

THE ESTIMATION OF OXIDATION DEGREE OF ACTIVE CARBONS BY SORPTION AND THERMOGRAVIMETRIC METHODS

B. Buczek

Faculty of Fuels and Energy, University of Mining and Metallurgy,
30-059 Cracow Poland

Introduction

Activated carbons are widely used as adsorbents to remove impurities from gas and water streams. They can also be used as catalyst supports as well as bulk catalysts, promoted or unpromoted with inorganic oxides and salts. Properties of activated carbons are strongly influenced by oxygen groups involved in the modification of surface with oxidizing gases or solutions. Depending on the formation conditions, affected by the nature of carbonaceous precursor, porous structure and ash content, surface oxides may impart basic or acidic properties to the carbon surface. Among others, terminal groups influence the distribution of active material in catalysts for selective reduction of nitric oxide with ammonia and thus their catalytic performance[1].

The subject of the work was to study the oxidation degree of active carbons obtained as a result of different procedures (liquid or gas phase treatment).

Experimental

The starting active carbon was obtained in an industrial process of steam activation of hard-coal carbonizate. In order to study the effect of various oxidizing agents on the properties of the active carbon, it was demineralized, carbonized and oxidized. The following carbons were prepared by these treatments: calcinated under nitrogen at 973K (CC) and subsequently oxidized with air as oxidant at 623-673K (C21). Oxidation in liquid phase was carried out starting from demineralized and carbonized sample CC using the concentrated (68%) nitric acid at 363K. After treatment with HNO₃ the sample was purified by washing and vacuum distillation at 473K (CN/O). In order to enhance the content of oxygen-containing groups on the surface of active carbon, potassium permanganate was also chosen. CC carbon underwent oxidation by boiling in 1.42% KMnO₄ solutions with or without the addition of H₂SO₄. After such treatments, samples were washed with a solution of HCl and dried at 293K (CM2/O and CM1/O, respectively).

The texture of active carbon samples was determined from low-temperature argon adsorption-desorption measurements in a standard volumetric equipment.

The concentration of oxygen-containing surface groups (and thus the oxidation degree) was investigated by:

- (i) water vapor adsorption at 298K using a microburette-type apparatus,
- (ii) thermogravimetric method with the analysis of the decomposition products (Mettler analyzer, Balzers mass spectrometer).

Results and Discussion

Texture parameters: specific surface area S_{BET} (Brunauer, Emmett, Teller method), micropore volume W_0 (from Dubinin-Radushkevich equation) and mesopore volume V_{me} and surface S_{me} (using the second variant of Dubinin's method) were calculated. The results are presented in Table 1.

Table 1. Porous structure of active carbons

Carbon	W_0 cm ³ /g	$B \cdot 10^6$ K ⁻²	V_{me} cm ³ /g	S_{me} m ² /g	S_{BET} m ² /g
CC	0.553	1.50	0.04	34.0	1125
C21	0.431	1.07	0.05	39.2	1142
CN/O	0.497	1.34	0.06	50.6	1220
CM1/O	0.427	1.02	0.06	54.0	1222
CM2/O	0.421	0.98	0.06	48.9	1210

The analysis of texture of all carbons indicates their well developed micro- and mesoporous structure. The oxidation process leads to a decrease in volume of micropores present in the carbons. In the case of oxidation with HNO₃ (CN/O) the observed changes in micropores appeared to be smaller.

Adsorption isotherms of water vapor were determined at 298 K. The character of the changes in adsorption of H₂O on the active carbons is illustrated by Figure 1.

The equation proposed by Dubinin and Serpinsky [2] describes the initial region and the main part of the sharply rising water isotherm and provides approximate information on the number of primary adsorption centers i.e. surface oxygen groups capable of forming hydrogen bonds with water molecules. The equation was used to find the number of surface oxygen groups $n \cdot 10^{17}$ [1/m²] per 1 m². For the series of carbons, it was: CC, 3.16; C21, 6.80; CN/O, 12.14; CM1/O 14.38; CM2/O, 13.93.

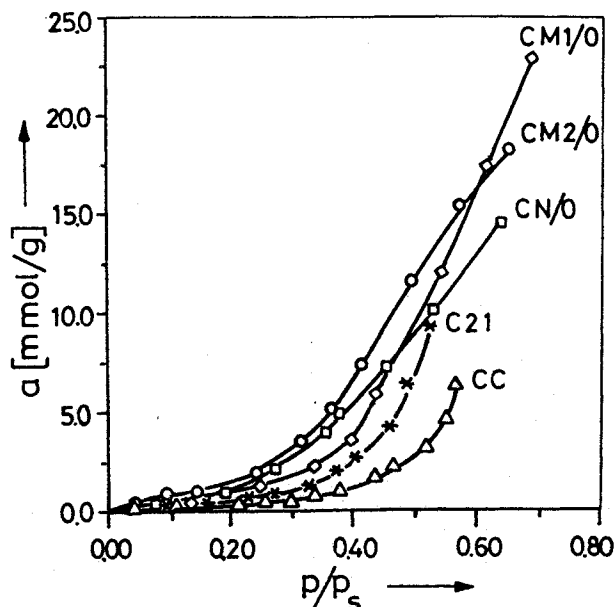


Figure 1. The adsorption isotherms of water vapor

Thermal analysis of active carbons was carried out within the temperature range of 298-1273K simultaneously with the analysis of decomposition products. On the basis of our results, 453K was assumed to be the final temperature where H₂O desorption ceases. Using DTA curves the temperature of 973K was adopted as the initial point of CO formation and the end of CO₂ formation [3]. The results of the analysis and calculations are summarized in Table 2.

Table 2. Mass loss calculated from TG curves.

Carbon	mass loss in various temperature ranges, Δm wt. %			
	298-453K	453-973K	973-1273K	453-1273K
CC	0.53	0.94	2.05	2.99
C21	0.11	3.10	3.32	6.42
CN/O	0.73	8.47	4.10	12.57
CM1/O	0.98	9.36	5.06	14.42
CM2/O	0.77	8.13	6.07	14.20

The mass losses found within the discussed temperature range show that more gases form in the case of oxidized carbons than for CC sample. For the gas-phase oxidized carbon, the total observed mass loss is much lower than for those oxidized in liquid phase. In the case of CC and C21, the amount of formed CO is higher than that of CO₂, while an opposite effect was found for liquid-phase oxidized carbons

Plotting the water adsorption results against those of the thermogravimetric analysis, a linear correlation between the two methods is evident. In order to quantify this relationship, numerical data is shown in Figure 2.

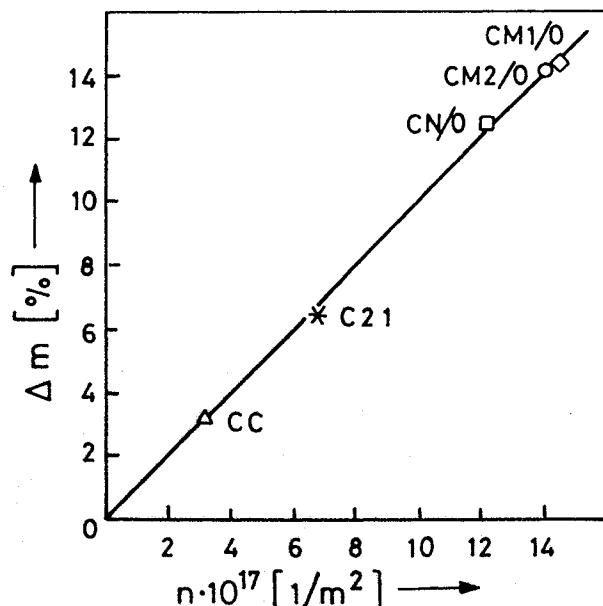


Figure 2. Plot of mass loss vs. number of oxygen groups

Mass loss (Δm) within the temperature range 453-1273K is used for the vertical axis whereas the number of oxygen groups, n per 1 m² of the carbon marks of the horizontal axis. A curve of best fit through the experimental points was obtained using the least squares method with the determination coefficient of 0.99. The straight line describing the relationship indicates that as the surface concentration of adsorption sites increases the loss of mass due to decomposition reaction is greater.

Conclusions

The oxidation process in liquid phase leads to a higher oxidation degree of carbons than the use of air as oxidant. Using two independent methods, the differences in surface properties of oxidized active carbons were confirmed. It is necessary for further characterization of carbonaceous surface to determine directly the oxygen groups and their population.

Acknowledgements

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References

1. Grzybek, T., *Fuel*, 1990, 69, 604.
2. Dubinin, M. M. *Carbon*, 1980, 18, 355.
3. Buczek, B., Grzybek, T., Bernasik, A., *Fundamentals of Adsorption* ed. by M. D. Le Van, Kluwer Academic Publishers, Boston/Dordrecht/London, 1996, pp.109.