Adsorption of $H_3PW_{12}O_{40}$ by porous carbon materials

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Adsorption of $H_3PW_{12}O_{40}$ from water and organic oxygen-containing solvents (AcOH, Me_2CO, MeOH) by carbon mesoporous materials, *viz.*, Sibunit and catalytic filamentous carbons (CFC), was studied. The amount of irreversibly sorbed heteropolyacid is 50—100 mg g^{-1} of support and decreases in the series of solvents: $H_2O > Me_2CO > AcOH > MeOH$. The adsorption capacity of CFC depends on the specific surface, total pore volume, and microstructure of the CFC fiber.

Key words: adsorption, heteropolyacids, catalytic filamentous carbon, Sibunit.

Heteropolyacids (HPA) are strong Brönsted acids and find wide use as homogeneous and heterogeneous catalysts.[1,2] The study of the catalytic and physicochemical properties of HPA is mainly focused on bulky acids; however, supported systems are also of great interest because their activity is not sometimes inferior to that of bulky HPA.

Interest in HPA heterogenation on the support surface as a method for preparation of catalysts for liquid-phase reactions of different types has considerably increased in recent time. Various materials were used as supports.[3—5] Depending on the type of the support, the acid strength of the supported HPA decreases in the series: $SiO_2 > Al_2O_3 >$ carbons,[5] indicating the strong interaction between the HPA and carbon surface. The determination of the heat of adsorption of ammonia showed that the strength of the acidic sites of HPA on active carbon (AC) depends on the amount of supported HPA; however, it is much lower than that for HPA supported on silica gel.[6] The nature of AC-supported HPA particles substantially depends[7] on their concentration in a solution used for preparing supported catalysts. Heteropolyacids precipitated from concentrated aqueous solutions retain Keggin structure on the carbon surface, whereas precipitation from dilute solutions completely destroys their structure. The dispersity and amount of adsorbed HPA can be varied by changing the solvent nature.[3]

In this work, we studied adsorption of $H_3PW_{12}O_{40}$ by porous carbon materials of different natures (Sibunit and catalytic filamentous carbon (CFC)) from water and oxygen-containing solvents (AcOH, MeOH, Me_2CO).

Experimental

Heteropolyacid $H_3PW_{12}O_{40} \cdot 15.41H_2O$ (reagent grade) recrystallized from water was used. Solvents (AcOH, Me_2CO (special purity grade), and MeOH) were used as received.

Carbons of different trade marks (Sibunit-5 (S-5), Sibunit-36P (S-36P), Sibunit-1099 (S-1099), and CFC obtained by methane decomposition using catalysts based on metals of the iron subgroup[8]) were pre-washed in the corresponding solvent and dried in air. Some samples of S-1099 were additionally treated with H_2O_2 (S-1099 (H_2O_2)), HCl (S-1099 (HCl)), or $KMnO_4$ (S-1099 (MnO_4^-)). After refluxing in HCl, the S-1099 sample was washed with water until no Cl ion was found in the filtrate. After refluxing in a solution of $KMnO_4$, the S-1099 sample was contacted with a solution of HCOONa for 1 h and then refluxed in HCl, and the Cl ions were removed with water. The main characteristics of the supports are presented in Table 1.

Adsorption measurements were carried out in a periodically agitated reactor held at a constant temperature (±0.1 °C). The adsorbent (1 g) was loaded into the reactor and heated for 0.5 h *in vacuo* (10 Pa, 120 °C), and HPA (10 mL, 10—150 g L^{-1}) was added. Samples of the solutions (0.1 mL) were taken at certain time intervals, and after dilution the HPA concentration in the solution was measured by spectrophotometry on a Specord M-40 instrument (ν = 32000—42000 cm^{-1}, error of measurement ±10%). In studying HPA desorption from the support, the solution was separated by vacuum filtration, and a pure solvent or a solution of HPA (10 mL) with the concentration lower than the equilibrium one was added to the adsorbent (1 g). The time needed to achieve equilibrium was <2 h. The limiting values of HPA adsorption (a_{max}) were determined from a point where a plateau portion of the adsorption isotherm cuts the adsorption axis. The irreversible adsorption (a_{ir}) was determined by boiling

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Table 1. Main characteristics of carbons

Carbon	S_{sp}	S_{meso}	ΣV_p	V_{meso}	V_{μ}	D_m /Å	Content of metal (wt.%)
	$m^2\ g^{-1}$		$cm^3\ g^{-1}$				
S-1099	402	528	0.6	0.6	0	62	—
S-1099 (HCl)	454	528	0.6	0.6	0	62	—
S-1099 (H_2O_2)	531	528	0.6	0.6	0	62	—
S-5*	200	—	—	—	—	400	—
S-36P*	403	—	0.7	0.3	0.3	—	Fe <1
CFC-1	100	—	0.3	—	0	100	Ni < 1
CFC-2	179	—	0.4	—	—	80—90	Ni, Cu ~0.5
CFC-3	125	—	0.4	—	0	129	Fe <1

* d = 2—3 mm.

1 g of the HPA/C[*] sample in a pure solvent (20 mL) followed by the separation of it by vacuum filtration and burning the sample at 800 °C in a muffle furnace. The a_{ir} value was calculated from the amount of the solid residue.

For IR spectroscopic studies, powdered $H_3PW_{12}O_{40}/C$ samples were sputtered on the NaCl plate. The IR spectra were recorded on a FTIR-8300 spectrometer (Shimadzu) in the 700—1800 cm^{-1} region with a resolution of 4 cm^{-1}.

The porous structure of the supports was determined from the adsorption isotherm of N_2 (77 K). The specific surface (S_{sp}) was calculated by the Brunauer—Emmett—Teller (BET) method. In addition, comparison plots[9] were used to determine the surface of mesopores (S_{meso}) and the volume of micropores (V_{μ}). The mean pore diameter (D_m) was determined using the equation $D_m = 4V_p/S_{sp}$, where V_{pore} is the pore volume.

Samples for transmission electron microscopy (TEM) were prepared by ultrasonic dispersion of $H_3PW_{12}O_{40}/C$ in hexane followed by supporting the suspension on a standard network covered with a perforated carbon film. TEM studies were carried out on a JEM-2010 instrument.

Results and Discussion

Adsorption of HPA on Sibunit. Adsorption of HPA on Sibunits from mixtures with water or organic solvents (MeOH, AcOH, Me_2CO) was studied. Initial regions of the adsorption isotherms are associated with irreversible sorption of HPA (~50—100 mg of HPA per 1 g of support) (Fig. 1, Table 2). The data on irreversible adsorption agree with the published results,[3,4] which emphasize that HPA cannot completely be desorbed from the carbon surface even on boiling in water and MeOH. This indicates the strong interaction of the HPA molecules with the support surface and the possibility of capsulation of sufficiently large HPA molecules (adsorption surface 100 Å)[1] in the narrowest pores of the adsorbent due to the adsorption deformation of the carbon.[10] The adsorption isotherms are of Langmuir type, and the adsorption and desorption curves coincide (see Fig. 1). For all studied solvents, the adsorption isotherms exhibit a plateau. The a_{max} and a_{ir} values are presented in Table 2.

The solvent noticeably affects the adsorption value. The a_{max} values for solvents show the decreasing order: $H_2O > Me_2CO > AcOH > MeOH$. The series does not correspond to the sequence of varying dielectric constants and solubilities of HPA in these solvents. This can be explained by HPA adsorption on the hydrated surface because water plays the binding role in the formation of the crystal structure of HPA.[2] Adsorption from organic solvents decreases with an increase in the solvent polarity, which agrees with the competitive adsorption of the solvent and HPA molecules on the carbon surface.

The size of granules and the type of Sibunit have a negligible influence on HPA adsorption from solutions (see Table 2). This indicates that adsorption on the external surface of the support is insignificant, whereas adsorp-

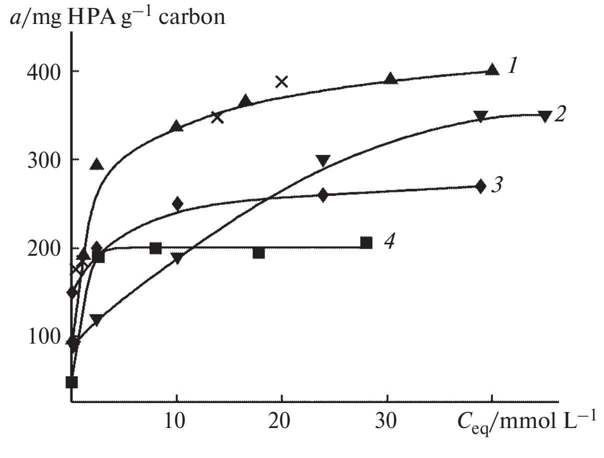

Fig. 1. Adsorption isotherms of $H_3PW_{12}O_{40}$ on Sibunits of different modifications: *1*, adsorption on S-1099 from a mixture with water; *2*, adsorption on S-5 from a mixture with Me_2CO; *3*, adsorption on S-5 from a mixture with AcOH; and *4*, adsorption on S-1099 from a mixture with MeOH (a is adsorption, C_{eq} is equilibrium concentration). Desorption is marked by crosses.

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[*] Hereinafter the porous carbons of different trade marks discussed in the work are implied.

Table 2. Adsorption of $H_3PW_{12}O_{40}$ on carbons of different trade marks

Carbon	D_m /Å	S_{sp} /m^2 g^{-1}	ΣV_p /cm^3 g^{-1}	H_2O		MeOH	
				a_{max}	a_{ir}	a_{max}	a_{ir}
				mg g^{-1}			
S-1099 (d = 2—3 mm)	62	402	0.6	402	100	199	25
S-1099 (d < 0.25 mm)	62	402	0.6	406	100	199	20
S-1099 (H_2O_2) (d = 2—3 mm)	62	531	0.6	245	60	169	5
S-1099 (HCl) (d = 2—3 mm)	62	454	0.6	275	50	250	20
S-5 (d = 2—3 mm)[a]	—	200	—	550	70	165	40
S-36P (d = 2—3 mm)	—	403	0.7	385	10	—	—
CFC-1	100	100	0.3	79	0	18	0
CFC-2	80—90	179	0.4	380	0	140	0
CFC-3	129	125	0.4	260	50	—	—
CFC-3 [b]	129	125	0.4	320	80	—	—

[a] Data of adsorption: a_{max} = 360 mg HPA g^{-1} carbon, a_{ir} = 80 mg HPA g^{-1} carbon (from Me_2CO); a_{max} = 320 mg HPA g^{-1} carbon, a_{ir} = 50 mg HPA g^{-1} carbon (from AcOH).

[b] The carbon was washed free from the Fe ions.

tion on the porous internal surface of carbon makes material contribution. However, a_{max} values do not correlate with surface area S_{sp} determined by the BET method and, correspondingly, with D_m values (see Table 2). Since the correlation was absent for the adsorption of $H_4SiW_{12}O_{40}$ on SiO_2,[3] it was assumed that HPA adsorption is substantially affected by the competitive adsorption of the solvent and water and a considerable change in the sizes of the HPA molecule in a solution due to solvation and association effects.

The nature of surface sites of Sibunit has a strong effect on the adsorption (see Table 2). The a_{max} value decreases in the series of supports pre-oxidized by various reagents: S-1099 > S-1099 (HCl) > S-1099 (H_2O_2). The acidity of the surface carbon sites changes in the same sequence.[8] Thus, the oxidation of the Sibunit surface reduces the sorption activity of the HPA anion, and this feature agrees with the electrochemical theory of electrolyte adsorption.[8]

According to IR spectroscopic data (Fig. 2), the structure of the Keggin anion $[PW_{12}O_{40}]^{3-}$ remains unchanged on the Sibunit surface. The IR spectrum of the $H_3PW_{12}O_{40}$/C samples exhibits strong bands at 820, 896, 980, and 1077 cm^{-1} attributable to the HPA with the Keggin structure.[1,2] At the same time, additional bands are observed in regions of 1100—1300 and 1400—1600 cm^{-1}. After preliminary oxidation of the Sibunit surface with H_2O_2 the relative intensity of these bands decreases (see Fig. 2), and they completely disappear upon strong oxidation of the carbon with $KMnO_4$. This indicates that the appearance of these bands can be due to both the interaction of $H_3PW_{12}O_{40}$ with the surface groups of the carbon (carboxylic, lactonic, *etc.*) to form the intermolecular hydrogen bond (owing to the π-electron interaction) and some oxidation of the carbon surface by the adsorbed HPA molecules.

Adsorption of HPA on filamentous carbon. CFC with different structural and textural characteristics were used in the work (see Table 1). Figure 3 presents the microstructure of the fiber of different types used. It is seen that in the CFC-1 fiber graphite-like layers represent nested cones, and head ends of the planes of the graphite-like carbon enter the fiber surface.[11] In CFC-2 the graphite-like layers are perpendicular to the fiber axis with the head ends entering the fiber surface. CFC-3 represents the so-called carbon nanotubes in which seven to ten graphite-

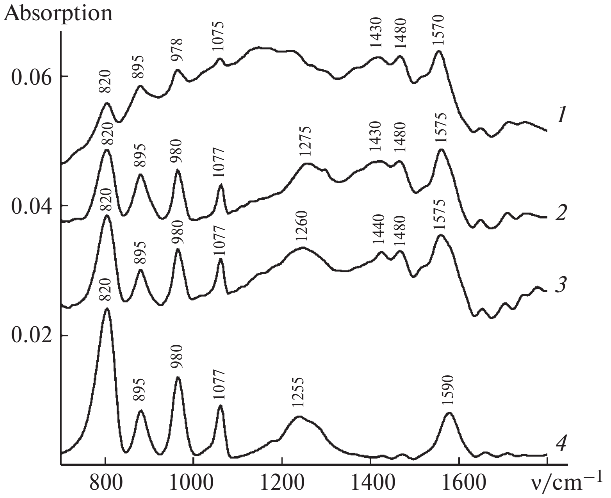

Fig. 2. IR spectra of $H_3PW_{12}O_{40}$ supported on Sibunit treated with different reagents: *1*, 5% $H_3PW_{12}O_{40}$ on S-1099 (H_2O), *2*, 25% $H_3PW_{12}O_{40}$ on S-1099 (H_2O); *3*, 25% $H_3PW_{12}O_{40}$ on S-1099 (H_2O_2); and *4*, 25% $H_3PW_{12}O_{40}$ on S-1099 (MnO_4^-).

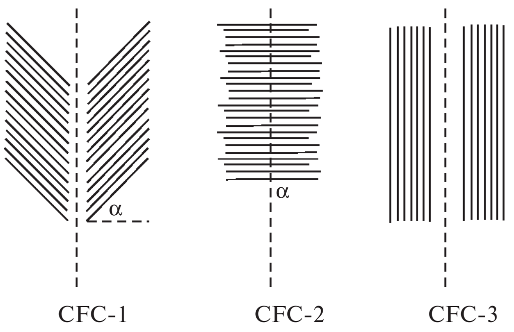

Fig. 3. Schematic representation of the fiber microstructure of CFC of different types.

like layers are parallel to each other and to the fiber axis and are formed by nested cylinders with increasing diameters. The nanotubes have a diameter of 25—30 nm, and the size of the hollow internal channel is[12] ~10 nm.

The adsorption isotherms of $H_3PW_{12}O_{40}$ on CFC in the studied region of coverage of the surface by the HPA molecules are of the Langmuir type (Fig. 4). Adsorption of CFC-1 and CFC-2 is reversible regardless of the solvent type. The adsorption curve coincides with the desorption curve. CFC-3 material is similar to Sibunits in adsorption properties. Approximately 80 mg of HPA per g of the support (CFC-3) is irreversibly adsorbed (see Fig. 4). The difference in adsorption behavior is probably related to the presence of minor amounts of iron ions in CFC-3 (see Table 1).

The influence of the solvent nature on the character of adsorption is the same as in the case of Sibunit (see Fig. 4). For different solvents a_{max} values decrease in the series: $H_2O > Me_2CO > MeOH$ (see Table 2).

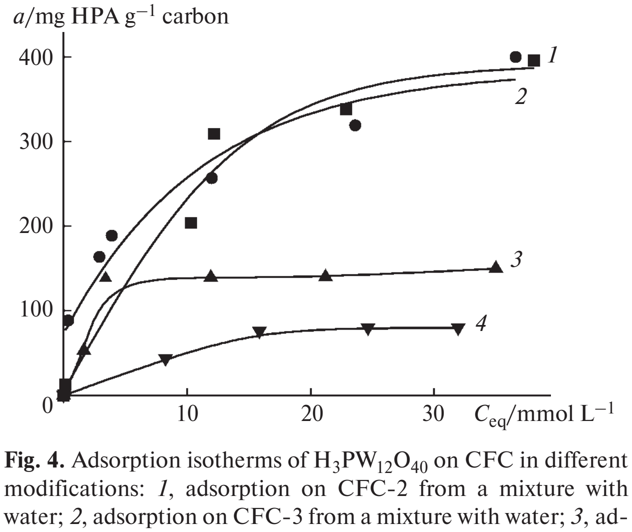

Fig. 4. Adsorption isotherms of $H_3PW_{12}O_{40}$ on CFC in different modifications: *1*, adsorption on CFC-2 from a mixture with water; *2*, adsorption on CFC-3 from a mixture with water; *3*, adsorption on CFC-2 from MeOH; and *4*, adsorption on CFC-1 from a mixture with water (*a* is adsorption; C_{eq} is equilibrium concentration).

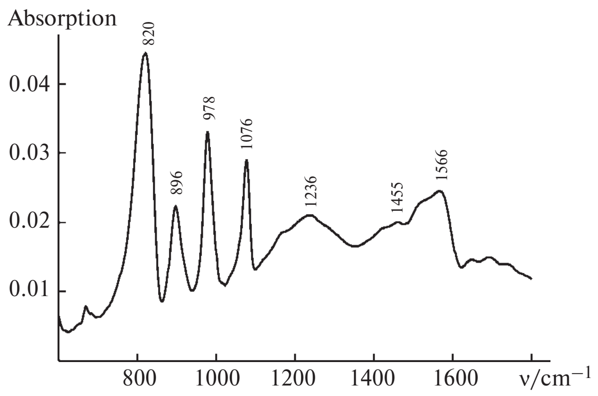

Fig. 5. IR spectra of $H_3PW_{12}O_{40}$ supported on CFC-2.

When $H_3PW_{12}O_{40}$ is adsorbed on CFC, the structure of the $[PW_{12}O_{40}]^{3-}$ anion remains unchanged (Fig. 5). The character of the IR spectra does not change, they are similar to those of $H_3PW_{12}O_{40}$ supported on the Sibunit surface.

As can be seen in Fig. 6, *a*, in the studied interval of HPA concentrations, the experimental data do not obey a linear function in the coordinates $1/\theta—1/C_{eq}$ of the linear form of the Langmuir equation ($\theta = a/a_{max}$). The Freundlich equation turned out to be one of the most successful empirical equations for the description of adsorption isotherms[9]

$$X/m = kC^n, \tag{1}$$

where X is the amount of the adsorbed substance, m is the adsorbent weight, and k and n are constants determined from the plot $\log(X/m) = \log k + n\log C$. As can be seen in Fig. 6, *b*, HPA adsorption obeys Eq. (1) for all carbons studied. Therefore, the surface of carbon materials can be considered non-uniform with respect to HPA adsorption. Non-uniformity of the carbon surface with respect to the adsorption of inorganic acid was reported previously.[13,14] Based on the CFC microstructure, one can assume that weak adsorption sites are typical of CFC-1. They appear only on the planes of graphite-like carbon shift entering with head ends the fiber surface (see Fig. 3). Moderate adsorption sites are characteristic of CFC-2 and appear both on planes of graphite-like carbon and on defects of packing of the graphite-like layers in the fiber (see Fig. 3). Most likely that it is these sites on which the reversible adsorption of HPA on CFC-1 and CFC-2 occurs. The difference in adsorption capacities for these samples can be explained by different values of S_{sp} and the total pore volume and the substantial differences in microstructure of the CFC filaments. According to the TEM data, due to the large size of the molecule, the adsorption of $H_3PW_{12}O_{40}$ occurs predominantly on the external fiber surface of both CFC-1 and CFC-2 (Fig. 7). Individual HPA molecules can fill voids appeared due to defects in

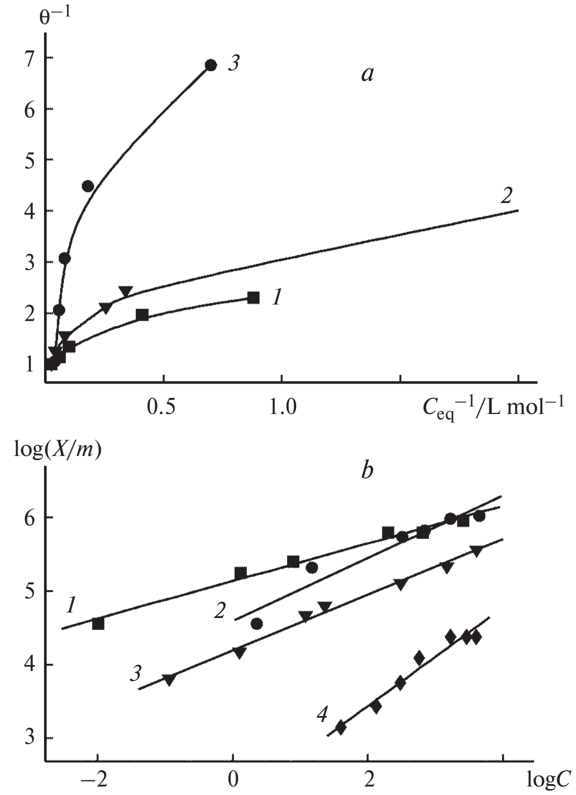

Fig. 6. Adsorption isotherms of $H_3PW_{12}O_{40}$ on carbons of different trade marks from aqueous solutions in the Langmuir coordinates $1/\theta$—$1/C_{eq}$ (*a*) and in the coordinates of the Freundlich equation log(*X*/*m*)—log*C* (*b*): *1*, S-1099; *2*, CFC-3; *3*, CFC-2; and *4*, CFC-1.

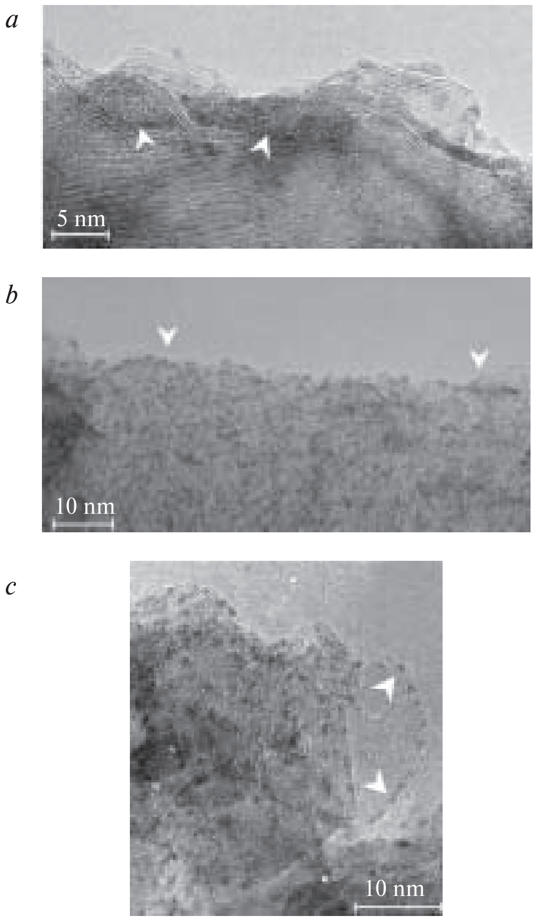

Fig. 7. TEM data for $H_3PW_{12}O_{40}$ on CFC-2, amplification 600 000.

packing of the graphite-like layers in the fiber and become centers of further adsorption (see Fig. 7, *a*). Depending on the amount of supported $H_3PW_{12}O_{40}$, surface aggregates of three types are formed. The first type is presented by the most highly dispersed particles with the size ≥20 Å (probably, individual particles or their small associates) (see Fig. 7, *b*), which exist on the sample with low amounts of supported acid. The second type represents species aggregates with the size ~50 Å (see Fig. 7, *c*), which uniformly cover the whole external surface of the fiber. In addition to the particles indicated above, there are the largest HPA aggregates with the size ≥150 Å (see Fig. 7, *a*). The formation of three HPA forms, which are discernible by electron microscopy, on the support surface has been observed previously[3] for the adsorption of $H_4SiW_{12}O_{40}$ on SiO_2 and AC. At the same time, only large crystalline agglomerates were observed on the carbon film.

The CFC-3 material is predominantly characterized by weak and strong adsorption sites. Reversible adsorption occurs, most likely, on the surface of the carbon nanotube, whereas irreversible HPA adsorption occurs on the sites arranged inside the hollow channel of the CFC nanotube. According to the TEM data, the adsorption of $H_3PW_{12}O_{40}$ on the CFC-3 surface occurred predominantly on the external surface of the fiber (Fig. 8). How-

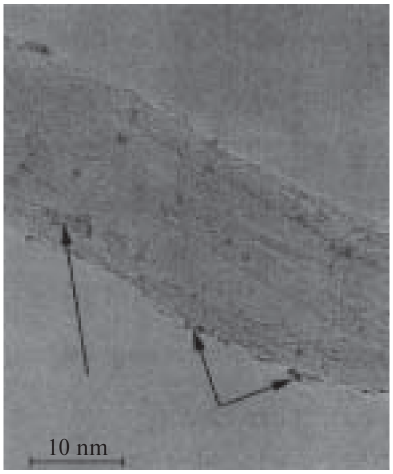

Fig. 8. TEM data for $H_3PW_{12}O_{40}$ on CFC-3, amplification 600 000.

ever, as can be seen in Fig. 8, HPA can also be sorbed on the sites arranged inside the hollow channel of the CFC nanotube. All these data agree well with the fact that the value of irreversible adsorption on CFC-3, which was not washed from the Fe ions, is lower (see Table 2) than that on CFC-3 preliminarily stored in a solution of HCl to remove the Fe ions.

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