

SURFACE CHEMICAL FUNCTIONALITY OF ACTIVATED CARBONS AND ADSORPTION OF POLAR MOLECULES AT LOW RELATIVE PRESSURE

Issa I. Salame and Teresa J. Bandosz*

Department of Chemistry, The City College and The Graduate School of The City University of New York, New York, NY 10031: *E-mail: tbandosz@scisun.sci.cuny.cuny.edu

Introduction

The objective of this paper is to show how washing with methanol modifies the surface of activated carbon and how this modification affects the process of water adsorption. Based on the results obtained we underline the possibility of chemical transformations which may take place during the water adsorption process. This is very often neglected in the interpretation of data and the discussions are limited only to the physical adsorption phenomena.

Experimental

Materials: Activated carbon WVA 1100 (Westvaco, wood based, H₃PO₄ activation) was chosen for this study. The initial sample, referred to as W, was oxidized with ammonium persulfate (W-APS). Then both, initial and oxidized samples, were washed with methanol in Soxhlet apparatus for 3 days (W/M and W-APS/M).

Methods: The oxygenated surface groups were determined according to the method of Boehm [1]. Potentiometric titration measurements were performed with a DMS Titrimo 716 automatic titrator (Metrohm). FTIR spectra were collected using a Nicolet Impact 410 with DRIFT unit. Thermal analysis was carried out using TA Instruments Thermal Analyzer. Nitrogen isotherms were measured using a ASAP 2010 (Micromeritics) at 77K. Water sorption experiments were carried out at different temperatures close to ambient (283 K-303 K) using Micromeritics ASAP 2010 with vapor sorption kit.

Results and Discussion

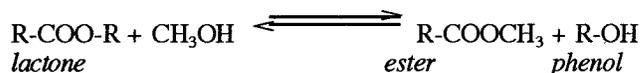
The structural parameters calculated from nitrogen adsorption isotherms are collected in Table 1. As expected, washing with methanol did not cause any significant changes in the structure of carbon samples.

The effect of methanol washing on surface chemistry is much more pronounced (Tab.1); the number of phenols doubled along with a significant decrease in the number of lactones and a small decrease in the population of carboxylic groups. It is noteworthy that the total number of groups was not affected to great extent. Similar changes in surface chemistry after washing with methanol are also observed on pK_a distributions [2].

After washing with methanol the relative intensity of bands at 1699, 1593 and 1288 cm⁻¹ representing vibrations

of C=O, C-O and C-O bonds is unchanged. Indeed, the introduction of methanol, even though resulting in a decrease in the number of carboxylic groups and lactones accompanied by an increase in phenols, should not create more oxygen-carbon bonds.

An increase in the number of phenols accompanied by a decrease in lactones and carboxyls detected consistently using various methods suggests that during washing with methanol esterification occurs. If the necessary energy is supplied (the system is kept at high temperature around the boiling point of methanol) the following pathways of reactions are expected [3]:



Then, when exposed to water in "wet" titration methods hydrolysis occurs:

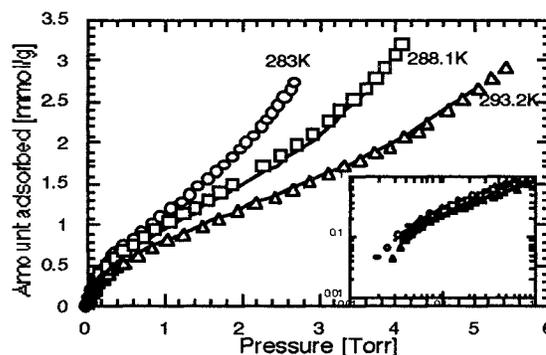
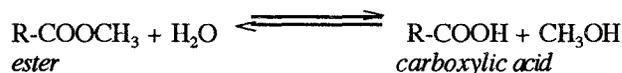


Fig. 1. H₂O isotherm for the W sample

If the mentioned above hydrolysis occurs, the indication of it should be revealed on the water adsorption isotherms. Indeed in the cases of the W and W-APS samples a good reproducibility was obtained (Fig.1). On the other hand, in the case of samples after methanol

treatment the low pressure ranges of the isotherms sometimes cross each other and it is hard or almost impossible to get good reproducibility (Fig.2). When water molecules are adsorbed on the carbon surface decorated with esters hydrolysis takes place resulting in the production of carboxylic surface groups and methanol molecules. The presence of methanol contributes to the vapor phase pressure and may block some centers for water adsorption. Apparent result of this is the measured isotherm which represents sorption of water-methanol mixture.

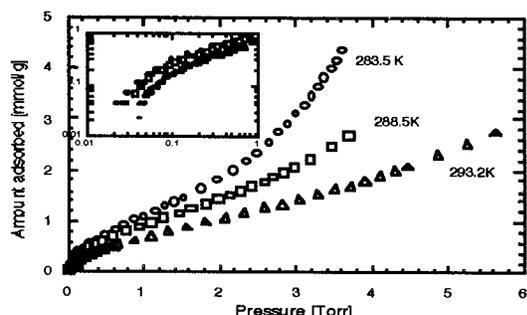


Fig. 2. H₂O isotherm for the W/M sample

The correct measurement of isotherms at two temperatures (at least) is necessary to calculate isosteric heats of adsorption, Q_{st} , provided that the process is reversible and equilibrium is reached [4, 5]. This allows one to calculate Q_{st} which will represent the meaningful quantity. The results are presented in Figure 3. The obtained heats of water adsorption show common features in their shape: an initial increase reaching the plateau at the value of Q_{st} close to 45 kJ/mol (Fig. 3) [4, 6].

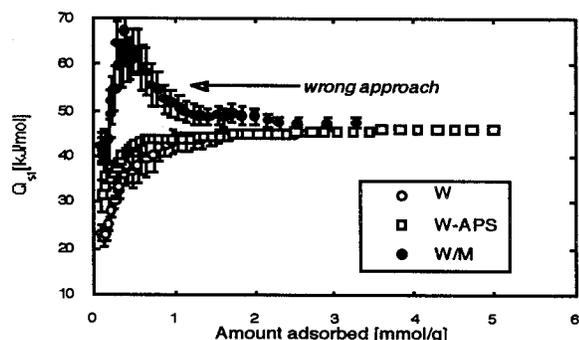


Fig. 3. Isosteric heats of water adsorption

To underline the proper conditions for calculation of the isosteric heat of adsorption a deliberate attempt was made to calculate the heat from the isotherms obtained for the W/M sample (Fig.3). The quantity obtained starts from much higher value than for other samples (~40 kJ/mol), reaches its maximum at about 70 kJ/mol and decreases to about 45 kJ/mol. Based on the discussion presented above, this Q_{st} does not represent the isosteric heat of water adsorption and we mark it in Figure 4 as a wrong approach. Moreover, the calculated error is high.

Conclusions

The results presented in this paper show significant changes in surface chemistry due to washing with methanol. These changes are due to the reaction of esterification leading to an increase in the number of phenols and esters. The esters, when in contact with water are hydrolyzed giving carboxylic acids and methanol as products. When the probability of such reaction exists one can not use the isotherms to calculate the isosteric heats of adsorption due to irreversibility, non-equilibrium conditions and the presence and adsorption of another component, methanol.

Acknowledgment

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References

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Table 1. Structural parameters and the results of Boehm titration [mmol/g]

Sample	S_{BET} [m ² /g]	V_{mic} [cm ³ /g]	carboxylic	lactonic	phenolic	basic	all acidic
W	1710	0.645	0.250	0.250	0.325	0.225	0.825
W-APS	1470	0.541	1.238	0.288	0.625	0.113	2.151
W/M	1730	0.561	0.200	0.125	0.925	0.350	1.250
W-APS/M	1460	0.474	0.980	0.050	1.275	0.050	2.305