

Removal of Formaldehyde at Low Concentration Using Various Activated Carbon Fibers

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ABSTRACT: Adsorption of low concentration formaldehyde on pitch-based, rayon-based, and PAN-based activated carbon fibers (ACFs) and an unactivated PAN-based carbon fiber (PAN-CF) was investigated by a dynamic method. The pore structure and surface chemistry of these samples were characterized by liquid nitrogen adsorption, elemental analysis, and X-ray photoelectron spectroscopy. Results revealed that the pore structure, especially surface chemical composition, greatly influence the formaldehyde adsorption. PAN-

based ACFs showed the highest formaldehyde adsorption capacity because there are more abundant nitrogen-containing groups, especially pyrrolic, pyridonic, pyridinic, and quaternary on the surface. The breakthrough time and formaldehyde adsorption capacity of one kind of PAN-ACF were 361 min and 0.478 mmol/g, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2151–2157, 2007

Key words: adsorption; structure; surface; ESCA/XPS

INTRODUCTION

Formaldehyde is one of the main pollutants in the atmosphere. In indoor air, formaldehyde mainly comes from decorating materials, paint, furniture glue, and chemical fiber carpets,^{1,2} and the concentration of formaldehyde is always relative low (<20 ppm). Even if the concentration of the formaldehyde is low, it can cause symptoms such as headache, nausea, coryza, pharyngitis, emphysema, lung cancer, and even death, so it is necessary to take effective measures for its removal. Adsorption by carbonaceous adsorbents is the most widely used method to purify the polluted air. The performance of carbons is strongly influenced not only by the porosity but also by the surface chemistry.³ The introduction of heteroatoms may also significantly influence the adsorption properties especially for polar or polarizable organic molecules. However, there are few publications relating to the adsorption of formaldehyde at low concentration by activated carbons.^{1–5} Rong et al. studied the effect of heat treatment of rayon-based activated carbon fibers (ACFs) on the adsorption of formaldehyde.² It was found that heat treatment in an inert atmosphere for rayon-based ACFs resulted in an increase in the adsorption capacities and

prolongation of the breakthrough time on formaldehyde removing. Boonamnuyvitaya et al. prepared activated carbons from coffee residues and investigated their formaldehyde adsorption at high concentration (13,767–74,216 ppm).³ It was reported by Tanada et al. that the presence of nitrogen on the carbon surface facilitates formaldehyde removal in formalin.⁴ Formaldehyde adsorption at 45% relative humidity on polymer-based activated carbons with different surface chemical structures was investigated by Laszlo.⁵ It was found that porous carbons derived from polyacrylonitrile (PAN) showed larger formaldehyde adsorption capacity, which originated from its abundant nitrogen functionalities on the surface. However, all of the earlier researches about formaldehyde adsorption were carried out with the participation of water, and the relationship between physic-chemical structures of adsorbents and formaldehyde adsorption properties was still not clarified.

The aim of the present study is to investigate the adsorption behavior of low concentration formaldehyde on various ACFs, and on the basis of systematical analysis of the pore and surface chemical structures, the relationship between the structures of ACFs and their formaldehyde adsorption properties were elucidated.

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EXPERIMENTAL

Chemicals and materials

Different kinds of ACFs such as pitch-based ACFs (OG5A, OG15A), rayon-based ACF (KF1500), and

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PAN-based ACFs (FE100, FE200, and FE300) were used in the experimental. To find the effect of pore structure on the adsorption of formaldehyde at low concentration, the formaldehyde adsorption behavior of PAN-based carbon fiber (PAN-CF), which was carbonized at 800°C, was also investigated. The standard formaldehyde gas (20 ppm), which was diluted by pure nitrogen, was obtained from Asahi Gas Company (Fukuoka, Japan).

Characterization

Nitrogen adsorption/desorption isotherms of ACFs were measured at 77 K using Sorptomatic 1990 instrument. Samples were out-gassed at 200°C in vacuum ($P < 10^{-8}$ bar). The surface area was calculated according to the BET model. The total pore volume was obtained from the amount of nitrogen adsorbed at a relative pressure of 0.95, with the assumption that the pores were then filled with liquid nitrogen. Dubinin–Radushkevich (D-R) approach was used to determine the micropore volume.

Element analysis of carbon, hydrogen, nitrogen, and oxygen (by difference) of the samples was carried out using Perkin–Elmer CHN Elemental Analyser, model 2400. The sample was desiccated thoroughly before measurement.

The surface chemical composition of the samples was determined by ASCALab220i-XL electron spectrometer from VG Scientific using 300 W Al K α radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The constant pass energy was 100 and 30 eV for wide-scan and detailed peak analysis, respectively. High resolution spectra of the N1s signals were recorded in a step of 0.05 eV. After subtraction of the linear base line, curve fitting was performed assuming Gaussian peak shapes.

Formaldehyde adsorption

A laboratory fixed-bed unit was setup to obtain the equilibrium data of adsorption of formaldehyde at 30°C; 0.1 g of sample was loaded for every test. The flow rate is 100 mL/min. The outlet concentration of formaldehyde is detected by model 4160 formaldehyde analysis instrument (JMS Company, Tokyo, Japan). The breakthrough time is defined as the time at which the output concentration (C) reaches 1% of the inlet concentration (C_0).⁶ The saturated amount of formaldehyde adsorbed on ACFs at equilibrium is calculated according to the following equation: $W = PV/(RT)/m$, where W is the adsorbed amount of formaldehyde per unit gram of ACF, P is atmospheric pressure (1 atm), V is the volume of adsorbed formaldehyde, which was calculated from the integrated area over breakthrough curve $\times 10^{-6} \times 0.1$ L/min, R

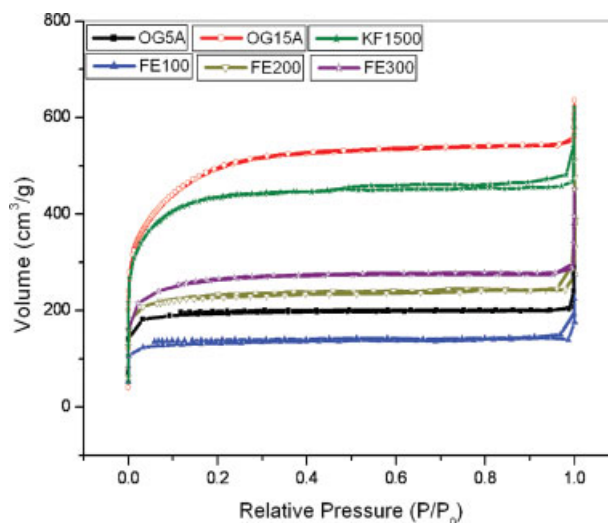


Figure 1 Nitrogen adsorption/desorption isotherms of various ACFs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

is universal gas constant ($0.08204 \text{ atm mol}^{-1} \text{ K}^{-1}$), and T is adsorption temperature (303.15 K).

RESULTS

Nitrogen adsorption isotherms and pore structure of different ACFs

Figure 1 shows the nitrogen adsorption isotherms of ACFs. It was found that the isotherms of the sample are all of type I according to the classification of IUPAC,⁷ which exhibit mainly microporous characteristics.

Table I lists the porous parameters of various ACFs. It was found that the porous structure of ACFs was greatly influenced by raw materials. As for PAN-based ACFs, the order of surface area and pore volume is as follows: FE100 < FE200 < FE300, and for Pitch-based ACFs, OG15A shows higher surface area and larger pore volume than OG5A. Among these samples, OG15A shows the highest surface area ($1516 \text{ m}^2/\text{g}$) and larger pore volume ($0.84 \text{ cm}^3/\text{g}$), followed by KF1500 ($1271 \text{ m}^2/\text{g}$, $0.96 \text{ cm}^3/\text{g}$), whereas FE100 exhibits the smallest surface area ($378 \text{ m}^2/\text{g}$) and pore volume ($0.22 \text{ cm}^3/\text{g}$).

Elemental composition of different ACFs

Table II lists the elemental composition of the samples. Results reveal that for all samples the N/C ratio greatly differs, while the O/C ratio is similar. Among the samples studied, PAN-based ACFs contain the most abundant nitrogen, especially FE100, which might originate from the polymer precursor. Pitch-based ACFs (OG5A and OG15A) contain small amount of nitrogen compared with other samples. Moreover, PAN-CF has more abundant oxygen and nitrogen contents compared with PAN-based ACFs.

TABLE I
Porous Structure Parameters and Formaldehyde Adsorption Properties of ACFs

Sample	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	Breakthrough time (min)	Adsorbed formaldehyde amount at saturation (mmol/g)
FE100	378	0.22	0.21	361	0.478
FE200	679	0.38	0.37	193	0.274
FE300	794	0.43	0.43	109	0.127
KF1500	1275	0.72	0.72	14.2	0.035
OG5A	573	0.31	0.31	14.7	0.020
OG15A	1516	0.84	0.83	5.2	0.010

S_{BET} : calculated between P/P_0 from 0.05 to 0.35; V_{total} : total pore volume at relative pressure 0.95; V_{micro} : calculated from Dubinin–Radushkevich (D-R) approach; formaldehyde adsorption amount at saturation were calculated from breakthrough curves.

X-ray photoelectron spectroscopy analysis of different samples

Table III shows the molar fraction of O/C and N/C in the external surface of the samples, and the molar fraction of different nitrogen-containing groups calculated by peak area at different binding energies. It can be seen that among the samples the PAN-CF has most abundant nitrogen functional groups. PAN-based ACFs, especially FE100, have larger amount of oxygen and nitrogen containing functional groups on the surface compared with other samples. KF1500 and OG5A have similar oxygen functional groups, and OG15A has smallest amount of oxygen functional groups on the surface. As for FE100, 200, and 300, it can be found from Tables II and III that elemental analysis shows higher N and lower O contents than XPS data. As is well known, XPS data reflects only the compositions of the external portion within 3 nm below the solid surface.⁸ The reasons might be as follows: the oxygen atoms are preferentially located on the surface of the PAN-based ACFs, by contrast, the nitrogen atoms are incorporated in graphene layers and are thus presumably more abundant in the micropores.^{3,9}

The broad N1s spectrum, ranging from 390 to 410 eV, of PAN-based ACFs and PAN-CF in the XPS spectra, as shown in Figure 2, might be comprised of

peaks of several nitrogen-containing functional groups with different binding energies, which were assigned to pyridinic nitrogen (N-6) at 398.5 ± 0.2 eV, pyrrolic or pyridonic nitrogen (N-5) at 400.5 ± 0.2 eV, quaternary nitrogen (N-Q) in the aromatic grapheme structure at 401.4 ± 0.2 eV, and nitrogen oxide or nitrate structures (N-X)¹⁰ at 403 ± 0.2 eV (see Fig. 3).⁵ So the N1s spectrum of each sample was treated using XPS Peak Fitting Program to obtain the relative amount of each nitrogen-containing groups (see Table III). It can be seen that pyridinic and pyrrolic or pyridonic nitrogen account for the majority of the nitrogen functionalities, whereas the quaternary nitrogen and nitrogen oxide are the minor species for PAN-based ACFs. It should be noticed that FE100 has larger amount of pyrrolic or pyridonic nitrogen (2.160%) than FE200 (0.996%) and FE300 (0.930%). PAN-CF has the largest amount of pyrrolic or pyridonic nitrogen (3.005%) and pyridinic nitrogen (3.833%).

Formaldehyde adsorption properties of different samples

Figure 4 shows the breakthrough curves obtained at the formaldehyde concentration of 20 ppm over various sample beds. Table I also lists the breakthrough

TABLE II
Elemental Composition of Various Samples

Sample	C (wt %)	H (wt %)	N (wt %)	O (diff) (wt %)	O/C (atom ratio)	N/C (atom ratio)
PAN-CF	75.54	1.12	15.76	7.58	0.075	0.179
FE100	81.31	0.71	10.86	7.12	0.066	0.114
FE200	84.45	0.91	5.65	8.99	0.080	0.057
FE300	84.51	0.73	4.28	10.48	0.093	0.043
KF1500	88.03	0.63	1.61	9.73	0.083	0.016
OG5A	92.57	0.54	0.87	6.02	0.049	0.008
OG15A	92.83	0.79	0.39	5.99	0.048	0.004

Oxygen content: calculated by difference.

TABLE III
Molar Fraction of O/C and N/C in the External Surface of the Samples, and the Molar Fraction of Different Nitrogen-Containing Groups Calculated by Peak Area at Different Binding Energies

Sample	O/C	N/C	Pyridinic nitrogen at 398.5 ± 0.2 eV (mol %)	Pyrrolic or pyridonic nitrogen at 400.5 ± 0.2 eV (mol %)	Quaternary nitrogen at 401.4 ± 0.2 eV (mol %)	Nitrogen oxide at 403 ± 0.2 eV (mol %)
PAN-CF	0.052	0.080	3.833	3.005	0.795	0.320
FE100	0.230	0.054	0.737	2.160	0.385	0.857
FE200	0.138	0.030	1.050	0.996	0.470	0.015
FE300	0.141	0.031	0.734	0.930	0.670	0.245
KF1500	0.093	0.015	0.330	0.320	0.330	0.390
OG5A	0.097	0.006	0.149	0.126	0.113	0.182
OG15A	0.055	0.005	0.230	0.130	0.030	0.054

time and the amount of formaldehyde adsorbed on ACFs at equilibrium. It was found that the breakthrough time and calculated saturation adsorption amount are 361 min and 0.478 mmol/g for FE100, 193 min and 0.274 mmol/g for FE200, 109 min and 0.127 mmol/g for FE300, 14.2 min and 0.035 mmol/g for KF1500, 5.2 min and 0.010 mmol/g for OG15A, and 14.7 min and 0.020 mmol/g for OG5A, respectively.

PAN-based ACFs show higher formaldehyde saturation adsorption capacity and longer breakthrough time than pitch-based or rayon-based ACFs. The order of formaldehyde saturation adsorption amount is as follows: FE100 > FE200 > FE300 > KF1500 > OG5A > OG15A. However, the PAN-CF bed was penetrated totally after few seconds, which suggested that it has the lowest formaldehyde adsorption.

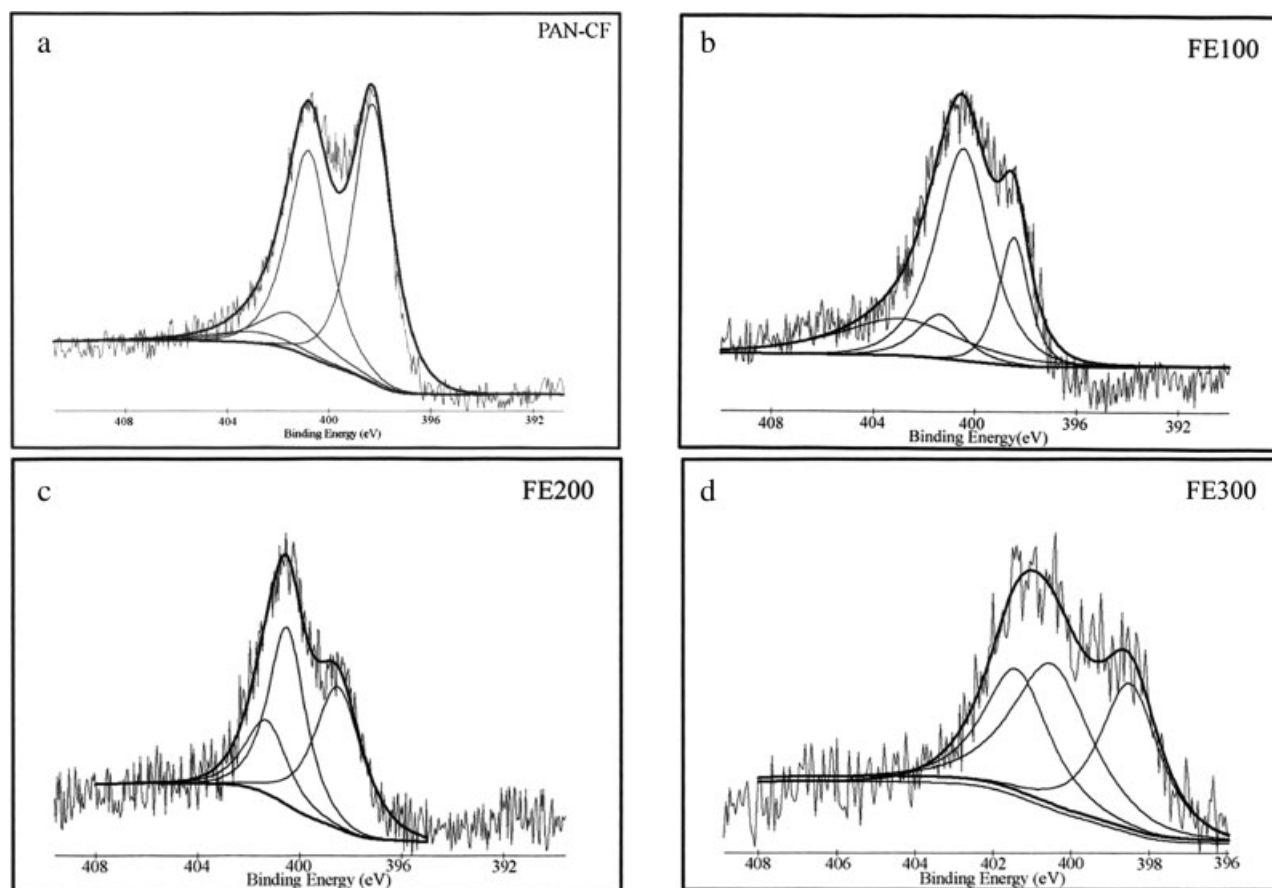


Figure 2 N1s XPS spectra of PAN-based CF and ACFs.

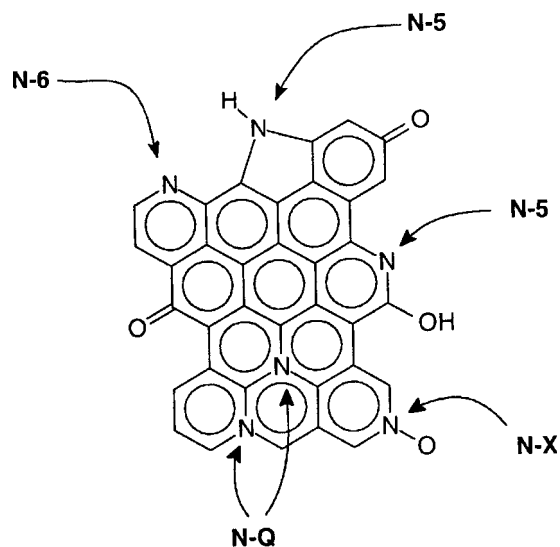


Figure 3 Nitrogen-containing functional groups in ACF.⁵ N-6: pyridinic-like structures; N-5: pyrrolic or pyridonic-N moieties; N-Q: quaternary nitrogen; N-X: nitrogen oxide or nitrate structures.

DISCUSSION

Pore structure versus formaldehyde adsorption capacity

As stated earlier, ACFs certainly show larger formaldehyde adsorption capacity than PAN-CF. Since PAN-CF exhibits a nonpore structure, it has poor formaldehyde adsorption capacity. From Table I, it can be found that although OG15A has larger surface area and pore volume than other samples its formaldehyde adsorption capacity is very low. At the same time, FE100 shows the highest formaldehyde adsorption capacity among the tested samples despite of its lowest surface area, which might imply that although surface area and pore volume have certain effect on

the formaldehyde adsorption, there is another key factor that might influence the adsorption behavior. Among these four kinds of ACFs, PAN-based ACFs have superior formaldehyde adsorption capacity, which might result from their special surface chemical composition.

Surface chemical composition versus formaldehyde adsorption capacity

Surface chemical composition of ACFs often refers to oxygen-containing and nitrogen-containing groups. To investigate the effect of surface chemical composition on the adsorption of formaldehyde, the relationship between the amount of adsorbed formaldehyde and elemental composition is exhibited in Figure 5.

From Figure 5, it can be seen that oxygen-containing groups have not so much relation with the formaldehyde adsorption capacity, while the nitrogen content (obtained from elemental analysis) shows a great effect on the formaldehyde adsorption capacity. The higher N/C ratio on the ACF, the larger formaldehyde adsorption capacity it exhibits. This trend is more obvious when the nitrogen content is higher (e.g., PAN-based ACFs and rayon-based ACF).

To further clarify the effect of nitrogen-containing groups on the formaldehyde adsorption performance of ACF, the relationship between adsorption amount and XPS data is plotted in Figure 6. Figure 6(a) shows the relationship between adsorption amount and total surface nitrogen content, and Figure 6(b) reveals the relationship between adsorption amount and specific nitrogen content, including pyrrolic or pyridonic nitrogen, pyridinic nitrogen, and quaternary nitrogen-containing groups. It agrees well with that nitrogen content control the formaldehyde adsorption capacity, especially for pyrrolic or pyridonic nitrogen,

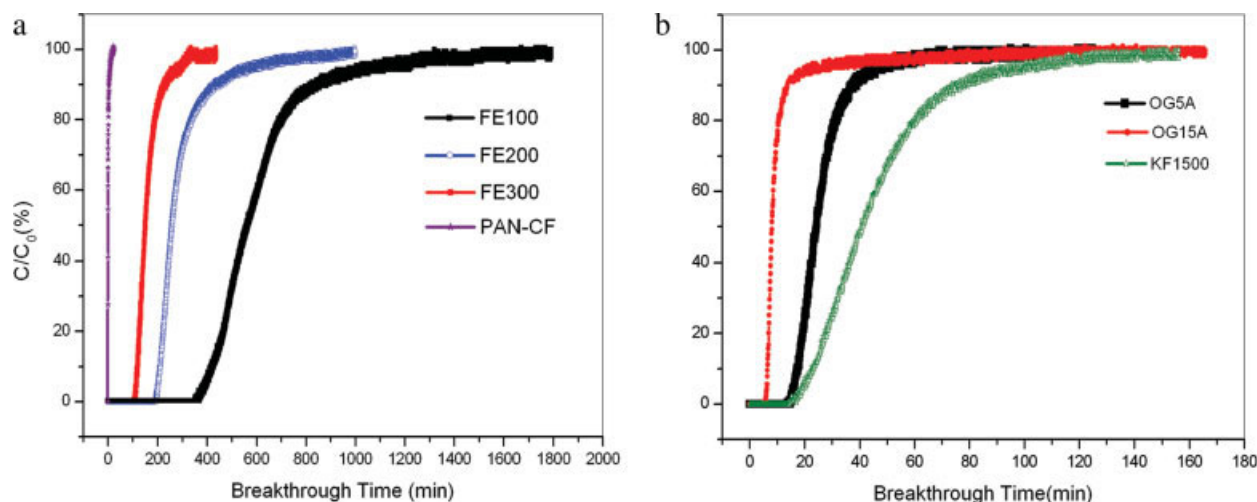


Figure 4 Breakthrough curve of formaldehyde (2×10^{-5}) on various samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

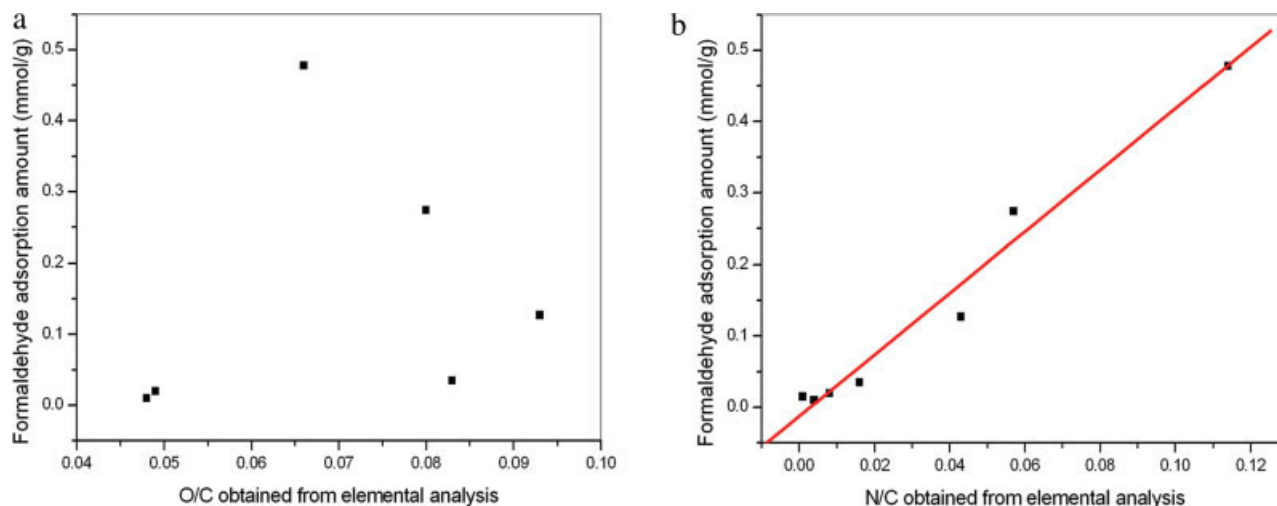


Figure 5 Relationship between adsorption amount and elemental composition. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

pyridinic nitrogen, and quaternary nitrogen-containing groups. The reason might be as follows: (1) the active hydrogen atom of pyrrole (one of N-5) might react with formaldehyde to form alcohol; (2) the nitrogen atoms in the N-6, N-5, and N-Q structure possess partly negative charge (δ^-) for its strong electronegativity, while carbon atom of formaldehyde shows slightly positive charge (δ^+) for its weaker electronegativity than oxygen atom. So the nitrogen atoms in the N-6, N-5, and N-Q structure of ACFs and carbon atom in the carbonyl of formaldehyde will attract each other for the electrostatic gravitation, which will lead to better formaldehyde adsorption capacity over ACF with higher pyrrolic or pyridonic nitrogen, pyridinic nitrogen, and quaternary nitrogen-containing groups.

CONCLUSIONS

Low concentration formaldehyde adsorption behavior of various ACFs prepared from different precursors was investigated. Results showed that the pore structure, especially surface chemical composition, could influence formaldehyde adsorption. Among the ACFs investigated, PAN-based ACFs showed the best formaldehyde adsorption capacity, which might be originated from the abundant nitrogen-containing groups, especially pyrrolic or pyridonic nitrogen, pyridinic nitrogen, and quaternary nitrogen-containing groups, which might promote the adsorption of formaldehyde. The breakthrough time and formaldehyde adsorption amount at saturation of FE100 were 361 min and 0.478 mmol/g, respectively.

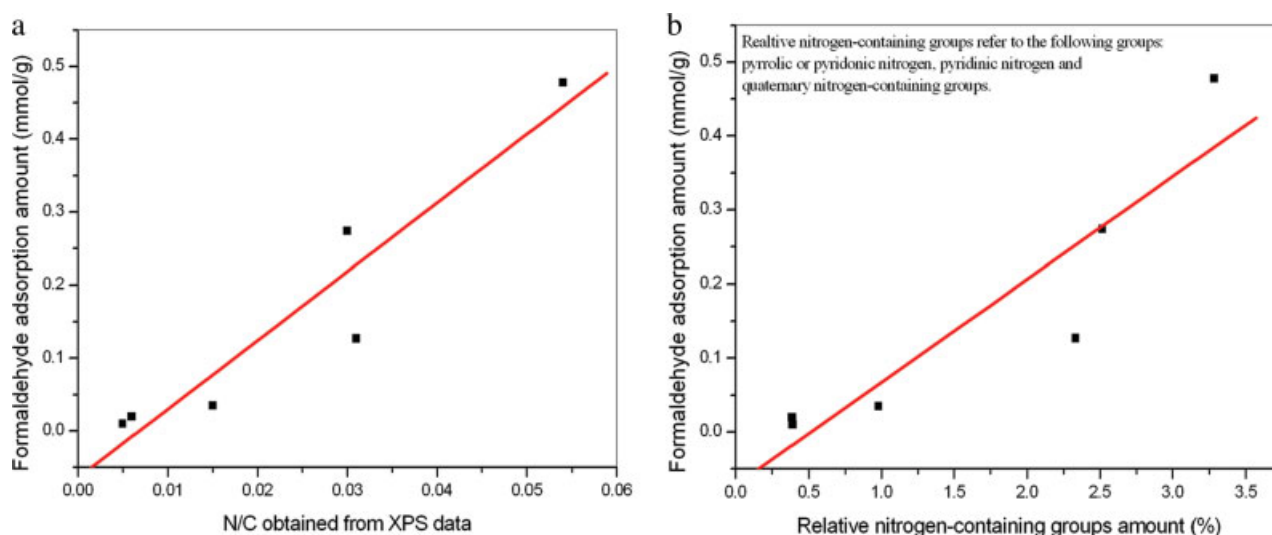


Figure 6 Relationship between adsorption amount and XPS data. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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