

The analysis of surface and pores of activated carbons by the adsorption of various gases

K. Nakai¹⁾, J. Sonoda¹⁾, S.Kondo²⁾ and I. Abe³⁾

1) Bel Japan Inc., Ebie, Fukushima-ku, Osaka 553

2) Fukui Inst. Tech., Gakuen, Fukui 910

3) Osaka Municipal Tech. Res. Inst., Joto-ku, Osaka 536

Abstract - The analysis of surface and pores of activated carbons oxidized to various degrees has been carried out on the basis of adsorption isotherms of nitrogen, water and several organic compounds. The reason for the large hysteresis of isotherms of water was ascribed to the structure formation of water in the micropores caused by the hydrophobic interaction at water-carbon interface.

INTRODUCTION

The surface of activated carbons has been characterized from physical, chemical and industrial points of view by many researchers. Among them, the pore structure analysis has been carried out on adsorption isotherms of microporous carbons such as molecular sieve carbons and carbon fibers intensively for the purpose of physical characterization.¹⁾ The influence of oxidative and reductive treatment of this material at various temperatures upon the surface properties is also one of the most important subjects to study from chemical view point. The surface oxidation of this material by various means gives a drastic change to the surface area and pore size as well as to chemical properties such as hydrophilicity to the hydrophobic surface.

The adsorption isotherms of various nonpolar and polar gases on this material can supply interesting information of not only of physical characterization such as microporosity and fractal property, but also chemical nature such as acidity and hydrophilicity can be studied.

The physical and chemical characterization is studied in this report on an activated carbon oxidized to various degrees with nitric acid. The detailed analysis of adsorption isotherms of various nonpolar and polar compounds gave some interesting results.

MATERIALS

Granular activated carbons "DIAHOPE" of Mitsubishi Chemical made by steam activation of coal were ground to powder less than 75 mesh. This material was boiled with nitric acid solution of 1, 6 and 12 mol/l concentration for 1 h. The original and acid treated materials were washed repeatedly with pure water until

the electric conductivity of washed water became less than $2 \mu\text{S}$. These were dried in vacuo at 383 K for 3 h. The original and acid-treated materials were called AC-0, -1, -6 and -12 respectively. The weight of these materials for measurement were measured without exposure to air after drying at 383 K in vacuo.

METHODS OF MEASUREMENT

The acidity and basicity of these materials were measured by back titration of the slurries of these materials by sodium hydroxide, sodium carbonate and hydrochloric acid by back titration in aqueous solution at 298 K at various equilibrium concentrations.²⁾ The results of these analyses are listed in Table I.

An automatic volumetric gas adsorption instrument BELSORP 28SA, the flow diagram of which is shown in Fig 1,³⁾ was used for the adsorption isotherm measurement of nitrogen of 99.9999 % purity at 77 K, ammonia of 99 % purity, n- and iso-butane of 99 % both dried with molecular sieve 5A at 273 K. The temperature change of liquid nitrogen bath by atmospheric pressure change was measured by nitrogen gas ampoule probe in this figure and this change of temperature was transformed to the change of saturation vapor pressure P_0 of liquid nitrogen. This corrected value was used to compute the precise values of adsorbed amounts near saturation pressure, $P/P_0=1$. Also, the pressure increase (the amount of gas feed) was controlled to a appropriately small amount automatically by an artificial-intelligence software, and hence a sharp rise of the adsorbed amount can be detected. Thus the initial rise of the isotherm was precisely measured. The fluctuation of liquid nitrogen level was about ± 0.5 mm. The evacuation of pretreatment and measuring system is carried out independently. Thus the total experimental error of the surface area measurement was less than about ± 0.5 %.

The adsorption isotherms of neopentane (tetramethyl methane) of 97 % purity, distilled water and methanol of analytical grade

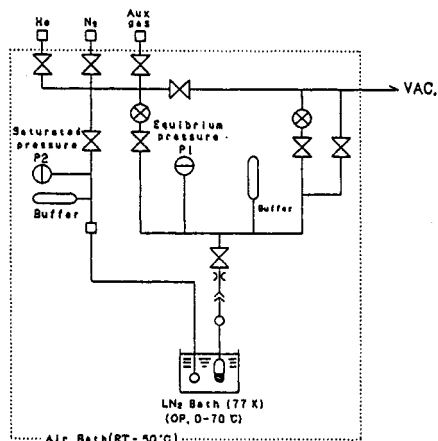


Fig. 1 The flow diagram of BELSORP 28SA

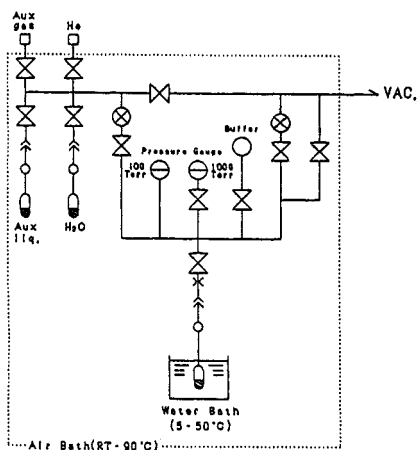


Fig. 2 The flow diagram of BELSORP 18

Table 1. The adsorbed amount of sodium carbonate, sodium hydroxide and hydrochloric acid on carbon adsorbents oxidized with nitric acid.

	adsorbed amount (mmol/g)		
	Na ₂ CO ₃	NaOH	HCl
AC-0	0.050	0.146	0.332
AC-1	0.199	0.511	0.214
AC-6	0.497	0.659	0.174
AC-12	0.750	1.222	0.039

were measured with an automatic volumetric gas adsorption instrument BELSORP 18 at 298 K, the flow diagram of which is shown in Fig. 2. All the stainless steel walls of the adsorption system was polished chemically so that the adsorbed amount of the adsorbates on these walls was very small as seen in Fig.3. This amount was measured without sample and was subtracted from the total adsorbed amount by computer so as to give the true isotherms. The measurement part was placed in a thermostat chamber. The liquid adsorbates were also placed in an ampoule in this chamber and gases evaporated from the ampoule were introduced to measuring system. These liquids usually dissolve gases from the air and these are removed by evacuation after carefully freezing the liquid at liquid nitrogen temperature. Freezing and evacuation cycles were repeated several times until no gases were remained in the liquid.

RESULTS AND DISCUSSION

The adsorbed amounts of sodium hydroxide, carbonate and hydrochloric acid increased as the function of oxidation (the concentration of nitric acid) as shown in Table 1. The consumption of sodium hydroxide and carbonate in the case of AC-12 was 10 times greater than that of AC-0. This indicates that the number of acidic functional groups increased on the surface as the oxidation is enhanced (markedly above 12 mol/l). In contrast, the rate of consumption of hydrochloric acid (the concentration of basic sites) decreased by the surface oxidation.

A marked increase of the adsorbed amount of ammonia at low pressure range is seen by the increase of concentration of nitric acid (the degree of oxidation) as illustrated in the ammonia adsorption curves of these samples in Fig. 4. This result also suggests the increase of the number of the surface acidic functional groups. Low pressure hysteresis was observed in these

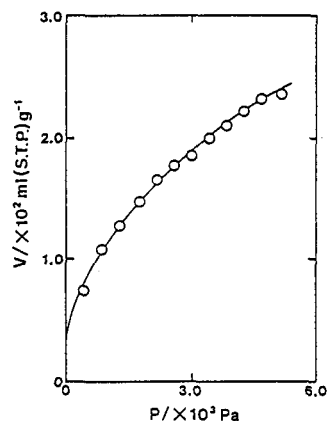


Fig. 3 The adsorbed amount of water on the walls

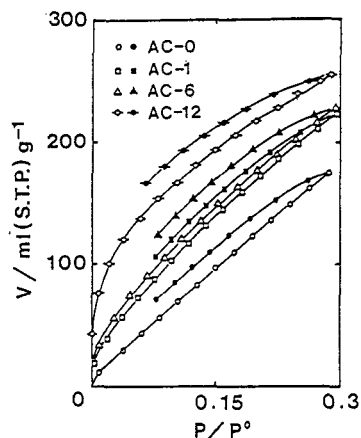


Fig. 4 The ammonia isotherms of AC-0 ~ 12

Table 2. BET surface area, A_{BET} , total, external and internal (pore) surface area, A_t , A_{ex} and A_{in} respectively, micropore volumes, V_p , and pore diameters $2t$ and D_{MP} , obtained from the t- and MP-methods.

	$A_{BET}(m^2/g)$	$A_t(m^2/g)$	$A_{ex}(m^2/g)$	$A_{in}(m^2/g)$	$V_p(ml)$	$2t(nm)$	$D_{MP}(nm)$
AC-0	1017	1093	90	1002	0.44	0.87	0.84
AC-1	1023	1062	80	983	0.42	0.86	0.84
AC-6	1052	1084	90	995	0.42	0.86	0.84
AC-12	829	881	62	819	0.38	0.92	0.90

curves, which also indicates the chemical adsorption of ammonia on the acidic sites.

All the nitrogen adsorption isotherms of these materials belong to approximately type I isotherm with slight adsorption hystereses in higher pressure range, as seen in Fig. 5 on AC-0 and -12 as the examples. This indicates that these materials are predominantly microporous with a very small amount of mesopores.

Fig. 6 shows the t-curve plot of the isotherm of AC-0 and -12 as the examples. The gradual inclination at the intercept of 2 straight lines indicates the distribution of micropore radii of this curve. Dubinin-Astakhov equation⁴⁾ was computed from these isotherms as shown in Fig. 7. These curves show the existence of a small amount of ultramicropores, the volume of which seems to decrease slightly by oxidation. The MP plots of these isotherms in Fig. 8 gave little smaller diameter of micropores with the increase of area in the larger pore diameter range of the distribution peaks. This tendency of increase of pore size is also shown in the t-curves mentioned above.

Table 2 summarizes surface properties of these materials obtained from the nitrogen adsorption isotherms, such as the total, external and internal surface areas derived from t-method and specific surface areas computed from BET equation, A_t , A_{ex} , A_{in} and A_{BET} , respectively, pore volumes, V_p , and the diameter of the micropores by t- and MP-methods⁵⁾, $2t$ and d_{MP} , respectively of all samples. Generally, A_{BET} , although applicable for mesopore materials, is nearly equal to A_t . There was only a small decrease of A_t which is parallel to the decrease of A_{in} on the samples AC-0, -1 and -6. This shows that the oxidation by nitric acid of these concentration was not so strong

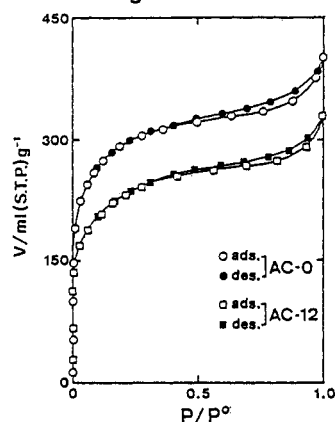


Fig. 5 The nitrogen adsorption isotherms on AC-0 ~ -12

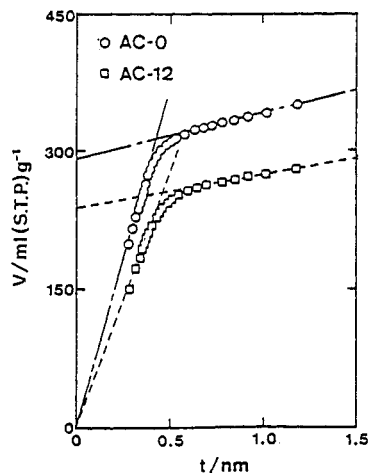


Fig. 6 The t-plots of AC-0 and -12

as to give a change to the bulk structure of this material. In contrast, A_t , A_{ex} , A_{in} and V_p were decreased and the micropore diameter increased appreciably in AC-12 which indicates that the oxidation by 12 mol/l nitric acid caused the enhanced change of not only the surface functional groups but also influenced the micropore structure.

The isotherms of n- and iso-butane and neopentane are shown in Fig. 9 on the sample AC-12 as the representative examples.

These isotherms belong to approximately type I with small amount of hysteresis in the mesopore range. This tendency is similar to those of nitrogen isotherms. The volumes of these adsorbates in the micropores were estimated from these isotherms under the assumption that the densities of these adsorbate in the pores are equal to these of bulk liquids and these are listed in Table 3, together with the minimum diameters, D_m of these molecules. The values in the brackets were obtained by dividing these values by those of the volumes of nitrogen in the pores. These values in the brackets of hydrocarbons are smaller than 1 and as the size of the molecules increased these values decreased as seen in each column of the table. This result indicates the relation of the sizes between the micropore and hydrocarbon become smaller as the oxidation is enhanced with almost the same density values in the brackets. The micropore volumes estimated by these hydrocarbons on each sample (in each column) decreased as the sizes of the molecules become larger. This indicates that the sizes of the micropores are close to the diameters of adsorbate.

The adsorption isotherms of water and methanol as illustrated in Fig. 10 on AC-12 are different from these mentioned above. These of water belong to type V being typical to the hydrophobic interface interaction with appreciable amounts of hystereses.^{6,7)} Small rise of adsorbed amount in low P/P_0 originate in a small fraction of hydrophilic interaction due to a small amount of acidic functional groups on the surface.

The fraction of the adsorbed amounts of water in the pore are smaller than 1 as seen in the brackets of Table 3 assuming the density of water inside micropores is equal to that of bulk water. This result contradicts with the following inference that the size of this molecule is smaller than that of nitrogen and water would fill even the ultramicropore of these materials,

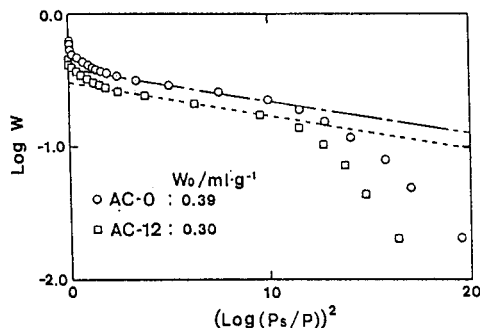


Fig. 7 The Dubinin-Astakhov plots of AC-0 and -12

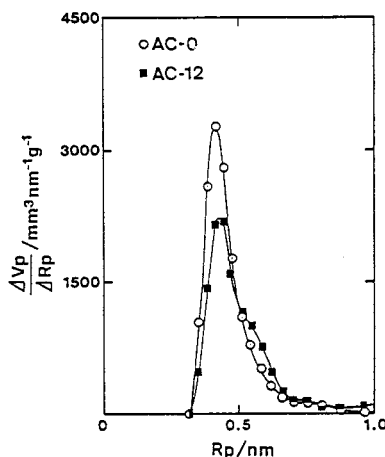


Fig. 8 The pore size distributions of AC-0 and -12 by MP method

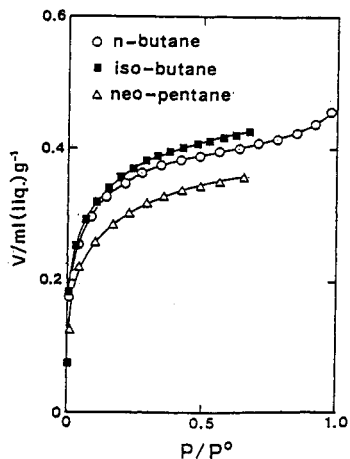


Fig. 9 The isotherms of hydrocarbons on AC-12

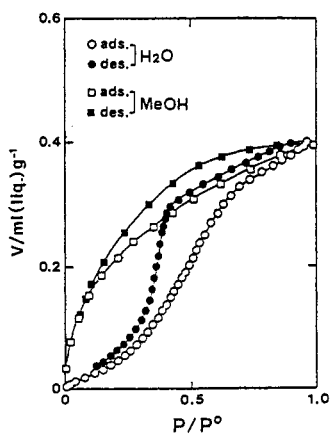


Fig. 10 The isotherms of water and methanol on AC-12

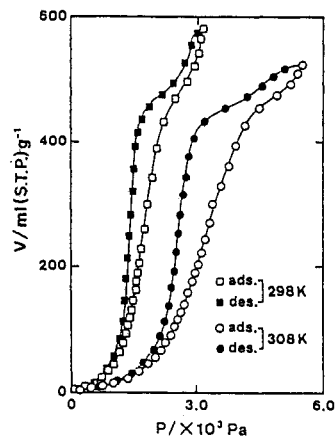


Fig. 11 The isotherms of water on AC-1 at 298 and 308 K

which should give rise to a larger fraction than 1. This contradictory result and the large adsorption hystereses of water may be explained as follows. The structure of water in these micropores would become more ordered than that of bulk water as the adsorbed amount is increased, because the hydrophobic interface interaction of water with the carbon surface would make the water hydrogen-bond stronger and would make the structure more ordered.⁸⁾ Then, the density of water inside the micropore would become lower than that of liquid water as the adsorption of water into the micropores proceeds. This would result in the decrease of water density in the pore. With this ordered structure, the vapor pressure of adsorbed water would become lower than that of bulk liquid water as the pores were filled. Thus, the desorption branch of the isotherm would show a large hysteresis. Fig. 11 shows the adsorption isotherms of water on AC-1 at 298 and 308 K. The energy of adsorption obtained from Clausius-Clapeyron equation by applying to these isotherms was a little more than the heat of condensation as seen in Fig. 12. This result supports the above interpretation.

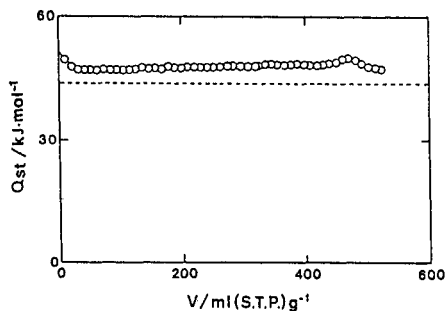


Fig. 12 The differential energy of adsorption of water on AC-1

The another possible interpretation for this hysteresis would be that there are a small degree of hydrogen-bond interaction of water with surface functional groups which lie mostly on the edge of the pores. This would make the desorption of water from the pores difficult.

The isotherm of methanol belongs to a mixture of types I and V, because methanol molecule is amphiphilic. A similar interpretation to water adsorption would be applicable to methanol, as is indicated in the small values of densities of methanol in the pores shown in the brackets of last line.

Table 3. The adsorbed volumes(ml) and the ratios of adsorbed volumes of each adsorbate to that of nitrogen in the brackets.

	AC-0	AC-1	AC-6	AC-12
Nitrogen	0.623 (1.0)	0.598 (1.0)	0.608 (1.0)	0.510 (1.0)
n-butane	0.545 (0.87)	0.522 (0.87)	0.520 (0.86)	0.457 (0.90)
iso-butane	0.487 (0.78)	0.449 (0.75)	0.470 (0.77)	0.370 (0.73)
Neopentane	0.450 (0.72)	0.410 (0.69)	0.421 (0.69)	0.344 (0.67)
Water	0.430 (0.69)	0.467 (0.78)	0.434 (0.71)	0.399 (0.78)
Methanol	0.450 (0.72)	0.474 (0.79)	0.461 (0.76)	0.394 (0.77)

REFERENCE

- (1) S.J. Gregg and K.S.W. Sing, "Adsorption, Surface and Porosity", 2nd ed., Academic Press, London (1982), p.262.
- (2) H.B. Boehm, "Advances in Catalysis", vol.16, Academic Press, N.Y., (1966), p.179.
- (3) H. Naono and M. Hakuman, J. Colloid and Interface Sci., 145, (1991) p.405.
- (4) M.M.Dubinin & V.A.Astakhov, Adv. Chem. Ser. No. 102, 69(1971).
- (5) R.Sh. Mikhail, S.Brunauer & E.E.Bodor, J.Colloid Interface Sci., 26, 45(1968).
- (6) J.C. Arnell and H.L. McDermott, Canad. J. Chem., 30,177(1952).
- (7) M.M. Dubinin, "Chemistry and Physics of Carbon", vol.2, Marcel Dekker, New York, (1966), p.51.
- (8) S. Kondo, T. Ishikawa and I. Abe, "Science of Adsorption", Maruzen, Tokyo, (1991), p.128.