetralin and *cis*- and *trans*-decalins.

It is evident that the highest activity was exhibited by the palladium catalyst based on a dendrimer-modified support: apparently, the presence of sulfo groups leads to a considerable decrease in the degree of hydrocracking of the substrate under the reaction conditions; for this reason, the formation of nanoparticles in the suspension is significantly slowed down.

Thus, mesoporous polymeric supports modified with sulfo groups and PPI dendrimers have been synthesized. The Pd and Pt catalysts prepared on the basis of these supports have been tested in the hydrogenation of phenylacetylene and naphthalene. It has been shown that the sulfonated Pd catalysts are most active in the phenylacetylene hydrogenation, whereas the Pt catalysts, conversely, exhibit an anomalously low activity. The dendrimer-containing catalyst exhibits a relatively low activity; however, it preserves a high styrene selectivity even with a significant increase in the reaction time. The highest activity in the naphthalene hydrogenation has been found for the Pd catalyst modified with third-generation PPI dendrimers.

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