Polymer-Modified Supported Palladium Catalysts for the Hydrogenation of Acetylene Compounds¹

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Abstract—Palladium catalysts supported on zinc oxide modified with polyethylene glycol or pectin were synthesized and investigated in the hydrogenation of acetylene compounds. It was established that the polymercontaining catalysts reduce acetylene hyrbons to olefins with high activity, selectivity, and stability. The composition and structure of the obtained composites were studied by elemental analysis, transmission electron microscopy, and XPS spectroscopy. It was found that the nanosized particles of palladium uniformly immobilized on the surface of zinc oxide were formed in the course of the synthesis of a supported polymer/oxide complex.

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INTRODUCTION

In spite of the comparatively short-term history of the development of the polymer-immobilized catalysts [1-4], their potential capabilities and disadvantages currently became clear. Among the disadvantages of polymer supports is their low surface area (as a rule, it rarely reaches tens of square meters per gram). A solution was found in the development of mixed-type carriers: polymers with functional groups were applied as a ligand layer, which is capable of chemically binding catalytic metal complexes, to traditional mineral carriers (metal oxides or activated soot) with high specific surface areas [5]. These systems combine the advantages of traditional homogeneous and heterogeneous catalysts: the retention of a polymer coil as a homogeneous microreactor and the easy separation and repeated use of a catalyst. In the general case, polymers can be bound to a powdered mineral support at any of the stages of its formation [6, 7]. For example, it is believed that the free-radical polymerization of acrylonitrile, vinylpyrrolidone, and vinylcarbazole initiated by benzovl peroxide in the presence of SiO₂ occurs with the formation of grafted chains on its surface. It is reasonable to assume that

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this is not the case at least because this reaction is noncompetitive with homopolymerization in solution followed by the covalent immobilization of grafted polymer chains. Nevertheless, adsorption polymerization methods and even the adsorption of polymers in the pores and on the surface of mineral supports are most promising for catalytic systems on mixed supports as the simplest in preparation.

In this work, we used water-soluble polymers of both synthetic and natural origin (polyethylene glycol and pectin) adsorbed on zinc oxide, on which palladium complexes were immobilized, for the preparation of catalysts on mixed supports. These polymers contained considerable amounts of functional groups (OH, COOH, CHO, NH₂, etc.). Because of this, on the one hand, they were adsorbed on an inorganic support and, on the other hand, they retained palladium complexes to form polymer–metal compounds of different composition and structure with them [10-13].

EXPERIMENTAL

Chemicals

n-Hex-2-yne and phenylacetylene of chemically pure grade were purified by distillation, and the purity was monitored by chromatography. Ethanol (reagent grade), PdCl₂ (reagent grade), HCl (reagent grade, $\rho =$ 1.19 g/cm³), KOH (reagent grade), polyethylene glycol ((PEG); weight-average molecular weight (M_w),

[†] Deceased.

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6000; Sigma-Aldrich), and beet pectin ((BP), $M_w = 15000$; uronide component content, 90.3%; the degree of esterification, 23.7%) were used without additional purification. Zinc oxide (chemically pure) with a specific surface area of 4.4 m²/g was used as an inorganic support.

Preparation of the 1%Pd/ZnO Catalyst

A 0.02 M solution of K_2PdCl_4 (5 mL) was added dropwise to a suspension of zinc oxide (1 g) in water (5 mL) under continuous stirring for 2 h. The resulting catalyst was kept in the mother liquor for 12–15 h; thereafter, it was washed with water and dried in air. The completeness of palladium immobilization was controlled by photoelectric colorimetry based on a difference between the concentrations of palladium ions in the mother liquor before and after the sorption of the metal ions.

Preparation of the 1%Pd–Polymer/ZnO Catalyst

The PEG and BP amounts for the preparation of the catalyst were taken in terms of one transition metal atom per monomer unit. A 5-mL portion of a 0.02 M solution of PEG (0.0042 g in 5 mL of water) or BP (0.0188 g in 5 mL of water) was added dropwise to a suspension of zinc oxide (1 g) in water (5 mL) at room temperature with continuous stirring for 2 h; then, 5 mL of a 0.02 M solution of K_2PdCl_4 was added for 3 h. The resulting catalyst was kept in the mother liquor for 12–15 h; thereafter, it was washed with water until a negative reaction for chloride ions and dried in air. The completeness of palladium immobilization was controlled by photoelectric colorimetry.

Hydrogenation of n-Hex-2-yne and Phenylacetylene

Hydrogenation was performed in a thermostatically controlled long-necked glass flask reactor in an ethanol solution (25 mL) at an atmospheric pressure of hydrogen and a temperature of 40° C with intensive stirring (600–700 rockings per minute). The catalyst (0.01 g) was preliminarily treated with hydrogen directly in the reactor for 30 min with intensive stirring; then, 2.23 mmol (0.09 mol/L) of a substrate was introduced. The substrate amount was taken based on the uptake of 100 mL of hydrogen. The rate of reaction was calculated from the hydrogen uptake per unit time.

The selectivity of the action of catalysts was evaluated as the fraction of the target product in the reaction products at a specified degree of conversion:

$$S = \frac{n_{\rm tp} \times \beta_{\rm reag}}{(n_{\rm reag}^0 - n_{\rm reag})\beta_{\rm tp}} \times 100\%, \tag{1}$$

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where *S* is selectivity, %; n_{reag}^{0} is the initial molar amount of the reagent; n_{tp} and n_{reag} are the molar amounts of the target product and the reagent, respectively, at the point in time when the selectivity was calculated; β_i are the stoichiometric coefficients of substances in the reaction equations, which are equal to unity in this case (for the hydrogenation of alkynes into alkenes).

Conversion was calculated via the formula

$$\alpha = \frac{m_{\text{reag}}^0 - m_{\text{reag}}}{m_{\text{reag}}^0} \times 100\%,$$
 (2)

where α is conversion, %; m_{reag}^0 and m_{reag} are the initial and current masses of the reagent, respectively.

The stability of catalysts was evaluated by carrying out the sequential cycles of substrate (2.23 mmol) hydrogenation on the same sample (0.01 g):

$$TON = 2370n, \tag{3}$$

where TON is the turnover number; 2370 is the turnover number per cycle; and n is the number of cycles carried out.

Error in parallel experiments was no greater than 5%.

Analysis of Catalysts

The analysis of catalysts by X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Axis Ultra DLD photoelectron spectrometer (Kratos Analytical LTD, United Kingdom). The area of analysis for each sample was $220 \times 220 \ \mu\text{m}^2$, and the depth of an analyzed layer was $1-2 \ \text{nm}$. The radiation source was a monochromated Al K_{α} line (1486.6 eV). The energy resolution of the instrument was $0.5 \ \text{eV}$ (for the Ag $3d_{5/2}$ line of silver). For the minimization of charging processes on the sample surface, the powder was pressed in indium foil, and the spectra were measured under identical conditions with the use of a neutralizer and calibrated based on the C1s line of aliphatic compounds (284.8 eV).

A Vario Micro cube elemental analyzer (Elementar Analysensysteme GmbH, Germany) was used in the organic microanalysis of the samples. The carbon content of the samples (CHNS/O) was determined by a method of combustion at 1150°C in the presence of pure oxygen with the subsequent reduction of oxides and separation on a chromatographic column with a thermal conductivity detector.

The palladium content of the mother liquors before and after the precipitation of K_2PdCl_4 was calculated from photoelectric colorimetry data, which were obtained on a Jenway 6300 spectrophotometer (Jenway, United Kingdom) based on calibration curves constructed at the wavelength $\lambda = 421$ nm.

| Sample | Element concentration, wt % | | |
|------------|-----------------------------|--------------------------|--|
| | C _{expt/calcd} | Pd _{expt/calcd} | |
| Pd-PEG/ZnO | 0.17/0.23 | 1.12/1.00 | |
| Pd-BP/ZnO | 0.57/0.67 | 0.96/1.00 | |

Table 1. Carbon and palladium contents of the 1%Pd–polymer/ZnO catalysts

The palladium content of the samples of catalysts was determined on an X-ArtM energy-dispersive X-ray fluorescence spectrometer (Komita, Russia).

The electron-microscopic studies were performed on a JEM-2100 transmission electron microscope (Jeol, Japan) with an accelerating voltage of 100 kV.

The specific surface areas (S_{BET}) of zinc oxide and a polymer-hybrid nanocomposite were measured by the low-temperature adsorption of nitrogen on an Autosorb-1 instrument (Quantachrome, the United States).

Chromatographic Analysis of the Reaction Products of the Hydrogenation of Unsaturated Compounds

The analysis was carried out on a Khromos GKh-1000 chromatograph (Khromos, Russia) with a flameionization detector in the isothermal regime using a BP21 (FFAP) capillary column with a polar phase (PEG modified by nitroterephthalate) 50 m in length and 0.32 mm in inside diameter. The column temperature was 90°C, and the injector temperature was 200°C; helium served as the carrier gas; the injected sample volume was 0.2 μ L. The liquid reaction mixtures were sampled two or three times in the course of an experiment.



Fig. 1. Survey XPS spectrum of 1%Pd–PEG/ZnO.

RESULTS AND DISCUSSION

The advantages of water-soluble polymers include their biodegradability, nontoxicity [14], and the possibility of synthesizing nanocatalysts in aqueous solutions, which is consistent with the principles of green chemistry [15]. In particular, polyethylene glycols are resistant to oxidation and the action of acids and bases; they possess moderate thermal stability, good solvating characteristics, and complex-forming properties with respect to many metals [16].

Synthesis of 1%Pd–Polymer/ZnO Catalysts

According to the photoelectric colorimetry data, 98–99% of the introduced palladium amount was precipitated on zinc oxide modified with BP and PEG. Palladium was also adsorbed quantitatively (to 96%) on ZnO without treatment by a polymer. Thus, in both of the catalysts, the palladium concentration of 1.0 wt % on a total catalyst component basis was close to calculated data.

The results of the X-ray fluorescence elemental analysis of 1%Pd–polymer/ZnO catalysts confirm the data obtained by photoelectric colorimetry. The carbon content determined by organic microanalysis is consistent with the calculated values and indicative of the immobilization of polymers on zinc oxide (Table 1).

The lines of zinc, oxygen, carbon, palladium, and chlorine were detected in the survey XPS spectrum of the 1%Pd–PEG/ZnO catalyst (Fig. 1). An analogous pattern was also observed in the XPS spectrum of 1%Pd–BP/ZnO.

According to the XPS data, palladium in 1%Pd– PEG/ZnO occurred in an oxidized state (Pd²⁺) with a $3d_{5/2}$ binding energy of ~337.4 eV (Fig. 2a). It is likely that a shift toward smaller energies was caused by the interaction of palladium with the modified support matrix and by the formation of a Pd–O bond [17, 18]. In the spectrum of the catalyst modified with pectin, peaks characteristic of both the oxidized (336.8 eV) and reduced (335.4 eV) forms of palladium were detected (Fig. 2b). Probably, the presence of palladium metal in the initial sample of 1%Pd–BP/ZnO was caused by its partial reduction with the functional groups of pectin in the presence of a basic oxide [19].



Fig. 2. The Pd3*d* XPS spectra of the samples of (a) 1%Pd–PEG/ZnO and (b) 1%Pd–BP/ZnO.

After the treatment of catalysts with hydrogen in a reactor at 40°C, palladium was completely reduced to a zerovalent state. The $Pd3d_{5/2}$ XPS spectrum (Fig. 3) exhibited a peak corresponding to the binding energy of palladium in the zerovalent state (~335.2 eV) [20, 21]. Polymer modification significantly affected the particle size of palladium and the distribution of the particles on the support. According to the transmission electron microscopy (TEM) data, the supporting of a palladium compound onto materials preliminarily treated with PEG or BP led to an increase in the dispersity of palladium. Thus, the metal particle sizes of Pd/ZnO prepared without a polymer were 30-35 nm (particles of size >40 nm were also detected), whereas the particle sizes of palladium in the polymer-modified catalysts decreased to 2-4 nm. The sufficiently uniform distribution of an active phase over the oxide surface treated with a polymer has engaged our attention (Fig. 4). Note that the catalysts obtained were characterized by a comparatively developed surface area and a porous structure. Thus, the values of S_{BET}



Fig. 3. The Pd3d XPS spectrum of the reduced sample of 1% Pd-PEG/ZnO.

and pore volumes for Pd-PEG/ZnO or ZnO were 7.9 and 0.035 or 4.4 and 0.025 cm 3 /g, respectively.

Catalytic Properties of 1%Pd–Polymer/ZnO in the Hydrogenation of Phenylacetylene

The polymer-modified catalysts manifested high activity in the reaction of phenylacetylene hydrogenation. Thus, under comparable conditions, the maximum rate of reaction on the polymer-modified catalysts was twice as high as that on a polymer-free analog (Fig. 5).

The rate of hydrogenation of phenylacetylene in the presence of 1% Pd/ZnO increased in the first three minutes and then slowly decreased after reaching 4.0×10^{-6} mol/s (Fig. 5, curve *I*). The maximum yield of styrene (65.7%) is observed after 16 min; in this case, the ethylbenzene content was 28.0% (Fig. 6a).

The hydrogenation of phenylacetylene in the presence of 1%Pd-PEG/ZnO (8.8 × 10^{-6} mol/s) and 1%Pd-BP/ZnO (8.1 × 10^{-6} mol/s) occurred at a high rate: in both cases, it sharply increased with passing through a maximum and then decreased (Fig. 5, curves 2 and 3). According to the data of the chromatographic analysis of the test samples taken in the course of hydrogenation, styrene accumulated on 1%Pd-PEG/ZnO in the initial period; then, it was reduced to ethylbenzene (Fig. 6b). The composition of the reaction mixture similarly changed in the hydrogenation of phenylacetylene on 1%Pd-BP/ZnO. The concentrations of styrene in the presence of the pectin-containing and PEG-modified catalysts reached optimum values (74.5 and 72.2%, respectively) after 7 and 6 min, respectively.

The complete conversion of phenylacetylene into ethylbenzene through the formation of styrene as an intermediate product was observed on all of the catalysts (Fig. 6). The curves of hydrogen uptake confirm the



Fig. 4. Micrographs of the samples of (a) 1% Pd/ZnO, (b) 1% Pd–PEG/ZnO, and (c) 1% Pd–BP/ZnO reduced with hydrogen in a reactor at 40° C and atmospheric pressure.

chromatographic analysis data: the volume of absorbed hydrogen on all of the catalysts was 100 mL (Fig. 7).

The styrene formation selectivity (S_{st}) for 1%Pd– PEG/ZnO and 1%Pd–BP/ZnO was 88.7 and 86.7%, respectively. The 1%Pd/ZnO catalyst exhibited lower selectivity. Both of the polymer-containing catalytic systems were sufficiently stable (TON = 11850-14220), as compared with the unmodified palladium catalyst (Table 2).

The styrene formation selectivity and the activity of the polymer-modified catalysts in the course of three repeated cycles decreased insignificantly (Fig. 8). Thus, in the hydrogenation of phenylacetylene in the presence of 1%Pd–BP/ZnO, the values of S_{st} in the first and third cycles were 86.7 and 83.4%, respectively (Fig. 9).

For the determination of the possibility of reducing phenylacetylene in the presence of styrene, we carried out experiments on the hydrogenation of their mix-



Fig. 5. Changes in the rate of phenylacetylene hydrogenation in the presence of (1) 1%Pd/ZnO, (2) 1%Pd– PEG/ZnO, and (3) 1%Pd–BP/ZnO. Conditions: catalyst sample weight, 0.01 g; temperature, 40° C; H₂ pressure, 0.1 MPa; solvent, ethanol (25 mL); and initial phenylacetylene amount, 2.23 mmol.

tures with ratios of 3:1, 1:1, and 1:3 between the components. We found that the rate of reaction decreased with the olefin content of the substrate, whereas S_{st} remained almost constant (Table 3). By this is meant that the hydrogenation of phenylacety-lene occurs consecutively through the stage of the formation of styrene.

Thus, based on the conducted investigations, we found that the modification of a palladium catalyst with polymers considerably increased its activity and selectivity. The activity and stability increased by a factor of 2, and S_{st} increased by 16–18% in comparison with that of the unmodified catalyst (Table 2).

Catalytic Properties of 1%Pd–Polymer/ZnO in the Hydrogenation of n-Hex-2-yne

All of the catalysts developed exhibited high activity in the stereoselective hydrogenation reaction of *n*-hex-2-yne. The rates of the reaction sharply increased in the first minutes to $(6.2-7.8) \times 10^{-6}$ mol/s and then, after passing through a maximum, decreased to $(1-2) \times 10^{-6}$ mol/s (Fig. 10).

An analysis of changes in the composition of the reaction mixture in the course of the hydrogenation of n-hex-2-yne showed that, in all cases, the process occurred selectively with respect to cis-2-hexene. At a substrate conversion higher than 97%, the concentration of cis-olefin reached a maximum value (85–89%); in this case, the fraction of hexane did not exceed 3%. Upon the continuation of the reaction, hexane and thermodynamically more stable *trans*-2-hexene were accumulated in the products (Fig. 11).

Thus, the hydrogenation reaction of *n*-hex-2-yne in the presence of all of the catalytic systems occurs at high rates with a high *cis*-hexene selectivity. The modification of a catalyst with a macroligand affects its stability, which is higher than the stability of the unmodified palladium catalyst (Table 4). Consequently, the role of the macroligand in these systems is reduced to a stabilizing function and its ability to the formation of the low-dimensional nanoparticles of an active phase



Fig. 6. Changes in the composition of reaction mixtures in the course of phenylacetylene hydrogenation in the presence of (a) 1%Pd/ZnO and (b) 1%Pd–PEG/ZnO: (*1*) phenylacetylene, (*2*) styrene, and (*3*) ethylbenzene. Conditions: catalyst sample weight, 0.01 g; temperature, 40° C; H₂ pressure, 0.1 MPa; solvent, ethanol (25 mL); and initial phenylacetylene amount, 2.23 mmol.

and the prevention of their aggregation in the course of a catalytic process. As a result, the activity and selectivity of the catalysts in the hydrogenation reactions of acetylene compounds considerably increases. Note



Fig. 7. Hydrogen uptake curves for the hydrogenation of phenylacetylene in the presence of (*I*) 1%Pd/ZnO, (*2*) 1%Pd–PEG/ZnO, and (*3*) 1%Pd–BP/ZnO. Conditions: catalyst sample weight, 0.01 g; temperature, 40° C; H₂ pressure, 0.1 MPa; solvent, ethanol (25 mL); and initial phenylacetylene amount, 2.23 mmol.



Fig. 8. Hydrogenation of the sequential portions of phenylacetylene in the presence of (*I*) 1% Pd/ZnO, (*2*) 1% Pd– PEG/ZnO, and (*3*) 1% Pd–BP/ZnO. Initial substrate amount, 2.23 mmol; catalyst sample weight, 0.01 g; solvent, ethanol (25 mL); temperature, 40°C; and H₂ pressure, 0.1 MPa.

that the results obtained can be valuable to petroleum chemistry for the removal of acetylene impurities in the synthesis of vinyl-type monomers from petroleum raw material, (for example, acetylene compounds

Table 2. Results of the hydrogenation of phenylacetylene (2.23 mmol) on palladium catalysts (0.01 g) in ethanol (25 mL) at 40°C and 0.1 MPa

| Catalysts | Maximum rate of reac- tion ($W_{\text{max}} \times 10^{-6}$, mol/s) | $S_{\rm st},$ % | Conversion, % | Stability (TON) |
|--------------|--|-----------------|---------------|-----------------|
| 1%Pd/ZnO | 4.0 | 70.1 | 93.7 | 7110 |
| 1%Pd-PEG/ZnO | 8.8 | 88.7 | 81.4 | 14 220 |
| 1%Pd-BP/ZnO | 8.1 | 86.7 | 85.9 | 11850 |



Fig. 9. Changes in the composition of the reaction mixture in the course of phenylacetylene hydrogenation in the presence of 1%Pd–BP/ZnO in the third cycle: (1) phenylacetylene, (2) styrene, and (3) ethylbenzene. Conditions: catalyst sample weight, 0.01 g; temperature, 40°C; H₂ pressure, 0.1 MPa; solvent, ethanol (25 mL); and initial phenylacetylene amount, 2.23 mmol.



Fig. 10. Changes in the rate of *n*-hex-2-yne hydrogenation in the course of reaction in the presence of (1) 1%Pd/ZnO, (2) 1%Pd–PEG/ZnO, and (3) 1%Pd–BP/ZnO. Conditions: catalyst sample weight, 0.01 g; temperature, 40°C; H₂ pressure, 0.1 MPa; solvent, ethanol (25 mL); and initial phenylacetylene amount, 2.23 mmol.



Fig. 11. Changes in the composition of the reaction mixture in the course of *n*-hex-2-yne hydrogenation in the presence of (a) 1%Pd/ZnO and (b) 1%Pd–PEG/ZnO: (1) *n*-hex-2-yne, (2) *cis*-2-hexene, (3) *trans*-2-hexene, and (4) hexane. Conditions: catalyst sample weight, 0.01 g; temperature, 40° C; H₂ pressure, 0.1 MPa; solvent, ethanol (25 mL); and initial *n*-hex-2-yne amount, 2.23 mmol.

30

Time, min

40

50

60

20

Table 3. Results of the hydrogenation of phenylacetylene–styrene mixtures on the 1%Pd–BP/ZnO catalyst (0.01 g) in ethanol (25 mL) at 40°C and 0.1 MPa

0

10

| Phenylacetylene : styrene ratio in the substrate | Maximum rate of reaction $(W_{\text{max}} \times 10^{-6}, \text{ mol/s})$ | $S_{ m st},$ % | Conversion, % |
|---|--|----------------|---------------|
| 3:1 | 7.8 | 87.3 | 88.2 |
| 1:1 | 7.6 | 88.9 | 93.8 |
| 1:3 | 3.9 | 90.1 | 97.4 |

| Catalysts | Maximum rate of reaction $(W_{\text{max}} \times 10^{-6}, \text{ mol/s})$ | <i>cis</i> -2-Hexene selectivi- ty, % | Conversion, % | Stability (TON) |
|--------------|---|--|---------------|-----------------|
| 1%Pd/ZnO | 6.2 | 86.1 | 98.8 | 9480 |
| 1%Pd-PEG/ZnO | 7.0 | 90.5 | 97.2 | 16590 |
| 1%Pd-BP/ZnO | 7.8 | 89.5 | 99.5 | 33180 |

Table 4. Results of the hydrogenation of *n*-hex-2-yne (2.23 mmol) on palladium catalysts (0.01 g) in ethanol (25 mL) at 40° C and 0.1 MPa

from ethylene, propylene, etc., which inhibit their catalytic polymerization).

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REFERENCES

- 1. Pomogailo, A.D., *Polimernye immobilizovannye metallokompleksnye katalizatory* (Polymeric Immobilized Metal Complex Catalysts), Moscow: Nauka, 1988.
- Pomogailo, A.D., *Kataliz immobilizovannymi kompleksami* (Catalysis by Immobilized Complexes), Moscow: Nauka, 1991.
- Bekturov, E.A., Kudaibergenov, S.E., Zharmagambetova, A.K., Iskakov, R.M., Ibraeva, Zh.E., and Shmakov, S.I., *Polimer-protektirovannye nanochastitsy metallov* (Polymer-Protected Metal Nanoparticles), Almaty: Inst. Organicheskogo Kataliza i Elektrokhimii, 2010.
- 4. Bukhtiyarov, V.I. and Slin'ko, M.G, *Russ. Chem. Rev.*, 2001, vol. 70, no. 2, p. 147.
- Pomogailo, A.D., in Kompleksnye metalloorganicheskie katalizatory polimerizatsii olefinov (Organometallic Complex Catalysts for Olefin Polymerization), vol. X: Sintez i svoistva polimerizatsionno-napolnennykh poliolefinov (Synthesis and Properties of Polymerization-Filled Polyolefins), D'yachkovskii, F.S., Ed., Chernogolovka, Moscow oblast: Inst. Khimicheskoi Fiziki, 1986, p. 63.
- 6. Kroker, R., Shneitsder, M., and Khamani, K., *Usp. Khim.*, 1974, vol. 43, p. 349.
- 7. Papirer, E. and Nguyen, V.T., *J.Polym. Sci.: Polym. Lett. Ed.*, 1972, vol. 10, p. 167.

- Ivanchev, S.S. and Dmitrenko, A.V., in Kompleksnye metalloorganicheskie katalizatory polimerizatsii olefinov (Organometallic Complex Catalysts for Olefin Polymerization), vol. X: Sintez i svoistva polimerizatsionno-napolnennykh poliolefinov (Synthesis and Properties of Polymerization-Filled Polyolefins), D'yachkovskii, F.S., Ed., Chernogolovka, Moscow oblast: Inst. Khimicheskoi Fiziki, 1986, p. 183.
- 9. Kritskaya, D.A. and Ponomarev, A.N., Vysokomol. Soedin., Ser. B: Khim. Polim., 1975, vol. 17, p. 67.
- Tal'roze, R.V., Shandryuk, G.A., Merekalov, A.S., Shatalova, A.M., and Otmakhova, O.A., *Polym. Sci.*, *Ser. B: Polym. Chem.*, 2009, vol. 51, nos. 3–4, p. 57.
- Bu, F.X., Hu, M., Xu, L., Meng, Q., Mao, G.Y., Jiang, D.M., and Jiang, J.S., *Chem. Commun.*, 2014, vol. 62, p. 8543.
- 12. Toshima, N., Adv. Mater. Res., 2009, vols. 317–318, p. 55.
- Kramareva, N.V., Finashina, E.D., Kucherov, A.V., and Kustov, L.N., *Kinet. Catal.*, 2003, vol. 44, no. 6, p. 793.
- 14. Leja, K. and Lewandowicz, G., *Pol. J. Environ. Stud.*, 2010, vol. 19, no. 2, p. 255.
- Sheldon, R.A., Arends, I., and Hanefeld, U., *Green Chemistry and Catalysis*, Weinheim: Wiley–VCH, 2007, p. 434.
- Chen, J., Spear, S.K., Huddleston, J.G., and Rogers, R.D., Green Chem., 2005, vol. 7, p. 64.
- 17. Parambhath, V.B., Nagar, R., and Ramaprabhu, S., *Langmuir*, 2012, vol. 28, p. 7826.
- Tarasenko, Yu.A., Boldyreva, N.A., Gerasimyuk, I.P., Lapko, V.F., and Yatsimirskii, V.K., *Katal. Neftekhim.*, 2003, no. 11, p. 53.
- Khazaei, A., Rahmati, S., Hekmatian, Z., and Saeednia, Sh., J. Mol. Catal. A: Chem., 2013, vol. 372, p. 160.
- 20. Crist, B.V., *Handbook of Monochromatic XPS Spectra*, Mountain View, Calif.: XPS International, 2004.
- 21. Temkin, O.N. and Bruk, L.G., *Russ. Chem. Rev.*, 1983, vol. 52, no. 2, p. 117.

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