

HIGH RESOLUTION ADSORPTION AND THERMOGRAVIMETRIC CHARACTERIZATION OF BASIC ACTIVE CARBONS

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Introduction

Active carbons are versatile adsorbents, which are widely used to remove a broad spectrum of organic and inorganic species from both gas and liquid phases. They also appear to be important catalysts and support substrates.

Novel applications of these materials often require additional modifications in order to improve the physical and chemical properties. It was shown recently [1] in contrast to the regular or oxidized active carbons that the basic active carbons retain stable adsorption properties even upon prolonged storage in the presence of moisture. The main contribution to the surface basicity arises from oxygen-free Lewis base sites on the basal planes. When these sites are occupied by oxygen-containing groups they become acidic. In order to remove the oxygen-containing surface groups and thus obtain a basic carbon surface the heat treatment in different gases such as ammonia, chlorine, etc., has been proposed. Also, basic active carbons have been recently obtained upon treatment in nitrogen and hydrogen atmosphere and studied by elemental analysis, electrophoresis, mass titration, and microcalorimetry [1,2]. The aim of this work was to study these basic carbons by high resolution adsorption and thermogravimetry.

Experimental

Basic active carbons were produced by high temperature treatment of the commercial NORIT C-granulated (Nc) carbon in the atmosphere of inert gases. Nitrogen (N950) and hydrogen (H950) treated samples of active carbons were obtained by heating up to 950°C in a flow of ultra-high-purity nitrogen or hydrogen at 25°C/min and holding them at this temperature for 3 hours.

Thermogravimetric measurements of the Nc, N950, and H950 samples of active carbons were performed in nitrogen atmosphere using a model TGA 2950 (TA Instruments, Inc., New Castle, DE) high resolution thermogravimetric analyzer. All measurements were carried out at the maximum heating rate of 5°C/min from room temperature up to 1000°C. Adsorption isotherms were measured for an ultra-high purity gaseous nitrogen at -195.5°C using a model ASAP2010 (Micromeritics, Inc.,

Norcross, GA) high resolution volumetric sorption instrument. The volume of nitrogen adsorbed was measured as a function of the equilibrium pressure over a range from 10^{-4} Torr to the saturation vapor pressure. Prior to adsorption measurements each carbon sample (about 0.2mg) was outgassed at 200°C for two hours under the vacuum of approximately 10^{-4} Torr.

The analysis of nitrogen adsorption isotherms involved the evaluation of the specific surface area according to the standard BET equation, and the total pore volume according to the single point method. The t-plot method, which is based on the comparison of the adsorption isotherm with the standard isotherm measured on a reference nonporous material, was used to obtain the micropore volume and the external surface area of the Nc, N950, and H950 carbons. The total volume of pores of the width less than 72.5 nm was calculated by converting the volume adsorbed at the relative pressure of 0.975 to the volume of liquid adsorbate.

The adsorption energy distribution functions were obtained by the INTEG program [3] based on the regularization algorithm. The Fowler-Guggenheim equation for localized monolayer adsorption with lateral interaction on the patchwise heterogeneous surface was used to represent the local isotherm. The interaction parameter was assumed to be equal $\omega/kT = 95K$ and the number of nearest neighbors was $z = 2$.

Results and Discussion

The equilibrium amount of nitrogen adsorbed on the Nc, N950 and H950 samples during the complete cycle of adsorption-desorption at -195.5°C is presented against the relative pressure in Fig. 1. All three isotherms are the type IV according to the IUPAC classification. Their hysteresis loops associated with the capillary condensation in mesopores may be classified as the type H4.

The total specific area S_{BET} , specific area of micropores S_{mi} , total specific pore volume V_p , specific volume of micropores V_{mi} along with their ratios are shown in Table 1. As can be seen, the high temperature treatment in an inert atmosphere decreases proportionally both the specific surface area and pore volume. However, the structural changes

caused by this treatment are relatively small in comparison to those related to the carbon surface.

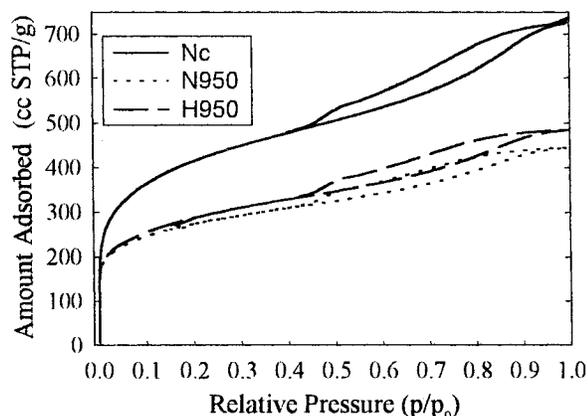


Figure 1. Nitrogen adsorption-desorption isotherms for original, nitrogen, and hydrogen treated carbons at -195.5°C .

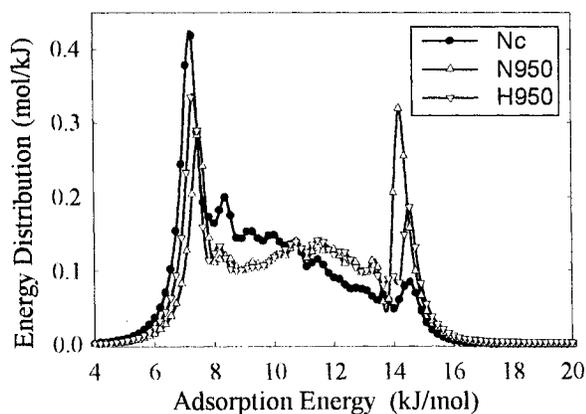


Figure 2. Nitrogen adsorption energy distribution functions for the original (Nc), nitrogen (N950), and hydrogen (H950) treated carbons.

In Fig.2 it is shown that the ratio of low energy sites to high energy sites alters in favour for the nitrogen treated carbons. The high energy peak, which is almost indistinguishable for the original carbon sample, becomes as high as the low energy one upon thermal treatment in nitrogen.

High resolution thermogravimetry yields characteristic temperature regions for weight loss or uptake due to chemisorption. The differential TGA curves shown in Fig.3 are completely different for all three samples. In the case of non-treated carbon destruction of most of the oxygen groups on the carbon surface occurs at the 300-700°C temperature range. This effect is much smaller for treated samples. In addition, it should be mentioned that the hydrogen treated carbon appeared to be stable upon changing nitrogen from prepurified grade to dry one in the

TGA measurements. In contrast, weight loss rate for the Nc and N950 samples increased about 1.5 times at the temperature range above 500°C.

Table 1. The BET specific surface area S_{BET} , specific surface area of micropores S_{mi} , total specific pore volume V_{t} , specific volume of micropores V_{mi} and their ratios obtained from nitrogen adsorption isotherms.

	S_{BET} m^2/g	S_{mi} m^2/g	$S_{\text{mi}}/S_{\text{BET}}$	V_{t} cm^3/g	V_{mi} cm^3/g	$V_{\text{mi}}/V_{\text{t}}$
Nc	1500	970	0.65	1.12	0.44	0.39
N950	970	660	0.68	0.68	0.30	0.44
H960	1030	670	0.65	0.75	0.31	0.41

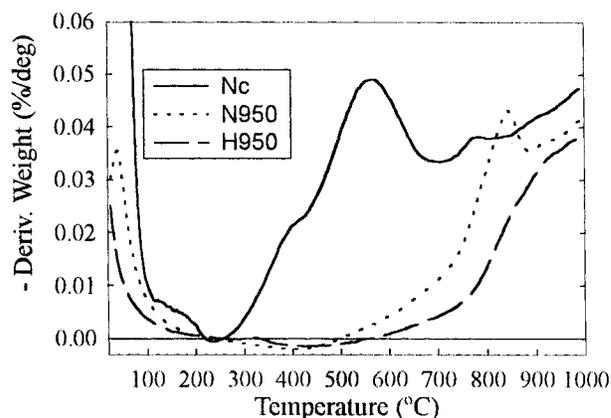


Figure 3. TGA differential curves measured in nitrogen.

Conclusions

High resolution adsorption and thermogravimetric studies reveal essential differences between the original, nitrogen and hydrogen treated active carbons. The relative adsorption is higher in the low pressure region for the N950 sample due to the large fraction of active sites of high adsorption energies. The TGA differential curves for the N950 and H950 samples show small changes in the 150-600°C range. In contrast, the weight loss for the sample Nc in this range is significant due to the decomposition of oxygen surface groups.

References

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