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Surface-Modified Carbons for the Drying of Gas Streams

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Abstract

As-received commercial activated carbons do not adsorb noticeable amounts of water vapor at lower relative vapor pressures (r.v.p.). Following surface oxidation with nitric acid, moisture sorption capacity at lower r.v.p. increases 100-fold. Exchange of surface H^+ ions of oxidized carbons by metal cations (Li, Na, K, Ca) brings about a further substantial increase in moisture sorption capacity. At lower r.v.p., water uptake on some of the cation exchanged samples is comparable to that on commercial zeolite molecular sieves. Following an adsorption run, moisture sorption capacity of ion-exchanged carbons can be fully restored upon outgassing at 140°C. This is in sharp contrast to the zeolite sieves which need to be heated to above 350°C to be completely regenerated.

INTRODUCTION

Probably the most important use of commercial zeolite molecular sieves, at the moment, is the removal of water from gas streams. Water is accessible to all types of A and X zeolites and is held strongly and preferentially to most other adsorbates. However, the zeolite sieves hold water so tenaciously that following adsorption of water vapor, complete regeneration is possible only at about 350–400°C. We have been able to produce novel modified carbons which have high moisture sorption capacities (in some cases as high as those of the zeolite sieves) but which, unlike the zeolite sieves, can be fully regenerated at much lower temperatures.

It is well known that a clean carbon surface is essentially hydrophobic in nature. However, surface properties and surface characteristics of carbons

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can be modified by the introduction of specific heteroatom functional groups on their surfaces (1). Most important of these functional groups are the carbon-oxygen complexes (1). These complexes in some cases are of such great importance that the reactions which seemingly appear to be of carbons are in reality of these complexes. We have recently shown that as-received commercial activated carbons, even though they have large surface areas ($\sim 1000 \text{ m}^2/\text{g}$), adsorb little or no ammonia from aqueous solution but ammonia uptake capacity increases appreciably upon surface oxidation (2). Further, oxygen complexes enhance water adsorption capacity of microcrystalline carbons; the effect is more pronounced at lower relative vapor pressures (1, 3, 4). Replacement of H^+ ions of acidic oxygen complexes by metal cations enhances moisture sorption capacity of carbons (5). Therefore, it appears that if the concentration of acidic surface complexes and, hence, of exchangeable metal cations can be significantly enhanced, it should be possible to prepare carbons having high moisture sorption capacities. In the present study, we have explored this possibility.

EXPERIMENTAL

Three commercial activated carbons supplied by different companies were used in the present study. They had BET N_2 surface areas in the range 830–975 m^2/g . The as-received carbons were oxidized with dry and moist air, ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$, hydrogen peroxide, and nitric acid. Details of the experimental procedure have been given elsewhere (2).

Surface H^+ ions of acidic oxygen groups present on the oxidized carbon surfaces were exchanged for metal cations (Li, Na, K, Ca) by treating 1 g portions of the carbon with 50 mL of appropriate 0.2 *N* alkali solution. The suspensions were shaken mechanically for 48 h after which the carbons were washed free of excess alkali with 60% alcohol.

Water sorption isotherms on carbons were measured gravimetrically at 20°C . Prior to making an adsorption run, the carbon samples were outgassed overnight at 140°C down to 10^{-6} torr. An arbitrary adsorption time of 1 h was allowed for each point on the isotherm. Details of the experimental procedure have been given elsewhere (4).

RESULTS AND DISCUSSION

Although commercial activated carbons have large surface areas, they adsorb little or no water vapor at lower relative vapor pressures (r.v.p.) (Figs. 1–3). Up to 0.6 r.v.p. the as-received carbon A (Fig. 1) adsorbs significantly more water vapor than carbons B and C (Figs. 2 and 3, respectively). It was thought that this behavior may be due, at least in part, to the presence of

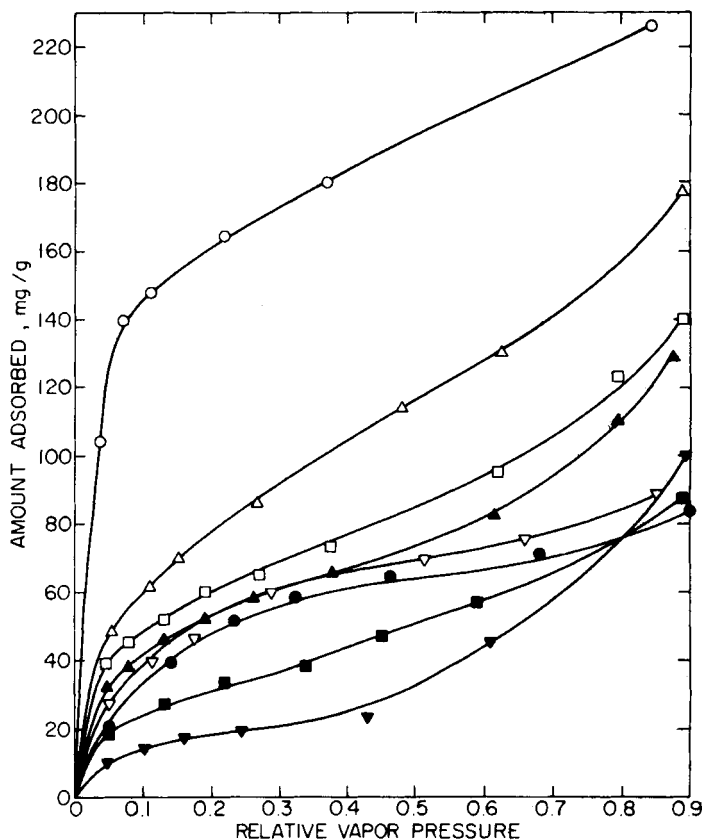


FIG. 1. Effect of surface oxidation on moisture sorption capacity of carbon A: (■) as-received; (▼) as-received treated with HCl. Carbon oxidized with: (●) dry air; (▽) moist air; (▲) H_2O_2 ; (□) $(\text{NH}_4)_2\text{S}_2\text{O}_8$; (△) 10 mL HNO_3 /g carbon; (○) 30 mL HNO_3 /g carbon.

some inorganic impurities which have been suggested earlier to enhance moisture sorption capacity of coals (4). Confirmation for this view comes from the fact that, following leaching with HCl, the moisture sorption capacity of carbon A decreases significantly over the entire r.v.p. range. The still higher moisture capacity of carbon A even after HCl treatment, compared to carbons B and C, could be due to the presence of a higher concentration of oxygen functional groups which, as will be discussed below, are conducive for water uptake.

The dramatic effect of oxygen complexes on moisture sorption capacity of carbons is brought out clearly in Fig. 1. We have recently reported (2) that

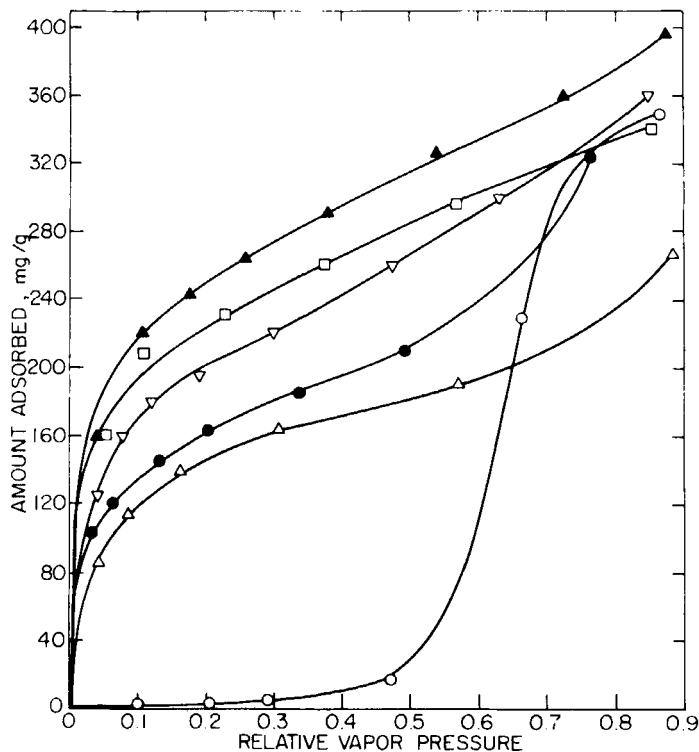


FIG. 2. Effect of cation exchange on moisture sorption capacity of carbon B: (○) as-received; (△) as-received oxidized with 30 mL HNO_3 /g carbon. Cation-exchanged samples: (●) Ca^{2+} ; (▽) K^+ ; (□) Li^+ ; (▲) Na^+ .

for a given carbon the efficacy of various oxidative treatments used in the present study to enhance surface acidity and, hence, concentration of oxygen complexes follows the order: $\text{HNO}_3 > (\text{NH}_4)_2\text{S}_2\text{O}_8 > \text{H}_2\text{O}_2 > \text{moist air} > \text{dry air}$. It is seen (Fig. 1) that the increase in moisture sorption capacity due to surface oxidation follows the same trend as the concentration of oxygen functional groups. It is noteworthy that at lower r.v.p. up to a 100-fold increase in moisture sorption capacities of activated carbons occurs following surface oxidation with 30 mL HNO_3 /g carbon. Thus surface oxidation places at our disposal a convenient method for increasing the moisture sorption capacity of otherwise hydrophobic carbons.

Adsorption-desorption isotherms on the as-received carbons were found to meet each other close to zero r.v.p. However, in the case of the oxidized samples, the two curves did not meet even at zero r.v.p. In these cases a part

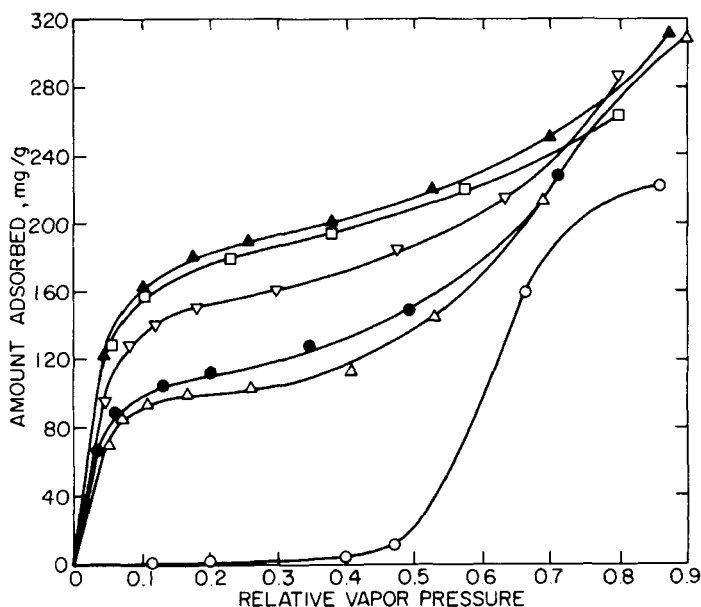


FIG. 3. Effect of cation exchange on moisture sorption capacity of carbon C: (O) as-received; (Δ) as-received oxidized with 30 mL HNO_3 /g carbon. Cation-exchanged samples: (\bullet) Ca^{2+} ; (∇) K^+ ; (\square) Li^+ ; (\blacktriangle) Na^+ .

of the adsorbed water was retained irreversibly even after outgassing at adsorption temperature (20°C). This amount was found to increase with an increase in the content of oxygen functional groups. This water could be completely desorbed upon degassing the carbon at 140°C , the temperature used for degassing the sample prior to making adsorption measurements.

The effect of different exchangeable cations on moisture sorption capacity of carbons B and C oxidized with 30 mL HNO_3 /g carbon is shown in Figs. 2 and 3, respectively. In each case, replacement of surface H^+ ions of the carbons by different metal cations results in an increase in moisture sorption capacity over the entire r.v.p. range. At a given r.v.p. the efficacy of different cations to enhance moisture sorption capacity follows the trend: $\text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{Ca}^{2+}$. It is noteworthy that at lower r.v.p. the Na^+ -exchanged samples adsorb twice as much water as the oxidized samples.

In the present study the highest moisture capacity at lower r.v.p. was observed for Na^+ -exchanged carbon A oxidized with 30 mL HNO_3 /g carbon (Fig. 4). For instance, 1 g carbon adsorbs 0.25 g water vapor at 0.05 r.v.p. To the best of our knowledge, carbons having such high moisture sorption capacities have never been reported before.

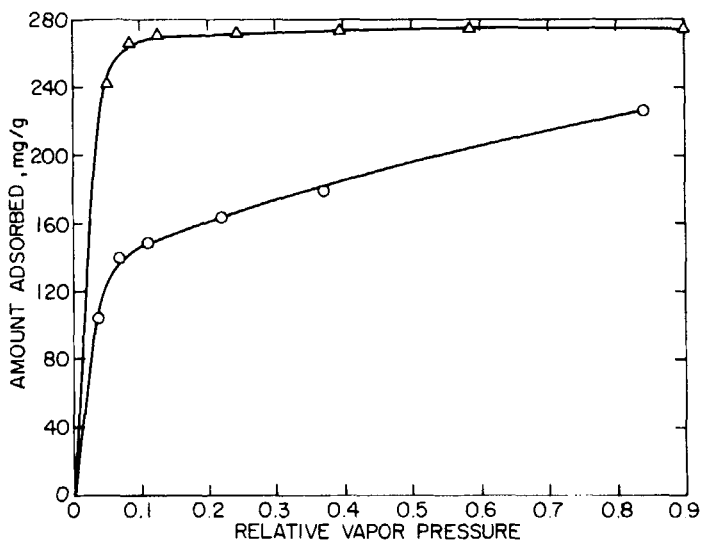


FIG. 4. Moisture sorption isotherms on oxidized and Na⁺-exchanged carbon A samples: (○) oxidized; (△) Na⁺-exchanged.

The results summarized in Table 1 show that above 0.05 r.v.p., water uptake on the Na⁺-exchanged carbon A is comparable to that on commercial zeolite molecular sieves. With our present experimental set-up, we cannot measure moisture sorption below 0.05 r.v.p.

Sorption-desorption isotherms on the cation-exchanged samples showed that the amount of water adsorbed irreversibly at zero r.v.p. was greater than

TABLE I

Moisture Sorption on Zeolites and Na-Carbon A

Zeolite	p/p_0	x/m^a	p/p_0	x/m	p/p_0	x/m	p/p_0	x/m
NaA	0.001	160	0.004	200	0.168	250	0.84	280
CaA	0.001	190	0.004	220	0.168	270	0.84	300
NaX	0.016	240	0.042	260	—	—	0.84	240
NaY	0.004	80	0.04	250	—	—	0.84	350
CaY	0.008	120	0.04	240	—	—	0.84	340
Chabazite	0.002	156	0.04	220	—	—	0.4	266
Mordenite	0.004	95	0.21	136	—	—	0.84	150
Na-carbon A	0.05	250	0.1	260	0.2	270	0.4	280

^aWater adsorbed, mg/g.

that on the oxidized samples. However, moisture sorption capacity was fully restored upon outgassing the carbon at 140°C. This is in sharp contrast to the zeolite sieves which need to be heated to above 350°C to be completely regenerated.

CONCLUSIONS

In view of the work conducted so far, the use of cation-containing active carbons for the drying of gases (and perhaps liquid) streams in place of the zeolites would seem to have some definite advantages. First, as discussed, the carbons can be regenerated by heating to a lower temperature than can the zeolites. This can be an important consideration today because of the high cost of energy. Second, the cost of producing these modified carbons is expected to be significantly less than that of producing the zeolites.

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