MODIFICATION OF ACTIVATED CARBON FIBERS BY DIRECT OXIDATION WITH AIR

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Introduction

The adsorbate-adsorbent interaction in the physical adsorption of gases by a solid is a function of the polarity of solid and the adsorptive. Varity of carbonaceous adsorbent, with a mainly nonpolar surface, is very useful for adsorption molecules of low polarity such as hydrocarbons but is not very adequate for the adsorption of polar molecules[1]. The adsorption properties of activated carbon fiber(ACF) as a typical microporous carbon result from their remarkable surface and structural properties. It is then easy to understand the need for a modification of the chemical nature of the carbon if one seeks to increase the adsorption capacity for polar molecules. Many research work[2,3,4] have been done in modification of the surface and porous structure to enhance the properties of ACF such as electric properties by fluorination, mechanical and thermal properties by siliconization, adsorption selectivity with pore size controlling by chemical vapor deposited and so on.

In the present work, polyacrylonitrile(PAN)-based ACFs were oxidized directly by air(oxygen) to investigate the adsorption behavior for the molecules with different polarity. The factors affected adsorption were analyzed from pore structure to surface chemistry.

Experimental

The oxidation of porous carbon with reagents such as air, nitric acid, hydrogen peroxide and so on, is rather simple and, if carried out under adequate conditions, may introduce noticeable changes in the chemical nature of the carbon surface without appreciably changing in its porosity[1]. In this way it is possible to prepare series of activated carbon with essentially the similar microporosity but different degree of oxidation and to carry out a systematic study of the adsorption of molecules with different polarity or polarizable extent. PAN-based ACF samples studied were produced in our laboratory at nitrogen atmosphere by steam activation from 820~850℃, then ACF samples were oxidized directly by air in the stainless steel tube reactor which can be heated electrically to a desired temperature such as 300~400℃ to obtain the samples with different surface oxygen functional groups, before oxidation all samples were outgassed at 950℃ in nitrogen to reduce the number of oxygen surface functional groups to a minimum. Then the adsorption capacity of oxidized samples for molecules with different polarity were investigated. The chemical components of oxidized samples were evaluated by Elementar analysensystem GmbH Vario EL (Germany). The factors conditioning the adsorption behaviour relative between microporosity and amount of oxygen surface groups of ACF were analyzed.

Results and Discussion

It is well known, owing to the nonpolar nature of carbon, the dispersion component of adsorption interaction plays the determining part in adsorption of substance on porous carbon, the phenomenon is known as physisorption. But for presenting of active sites on the surface of porous carbon, oxygen atoms are frequently fixed by chemisorption to form carbon oxygen surface complexes even at very low temperature. The samples outgassed at 950℃ were oxidized directly by air at 300~400℃ to obtain the samples with different oxygen content. Chemisorption proceeds, generally, more rapidly with rise in temperature, and therefore, like most chemical reactions, involves an activation energy. The adsorptive properties of porous carbon are determined not only by its porous structure but also by its chemical components. In graphite or graphite-like materials, with a highly oriented structure, the adsorption takes place mainly by the dispersion component of the van der Waals forces, but the random ordering of imperfect aromatic sheets in porous carbon results in incompletely saturated valences and unpaired electrons, and this will influence the adsorption behaviour, especially for polar or polarizable molecules. Oxygen surface groups are by far the most important in influencing the surface characteristics and adsorption behaviour of activated carbon, and as such they have attracted much attention in the last few years[5]. When molecular oxygen is introduced to an outgassed carbon surface it is either physically, reversibly adsorbed or it is chemisorbed on the surface. Which process predominates depends mainly on the temperature at which adsorption takes place. In general terms, although at low temperatures the adsorption is completely

reversible, as the temperature is increased, the chemisorption of oxygen increases and the molecules dissociate into atoms that react chemically with the atoms of carbon to form oxygen surface compounds. The chemical components of oxidized samples and adsorption amount for alcohol and benzene are shown in table 1. In the case of 300℃, with oxygen content increasing the adsorption amount of polar alcohol increases, it is shown that the oxygen atoms fixed on PAN-based ACFs are increased with temperature of chemisorption increasing. The adsorption amount of samples for nonpolar benzene keep constantly in a small range, this means that only the surface oxygen groups are changed but the porosity of PAN-based ACFs are not changed after oxidation at 300℃ even for 24 hours. But in the case of 400 ℃, from the adsorption measurement, both polar alcohol and nonpolar benzene improved with the increasing of oxidation time. This meant that not only chemisorption of oxygen took place but activation by oxygen occurred also, the yield decreased fleetingly as shown in fig. 1, thus the porosity may be changed at higher temperature. At present the porosity need to be characterized to interpret the phenomenon. It is our objective to obtain PAN-ACF samples with different surface functional groups, and more to develop adsorbents with high selectivity.

Conclusions

PAN-ACF samples with different oxygen content were prepared by direct oxidation with air. This means that the surface polarity of porous carbonaceous adsorbents can be changed by oxidation easily and the adsorption properties for different molecule of polarity can be affected by surface functional groups.

References

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Table 1 The chemical components and adsorption capacity of the oxidized samples

Samples		Element Analysis (%)				Adsorption Capacity (mg/g)	
		C	H	O	N	Alcohol	Benzene
Blank		73.29	1.87	13.98	10.62	163.73	178.41
950℃ outgassed		79.52	1.31	10.12	9.04	46.79	68.50
300℃	5hr	72.11	1.97	15.19	10.73	159.87	195.67
	10hr	70.71	2.06	16.39	10.84	172.78	195.76
	24hr	68.36	2.22	17.59	11.82	197.43	212.31
400℃	1hr	68.85	2.20	17.42	11.52	237.58	266.67
	5hr	67.09	2.22	20.35	10.34	280.64	325.74
	10hr	56.27	1.89	30.41	11.43	465.64	605.04

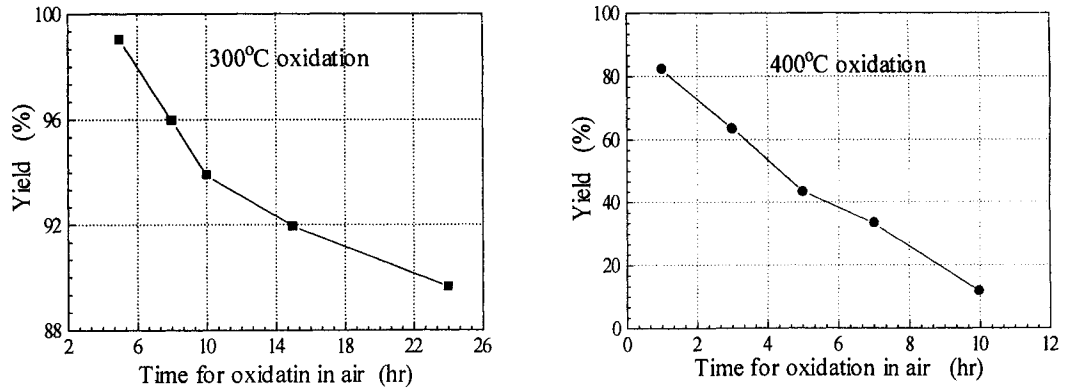

Fig. 1 The oxidation results of PAN-ACFs outgassed at 950℃ in nitrogen at different temperatures