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Short communication

# On the chemical structure of phosphorus compounds in phosphoric acid-activated carbon

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## Abstract

Chemical structure of phosphorus species in polymer-based phosphoric acid-activated carbon SP800 was investigated by X-ray photoelectron spectroscopy. It has been shown that most probable structure for phosphorus species is condensed phosphates bound to carbon lattice via C–O–P bonding.

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**PACS:** 82.80.Pv electron spectroscopy (X-ray photoelectron (XPS), Auger electron spectroscopy (AES), etc.); 68.49.-h surface characterization by particle-surface scattering; 82.45.Jn surface structure, reactivity and catalysis; 82.65.+r surface and interface chemistry, heterogeneous catalysis at surfaces

**Keywords:** Activated carbon; Phosphoric acid activation; X-ray photoelectron spectroscopy; Chemical structure

Phosphoric acid activation is widely used for production of activated carbons. Recent investigations have shown that carbons obtained by phosphoric acid activation show not only developed porosity but also exhibit significant cation exchange properties due to acidic surface groups [1,2]. Maximum amount of acidic surface groups was attained at 800 °C by carbonization of both styrene/divinylbenzene copolymer [1] or lignocellulosic precursor [2] in presence of H<sub>3</sub>PO<sub>4</sub>. The study of phosphoric acid-activated carbons by chemical analysis, FT-IR spectroscopy and potentiometric titration has shown that surface groups of phosphoric acid-activated carbons may be classified as phosphorus-containing, carboxylic, lactone and phenol-like groups. Phosphorus-containing surface groups were ascribed to condensed phosphates formed during pyrolysis of carbonaceous precursor in presence of phosphoric acid [1,2]. However, due to overlapping of many bands in FT-IR spectra it was not possible to establish the unambiguous structure of phosphorus-containing compounds in phosphoric acid-activated carbons.

In this study a polymer-based carbon SP800 obtained by phosphoric acid activation of styrene/divinylbenzene copolymer at 800 °C [1] was examined by XPS method.

XPS measurements were done in ES 2401 spectrometer using monochromatized Al K $\alpha$  radiation. A non-linear least-square curve fitting program (XPSPEAK 4.1 software [3]) with mixed Gauss–Lorentz product function and Shirley background was used to deconvolute XPS spectra. Atomic ratios were calculated from XPS spectra after correcting the relative peak areas by atomic sensitivity factors 0.25 for C1s, 0.66 for O1s and 0.39 for P2p, taken from [4].

The XPS survey spectrum of carbon SP800 indicates the presence of three distinct peaks due to carbon, oxygen and phosphorus. The contribution of other elements was insignificant. Table 1 shows that O/C and P/C atomic ratios representing surface composition are about two times higher than that obtained by elemental analysis [1]. The enrichment of surface with oxygen and phosphorus as compared to the bulk suggests that chemical activation of polymer precursor occurs superficially in case of carbon SP800. O/P atomic ratio shows that surface phosphorus-containing species are about the same composition as in the bulk, though slightly richer in oxygen.

C1s XPS spectrum (Fig. 1) was deconvoluted into six components with fixed positions adopted in the analysis of the C1s region of carbon materials [5–8]. The components (Table 2) represent graphitic carbon (peak 0, BE = 284.7 eV), aliphatic carbon (peak 1, BE = 285.2 eV), carbon in alcohol, ether groups and/or C–O–P linkage (peak 2, BE = 286.2 eV),

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Table 1

Comparison of surface (XPS data) and bulk (chemical analysis data) atomic ratios of SP800 carbon

Atomic ratios	XPS	Chemical analysis [1]
O/C	0.46	0.20
P/C	0.09	0.05
O/P	5.09	4.14

carbon in carbonyl groups (peak 3, BE = 287.5 eV), carboxyl and/or ester groups (peak 4, BE = 289.0 eV) and shake-up satellite due to  $\pi-\pi^*$  transitions in aromatic rings (peak 5, BE = 291.3 eV). 61% of carbon atoms are graphitic, 18% aliphatic and about 21% belongs to oxidized carbon. The BE of carbon bound to phosphorus (C–P bonding) is between graphitic and aliphatic carbons and thus cannot be clearly determined [4].

O1s spectrum of SP800 carbon was fitted to three peaks corresponding to double bonded oxygen in C=O and/or P=O groups (peak 6, BE = 530.9 eV), single bonded oxygen in C–OH, C–O–C and/or C–O–P linkages (peak 7, BE = 532.6 eV) and chemisorbed oxygen and/or water (peak 8, BE = 534.5 eV) [4].

P2p spectrum of carbon SP800 was successfully fitted to one peak with BE = 133.5 eV suggesting the existence of sole type of phosphorus compounds in the structure. The binding energy of the peak is characteristic of pentavalent tetracoordinated phosphorus [PO<sub>4</sub>] as in phosphates (Na<sub>2</sub>HPO<sub>4</sub>, BE = 133.4 eV [9]; K<sub>2</sub>HPO<sub>4</sub>, BE = 133.5 eV [10]) or in condensed phosphates (Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, BE = 133.5 eV [9]; (NaPO<sub>3</sub>)<sub>3</sub>, BE = 133.6 eV [11]). Polyphosphates in carbon SP800 were also revealed by FT-IR investigation [1]. Furthermore very acidic surface groups with *pK* about 1.8 and *pK* < 0 in carbon SP800 [1] is indicative of polyphosphates. The occurrence of condensed phosphates is supported by the fact that phosphoric acid readily produces polyphosphates at high temperature [12].

It is of interest to consider the way the polyphosphates are bound to carbon. The C1s and O1s spectra suggest P–O–C linkage, which is in line with previous FT-IR data [1]. On the other hand, the existence of C–P bonding cannot be ruled out on the base of XPS data. Indeed, P2p binding energies close to

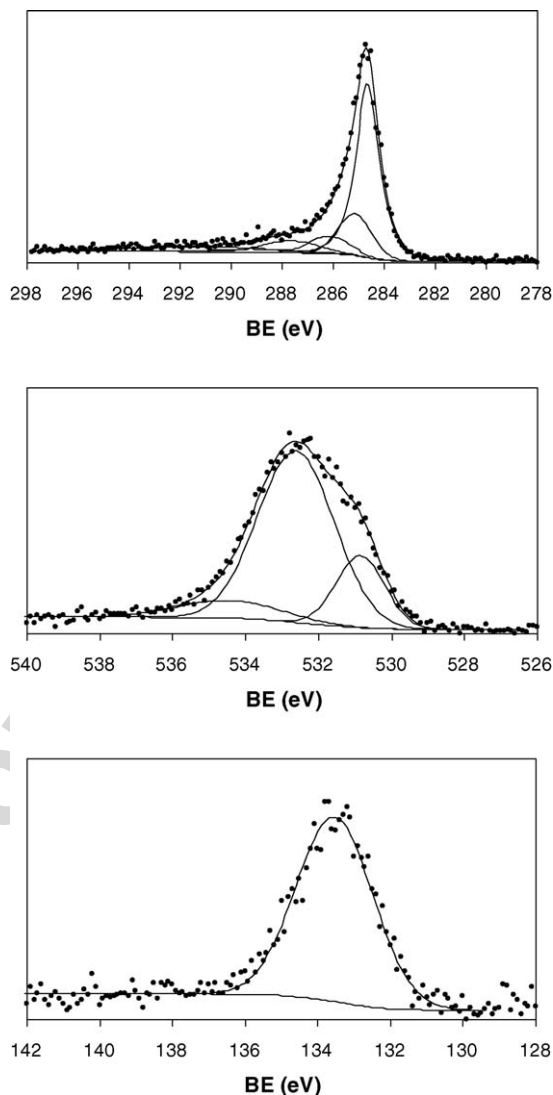


Fig. 1. High-resolution X-ray photoelectron spectra (C1s, O1s and P2p core level) of carbon SP800.

Table 2

Deconvolution results of XPS spectra of SP800 carbon

Region	Peak #	Position (eV)	Normalized area	FWHM (eV)	GL (%)	Assignment
C1s	0	284.7	13003	1.08	87	Graphite
	1	285.2	3924	1.57	0	Aliphatic
	2	286.2	1917	1.86	9	R–OH + C–O–C + C–O–P
	3	287.7	1844	2.61	0	C=O + >C=O
	4	289.2	641	3.02	84	COOH + –C(O)–O–C
	5	291.3	2079	7.18	0	$\pi-\pi^*$
O1s	6	530.9	1853	1.57	0	O=C + O=P
	7	532.6	6950	2.47	0	O–C + COH + C–O–C + P–O
	8	534.5	964	3.32	0	Chemisorbed O + H <sub>2</sub> O
P2p	9	133.5	1917	2.48	0	[PO <sub>4</sub> ]

GL: Lorentzian to Gaussian ratio.

133.5 eV were reported for diphenylphosphinic acid [13] and for triphenylphosphine oxide [10]. In addition, phosphinic acid has very acidic group with  $pK = 1.1$  [12] like surface groups of SP800 carbon. However, FT-IR study of SP800 carbon [1] did not reveal any bands in the region  $795\text{--}650\text{ cm}^{-1}$ , where C–P bond gives a medium-to-strong absorption [14]. Recently Lee and Radovic analyzed the stability of C–O–P and C–P–O bonding in context of oxidation inhibition of carbon materials [15]. Using quantum mechanical modeling they showed that the structure with C–O–P bonding is more stable and able to survive longer than the structure with C–P–O bonding.

It should be noted that there is no peaks in the P2p region corresponding to neutral phosphorus (BE = 130.2–130.9 eV) [9,10] or phosphorus (V) pentoxide (BE = 135.6 eV) [9].

Thus, present XPS investigation of phosphorus-containing carbon SP800 lends support to the evidence of existing condensed phosphates attached by C–O–P linkage to carbon matrix.

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