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Distribution of surface oxygen complexes on activated carbons from immersion calorimetry, titration and temperature-programmed desorption techniques

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Surface oxygen complexes on activated carbons essentially determine their surface chemistry, which is of great importance in their applications as adsorbents in aqueous solutions [1] and as catalysts and support for catalysts [2]. Different techniques are used to determine their chemical nature, their amount and the interactions with other molecules. In this letter it will shown that it is possible to know also their distribution by using three of the most common techniques such as: immersion calorimetry, titration and temperature-programmed desorption.

To carry out this work two oxidized activated carbons were used, samples AZ46-1 and AZ46-24, described in detail elsewhere [3]. Different portions of these carbons were treated in a helium flow at 20°C/min, up to final temperatures between 350 and 1000°C, in order to remove partly the surface oxygen complexes. The resulting portions were kept in humid air at room temperature for 2 years. These samples will be referred to in the text as AZ46-1 and AZ46-24 followed by a number corresponding to the outgassing temperature.

The surface oxygen complexes of these samples were studied by temperature-programmed desorption (TPD) as described previously [3]. All samples were heated in a He flow, from ambient temperature to 1000°C at 50°C/min, and the amounts of CO and CO_2 evolved were recorded as function of temperature. The total surface acidity of the samples was determined as explained elsewhere [3]. The various results are shown in Table 1.

The enthalpies of immersion of samples (Table 2) into benzene and water, $-\Delta_i H(C_6H_6)$ and $-\Delta_i H(H_2O)$, and the corresponding enthalpy of neutralization into NaOH 2N, $-\Delta_i H(NaOH)$, were determined with a calorimeter of the Tian-Calvet type [5,6]. The net enthalpy of neutralization, $\Delta_i H(NaOH)_{net} = \Delta_i H(NaOH) - \Delta_i H(H_2O)$, is proportional to the amount of acid present on the surface.

The enthalpy of $\Delta_i H(C_6H_6)$ increases with the outgassing temperature of the original samples, which suggests that the surface area and/or the micropore volume increase slightly during outgassing, as a result of gasification produced by the evolution of CO and CO_2.

The variation of the net enthalpy of neutralization of all acid groups, $\Delta_i H(NaOH)_{net}$, with the oxygen content of the samples is shown in Fig. 1. A similar pattern has been observed previously [4,5] with oxidized activated carbons of different origin. The present correlation leads to an energy of −15.9 J/mmol of surface oxygen (correlation coefficient 0.951), in good agreement with the result obtained earlier [4].

As reported earlier [4], $\Delta_i H(NaOH)_{net}$ corresponds to -41.1 ± 1.8 J/meq of acid at 293 K, in good agreement with direct titration. This means that in the present case 41.1/15.9=2.58 mmol of oxygen are involved per meq of surface acid group neutralized by NaOH. This is obviously more than the numbers of oxygen atoms expected for carboxylic (2), lactonic (2) and phenolic groups (1), which indicates that a certain amount of oxygen is not directly involved in the total acid groups.

The comparison of the amount of acid neutralized by NaOH with the amount of CO_2 evolved from the samples reveals a regular pattern. It appears that in general approximately half the meq of acidic sites correspond to oxygen evolving as CO_2 (Table 1, column 6) and containing two oxygen atoms. The other half must therefore correspond to groups evolving as CO and containing only one oxygen atom. Consequently, if half the acid groups contain two oxygen atoms and the other half only one oxygen atom, one obtains an average of 1.5 oxygen atom per acid sites. The correlation shown in Fig. 1 suggests 2.58 mmol oxygen/meq acid, which means that about 1 oxygen

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Table 1
Amounts of CO and CO_2 evolved up to 1000°C and total surface acidity of the activated carbons

Sample	[CO] (mmol/g)	[CO_2] (mmol/g)	[O][a] (mmol/g)	meq acid/g	mmol CO_2/ meq acid
AZ46-1	2.46	0.82	4.10	1.73	0.47
AZ46-1-350	2.40	0.46	3.32	1.04	0.44
AZ46-1-675	1.81	0.31	2.44	0.65	0.48
AZ46-1-1000	1.09	0.29	1.67	0.52	0.56
AZ46-24	3.96	1.55	7.06	2.62	0.59
AZ46-24-350	3.97	1.02	6.01	1.95	0.52
AZ46-24-675	2.76	0.42	3.60	0.93	0.45
AZ46-24-1000	0.96	0.30	1.56	0.38	0.79

[a] From the amounts of CO and CO_2 evolved up to 1000°C.

Table 2
Enthalpies of immersion of the activated carbons

Sample	$-\Delta_i H(C_6H_6)$ (J/g)	$-\Delta_i H(H_2O)$ (J/g)	$-\Delta_i H(NaOH)$ (J/g)	$-\Delta_i H(NaOH)_{net}$ (J/g)
AZ46-1	114.0	77.6	149.0	71.4
AZ46-1-350	118.8	63.6	106.4	42.8
AZ46-1-675	127.0	57.5	84.3	26.8
AZ46-1-1000	127.5	47.0	68.3	21.3
AZ46-24	113.2	95.0	202.5	107.5
AZ46-24-350	119.1	84.3	164.5	80.2
AZ46-24-675	122.7	69.9	108.1	38.2
AZ46-24-1000	123.1	50.8	66.5	15.7

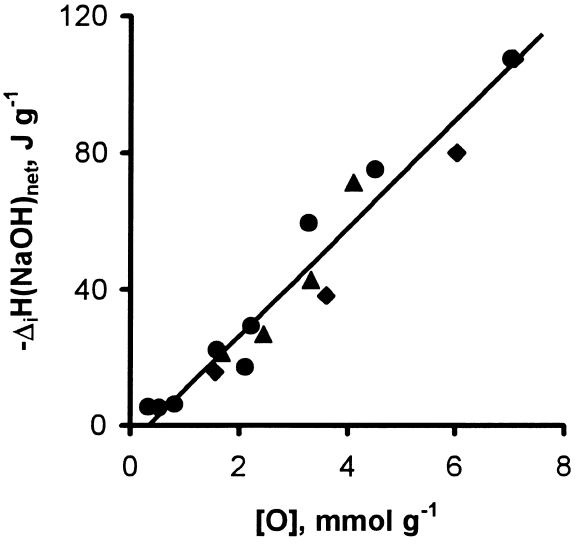

Fig. 1. Variation of the enthalpy of neutralization of the total acid groups with the total amount of oxygen on the surface. (●) Samples from Ref. [4]; (▲) AZ46-1 series; and (♦) AZ46-24 series.

(2.58–1.5) is not involved in the neutralization process. Thus, the distribution of the surface oxygen groups should correspond to the proportion of one 2-oxygen acid group, one 1-oxygen acid group and one non-acidic oxygen group.

It appears that the proportion 1:1:1 is quite regular and it reflects an interesting underlying pattern for the carbons of the present study and probably others. As reported earlier [6], the basic sites found on the surface of activated carbons, titrated with HCl, contain essentially little or no oxygen and they do not exceed 0.5–0.7 meq HCl. Moreover, their number tends to decrease when the carbons are subjected to oxidation.

Assuming that all surface oxygen functionalities have similar interactions with water, a simple correlation was obtained between the enthalpy of immersion into water, the oxygen content of the surface, the basic groups characterized by their meq HCl, the filling of the micropores and the wetting of the external (non-microporous) surface [6]. For a total of 27 well-characterized carbons of different origins and treatments, it was found that the interaction between water and the surface oxygen corresponds to −12.1 J/mmol of oxygen, against −10.3 J/meq

HCl for the basic groups [6]. At the same time [7], another correlation has been established between the enthalpy of immersion into water and benzene, and the amounts of surface oxygen [O] and basic groups [HCl]. The correlation showed that

$$\Delta_i H(H_2O)\,(J/g) = 0.21\Delta_i H(C_6H_6) - 9.9(J/mmol)\,([O + meq\,HCl]) \quad (1)$$

In view of the fact that the samples contain relatively high amounts of oxygen, one may, as a first approximation, neglect the basic sites and combine the data of Tables 1 and 2 with the previous set of data [7]. The overall correlation, illustrated by Fig. 2, leads to an interaction energy of -10 J/mmol of oxygen, which is virtually the same as obtained before. Since it is likely that the oxygen atoms belonging to different functionalities have different interaction energies with water, the good agreement found for the different carbons probably reflects a relatively constant ratio between the functionalities, i.e., approximately 1:1:1, as suggested in the present study. Further investigations will show under which conditions this proportion is valid and results will be published in due course.

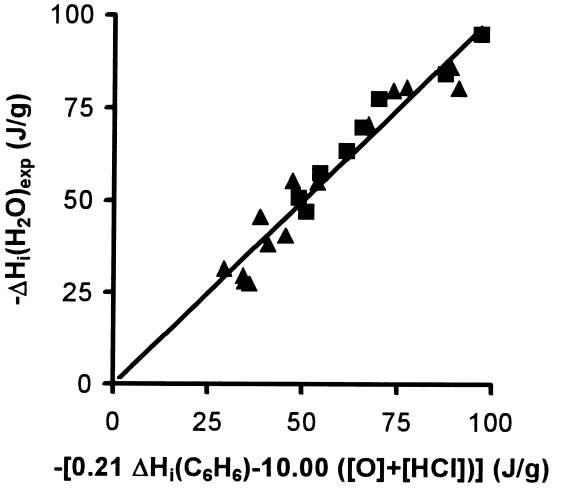

Fig. 2. Overall correlation between the enthalpy of immersion of activated carbons into water and the enthalpy of immersion into benzene and the total surface oxygen plus the total surface basic sites. (▲) Samples from Ref. [7]; and (■) samples from this work.

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