

CHARACTERIZATION OF NITROGEN- AND PHOSPHORUS-CONTAINING CARBON

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Introduction

It is well known that ash free activated carbons obtained at high temperature ($>700\text{ }^{\circ}\text{C}$) possess a relatively hydrophobic surface and show basic character in water electrolyte solutions [1]. The presence of functional groups on the surface of activated carbons can have a substantial effect on their adsorptive properties. In particular, a relatively small number of oxygen-containing groups gives rise hydrophilic centers and confers a capability to exchange cations in water solutions [2, 3]. Nitrogen-containing active carbons show increased anion-exchange capacity [3] and catalytic activity in red/ox reactions [4], while sulfur-containing carbons possess high affinity to Hg(II).

Active carbons containing heteroelements (O, N, P, S, etc.) can be obtained either by surface treatment of active carbons with various reagents (HNO_3 , O_2 , NH_3 , H_2S , SO_2 , etc.) or via pyrolysis of raw material containing these elements in different forms. This paper discusses the properties of carbon residue obtained from nitrogen- and phosphorous-containing polymer.

Experimental

The carbon residue (N,P-carbon) was obtained by carbonization of commercial ion exchange resin AFI-22 in argon atmosphere at $900\text{ }^{\circ}\text{C}$. AFI-22 resin was obtained by amination followed by phosphorilation of styrene-divinylbenzene copolymer and contains functional groups $\equiv\text{N}$ and $-\text{N}=\text{P}(\text{OH})_2$ [5].

The adsorption isotherms of benzene and water were determined gravimetrically at $20\text{ }^{\circ}\text{C}$. ESCA spectra were obtained with "Varian IEE-15" spectrometer (Varian, USA). TGA analysis was performed using Derivatograph Q-1500 (MOM, Hungary) in argon atmosphere with temperature rise $10\text{ }^{\circ}\text{C}/\text{min}$.

Results And Discussion

Carbonization of initial styrene-divinylbenzene copolymer in inert atmosphere results in formation of carbon residue with yield approximately 50%. The progress of pyrolysis can be classed into three steps. In the

first (up to $400\text{ }^{\circ}\text{C}$) weight decrease occurs due to the departure of water and decomposition products. In the second step, the weight of carbon residue decreases markedly (50% of total weight loss) in a narrow temperature range of $400\text{--}500\text{ }^{\circ}\text{C}$ with maximum at $450\text{ }^{\circ}\text{C}$. And in third step the weight decreases gradually.

According to chemical analysis (Tab. 1) carbon residue contains 9.5% of phosphorus. Phosphorus content even somewhat increased as compared to starting polymer, obviously, due to carbon loss with volatile products in the course of pyrolysis.

Tab. 1. Physical and chemical properties of N,P-carbon.

Parameter	AFI-22	N,P-carbon	SCS ₀ -1
Bulk density, g/cm^3	0.47	0.35	0.40
NaOH adsorption, meq/g	3.81	2.21	1.82
HCl adsorption, meq/g	0.15	0.10	0.09
Cu adsorption, meq/g	0.06	0.77	0.28
Ash content, %	-	17.62	0.03
P content, %	8.44	9.45	-

The ESCA spectra of both starting copolymer and carbon residue showed lines of C, N, P and O.

The C1s signal of N,P-carbon shows an asymmetric tailing which is characteristic to condensed aromatic systems and for carbon blacks. The C1s signal was fitted to three peaks, which were assigned to graphite, condensed aromatics (284.0 eV), aliphatics (285.0 eV) and COOH or COOR groups (289.6 eV).

N1s signal of N,P-carbon was fitted to three peaks 398.4, 400.8 and 404.5 eV. First and second peaks were observed on charcoal after treatment with NH_3 [6] and on synthetic carbon obtained by pyrolysis of vinylpyridine polymer [7]. These peaks were assigned to pyridine-like N and amines. Third peak was assigned to N-oxides.

P2p signal of N,P-carbon was fitted to two peaks at 132.7 and 136.3 eV. These peaks were assigned to oxides of tertiary phosphines and polyphosphates. This assignment is reasonable because oxides of tertiary phosphines are considered as most stable among all organophosphorus compounds.

No stable fitting of O1s signal of N,P-carbon was achieved.

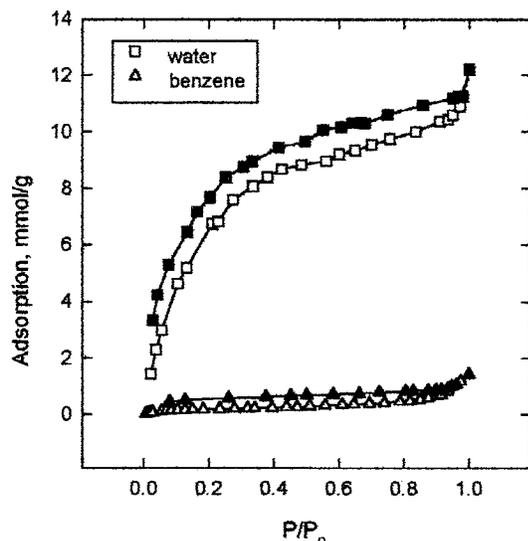


Fig. 1. Adsorption isotherms of water and benzene on N,P-carbon. Open symbols -- adsorption; closed symbols -- desorption.

Adsorption isotherm of benzene (Fig. 1) shows that N,P-carbon is mesoporous ($V_{me} = 0.12 \text{ cm}^3/\text{g}$) with negligibly small micropore volume ($0.0004 \text{ cm}^3/\text{g}$). Thus, phosphorus compounds in polymer do not act as activating agent during carbonization like phosphoric acid. The fact that mesopore surface area obtained by α_s method ($41.2 \text{ m}^2/\text{g}$) is close to BET surface area ($38.3 \text{ m}^2/\text{g}$) supports the absence of microporosity.

Adsorption isotherm of water vapor is convex upward at low relative pressure indicating high hydrophilic surface of adsorbent. Content of hydrophilic sites calculated from Langmuir equation is 11.72 mmol/g . For oxidized carbon SCS₀-1 this value is only 4.72 mmol/g .

Despite the fact that nitrogen increases anion-exchange properties of carbon [3], N,P-containing carbon shows high capacity for NaOH and copper (Tab. 1). Cu adsorption on N,P-carbon is more than two times above that on oxidized carbon SCS₀-1. Curve titration (Fig. 2) lies in negative region and implies the ability to exchange cations in wide range of pH. Distribution function shows only one peak at pK 8.62.

The distinctive characteristic of N,P-carbon as opposed to oxidized carbons is thermal and chemical stability. Both treatments at $900 \text{ }^\circ\text{C}$ in argon atmosphere and boiling in 1M NaOH during 1 hour cause only 5-10 % decrease in NaOH adsorption. High thermal and chemical stability may be attributed to formation of organophosphorus compounds like oxides of ternary phosphines or to polyphosphates.

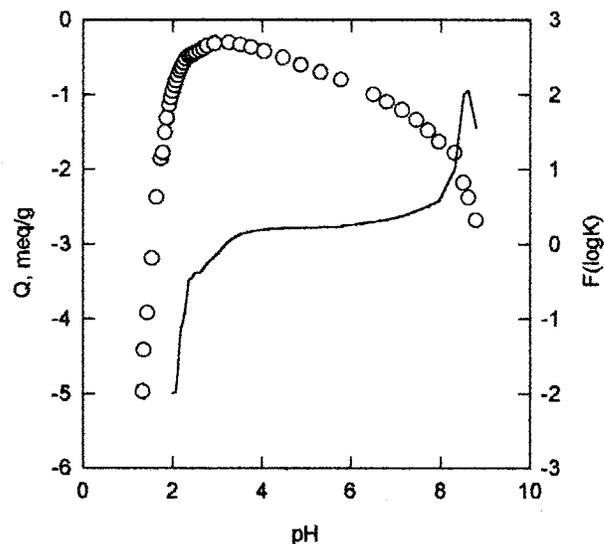


Fig. 2. Proton binding curve (symbols) and distribution function (line) of surface functional groups of N,P-carbon

Conclusions

The N,P-carbon obtained from nitrogen- and phosphorus-containing polymer possesses N, P and O-containing functional groups. This functionality makes carbon surface hydrophilic and confers cation-exchanging properties to the carbon. These properties may be utilized in potential application of N,P-carbon for adsorption of polar substances from gas phase or adsorption of cations from solutions.

References

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