CHARACTERISTICS OF DONOR – ACCEPTOR INTERACTIONS ON CARBONACEOUS MATERIALS

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Abstract

The influence of the amount and type of surface groups in the donor acceptor interactions was determined over two carbonaceous materials, a carbon black Clariant Graphtol Black BLN and an activated carbon Norit ROX 0.8. The materials were modified with nitric acid 5M during 6 hours at 80°C, oxygen diluted in nitrogen to 8.8% at 425°C during 10 hours, and hydrogen at 800°C during 6 hours. The textural properties were analyzed using t method and Dubinin-Radushkevich equation. The surface chemical characteristics were determined by temperature programmed desorption (TPD), zero charge point and iso-electric point. The characterization of the donor - acceptor interactions was made by inverse gas chromatography using acetone, dichloromethane and diethyl ether as probes. The dispersive component of free energy was higher for active carbons than for carbon blacks, which is related to the adsorption capacity of materials. The polar contribution to the free energy was about 18% for active carbons and about 40% for carbon blacks. The adsorption of polar probes shows the anphoteric character of materials and its relation with the increment of the oxygen content; when this content tends to zero, the carbonaceous materials behaves almost exclusively as electron donors. The acceptor behavior is more pronounce in the external surface than in the porosity of the material, due to the greater concentration of oxygenated groups at the outside.

Keywords: Activated carbon, Carbon black, chemically modified carbons, electrochemical properties, Surface oxide complexes.

Introduction

Adsorption on carbonaceous materials is mainly of dispersive interaction type, although surface chemistry plays an important role when specific interactions are considered; these interactions are strongly related to the presence of heteroatoms like nitrogen, oxygen and hydrogen, which determines the catalytic properties (Diaz, 2007), acid – base character, redox character and the adsorption of polar species (Figueiredo, 1999).

In the literature, the surface chemistry of carbonaceous materials has been characterized by several methods, such as inverse gas chromatography (IGC)(Voelkel, 2004), calorimetry and static gas adsorption (Stoeckli, 2001); the use of IGC is attractive because its simplicity and the broad physicochemical information that it provides. Working the IGC in the infinite dilution conditions, only few molecules are injected into the column of such form that the interactions between probe molecules are neglected and only the probe–solid interaction is taken into account. The retention volume measured for a giving probe passing through the column allows determine thermodynamic parameters such free energy, enthalpy and entropy of adsorption and the dispersive and specific components of the surface energy (Voelkel, 2004).

The acid – base behavior on carbonaceous materials can be analyzed from the point of view of donor – acceptor interactions. The acid character is commonly associated to the surface oxygen groups and the basic character to the delocalized π electrons on the carbon matrix. Using different polar probes on IGC, is possible to determine the donor – acceptor behavior of any material used to pack the chromatographic column (Voelkel, 2004). With the aim of study the effect of different surface groups and different textural properties on the donor – acceptor interactions in carbonaceous materials, the present work study a carbon black and an activated carbon, and its modifications by oxidizing and reducing treatments.

Methods

Two carbonaceous materials were selected, a carbon black Clariant Graphtol Black BLN (NH) and an activated carbon Norit ROX 0.8® (CA), the materials were modified by oxidative and reductive treatments.

Modifications
Each one of the carbonaceous materials was dried at 110°C during 12 hours before being modified.
Oxidative treatment with oxygen: The dried samples were heated in nitrogen at a rate of 10°C/min from ambient temperature to 425°C, when the treatment temperature is reached, the gas flow was settle to 250mL/min (8,8% of oxygen in nitrogen), the time of treatment was 10 hours. The samples were cooled in nitrogen atmosphere (samples NHO and CAO).

Oxidative treatment with HNO₃: The dried samples were treated with HNO_3 5M in relation 1g of sample to 10mL of acid; the samples were heated to reflux temperature during 6 hours, then they were washed with distilled water in sohxlet until constant pH of washing waters; then the samples were dried at 110°C during 12 hours (samples NHA and CAA).

Reductive treatment with hydrogen: The samples were heated in hydrogen (220mL/min) from ambient temperature to 800°C at a rate of 25°C/min and the treatment was performed during 6 hours. The samples were cooled until 200°C and then in nitrogen atmosphere to room temperature (samples NHH and CAH).

Textural characterization

The textural properties of the samples were determined by nitrogen adsorption isotherms at 77K in a Micromeritics Gemini III 2375. For each analysis 0.12 to 0.15g of sample were degasified at 350°C during 15 hours. The isotherms were analyzed by DR and t method.

Surface chemistry characterization

The zero charge point (ZCP) of the samples was determined by mass titrations as described elsewhere (Menendez, 1995). The isoelectric point (IEP) was determined using a zetameter as described elsewhere (Menendez, 1996). The content and type of the different surface oxygen groups was determined by temperature programmed desorption (TPD) of CO and CO_2. 200mg of sample were weighed and packed in a U shape reactor, using helium as carrier at a flow of 22.5mL/min. The heating rate was 5°C/min from room temperature to 1100°C. The detection of CO and CO_2 evolved was made in a Hewlett Packard 6890 gas chromatograph, equipped with a capillar column HP Plot Q of 30m in length, carrier gas flow was 20mL/min, injector and detector temperature were 250°C and oven temperature was 35°C. The deconvolution of CO and CO_2 spectra were made as described elsewhere (Figueiredo, 1999).

Inverse Gas Chromatography characterization

Infinite dilution experiments were carried out in a Hewlett Packard 5890 Series II chromatograph with FID detector. Teflon columns of 2,4mm of internal diameter and 30cm of length for carbon black or 5cm of length for activated carbons were filled with sample particles of diameter between 150 and 180μm. Columns were conditioned over night at 110°C in a helium flow of 40 mL/min. The experimental procedure for infinite dilution experiments are described in detail elsewhere (REF). Infinite dilution experiments were carried out at 110°C (isothermal) using series of n-alkanes (from C4 to C7), acetone, ethyl ether and dichloromethane as probes; the injector and detector temperatures were 250°C and the flow of helium was 40 mL/min.

Results and Discussion

Table 1 shows the textural characterization of samples; the treatments with oxygen and hydrogen produce and increment in micropore volume by the development of new porosity caused by the gasification of the material at the temperatures of modification, the treatment with nitric acid for activated carbon present a slight diminution of these parameters, since this treatment destroys the walls of pores diminishing the microporosity and increasing the mesoporosity of the material.

Table 2 shows the surface chemistry characterization of samples. For activated carbons the increase in carboxylic groups is significant for the sample modified with nitric acid, this treatment increase the content of phenol and carbonyl groups too. The modification with oxygen shows low content of carboxylic groups, but the increment in phenol and carbonyl groups is significant. The sample treated with hydrogen shows an important loose of all kind of oxygenated groups.

For carbon black the sample without treatment shows a great content of carboxylic, phenol and carbonyl groups indicating that this material has undergone some process of modification after its manufacture and before being used in this study; both oxidative treatments diminish the content of carboxylic group; the treatment with nitric acid reduce the content of phenol groups, while the treatment with oxygen increases the content of carbonyl groups; for carbon black the treatment with hydrogen reduce the content of oxygen surface groups appreciably.

The electrochemical characteristics of carbonaceous materials are related to the distribution of charges in their external and internal surface; the zero charge point allows to establish the distribution of net charge (external and internal), whereas the isoelectric point shows the distribution of charge on the external surface (Menendez, 1995). Table 2 shows that the modification of samples by oxidative treatments produce materials of acid character, related to high content of oxygen surface groups; whereas the treatments with hydrogen conduce to materials of basic character with minimum contents of oxygen surface groups. The samples CAA, NHO and CAH show a smaller IEP than ZCP, indicating that the treatments produce a greater content of oxygenated groups on the external than in the internal surface of the material; the samples CA and NHH show similar IEP and ZCP indicating a uniform distribution of the internal and external charge.

Table 3 shows the thermodynamic parameters obtained by inverse gas chromatography (IGC). For the activated carbons the dispersive component of surface energy diminishes with the oxidative treatments and grows with the hydrogen treatment. For carbon blacks, the untreated sample shows the lowest value of the dispersive component, although all carbon blacks show similar values.

Table 1. Textural characterization of samples.

Sample	S_{BET} m^2/g	t Method		DR Equation		
		W_0 cm^3/g	S_{meso} M^2/g	W_0 cm^3/g	E kJ/mol	E_0 kJ/mol
CA	1053	0,438	92	0,440	6,44	20,13
CAA	997	0,409	111	0,412	5,96	18,62
CAO	1296	0,530	140	0,514	6,18	19,31
CAH	1082	0,463	69	0,451	6,45	20,17
NH	94	0,001	91	0,038	5,32	16,61
NHA	132	0,004	121	0,053	5,28	16,50
NHO	225	0,042	127	0,094	6,44	20,12
NHH	137	0,011	110	0,056	5,27	16,46

Table 2. Electrochemical and TPD characterization of samples.

Sample	Oxygen surface groups					Electrochemical characterization	
	Carboxylic $(\mu mol/g)$	Anhydrides $(\mu mol/g)$	Phenols $(\mu mol/g)$	Lactones $(\mu mol/g)$	Carbonyl-quinones $(\mu mol/g)$	ZCP	IEP
CA	42,5	34,2	55,0	23,3	437,8	7.8	6.8
CAA	970,4	52,4	1756,9	170,2	1229,9	2.5	1.6
CAO	22,7	52,4	998,9	167,1	1995,5	4.2	2.5
CAH	14,9	5,3	16,4	12,4	181,3	10.4	6.8
NH	241,0	111,3	409,1	71,7	509,8	2.5	N. A.
NHA	92,7	57,8	247,1	50,5	378,2	2.8	N. A.
NHO	15,0	74,0	442,8	112,0	937,3	3.5	1.9
NHH	19,6	4,5	12,0	4,9	210,6	11.1	10.1

The original and modified materials by oxidative treatments have anphoteric behavior, as show the significant difference between the free energy of adsorption of the straight line of the n-alkanes and free energy of adsorption of polar probes (ethyl ether and dichloromethane that are related to acceptor and donor interactions respectively). For carbon blacks, a diminution in acceptor behavior was observed, related to reduction of oxygenated surface groups by the modification treatments.

The main contribution to the total free adsorption energy is from dispersive component, although in some cases the specific component plays an important role showing contributions as great as 46% (for acetone over NHA sample), specially when the material has low surface area and high content of oxygen groups, as shows in table 4.

Table 3. Adsorption thermodynamic parameters determined by IGC at 110°C.

Sample	Dispersive component γ_S^D (mJ/m^2)	Polar probe					
		Acetone		Ethyl ether		Dichloromethane	
		$-\Delta G_A$ (kJ/mol)	$-\Delta G_A^P$ (kJ/mol)	$-\Delta G_A$ (kJ/mol)	$-\Delta G_A^P$ (kJ/mol)	$-\Delta G_A$ (kJ/mol)	$-\Delta G_A^P$ (kJ/mol)
NH	125.70	21.81	9.47	30.80	12.83	20.50	7.22
NHA	142.38	23.76	10.97	27.92	9.15	21.69	7.90
NHO	157.07	22.12	8.68	28.52	8.79	23.04	8.54
NHH	174.00	25.68	11.52	25.11	4.32	24.78	9.51
CA	227.12	27.84	5.32	31.10	1.18	29.01	5.24
CAA	150.95	24.39	6.63	30.12	6.20	23.14	4.35
CAO	198.67	26.82	7.12	32.91	6.15	25.40	4.51
CAH	254.89	27.91	3.72	32.38	0.36	31.30	5.80

Table 4. Specific component contribution to the total free adsorption energy.

	$\Delta G_a^P/\Delta G_a^0$		
Sample	Acetone	Ethyl ether	Dichlorometane
CA	0,19	0,04	0,18
CAA	0,27	0,21	0,19
CAO	0,27	0,19	0,18
CAH	0,13	0,01	0,19
NH	0,43	0,42	0,35
NHA	0,46	0,33	0,36
NHO	0,39	0,31	0,37
NHH	0,45	0,17	0,38

Conclusions

The increase in the oxygen content of the sample causes a diminution in the alkane-solid interaction energy; the dispersive component of free adsorption energy is smaller for the carbon black samples and greater for activated carbons, indicating a proportional relation between the material adsorption capacity and the free adsorption energy. The adsorption of polar probes on carbonaceous materials shows that the surface tends to present an anphoteric character with the increment in the oxygen content; when the oxygen content decrease, the carbonaceous material behaves almost exclusively like a donor of electrons. The acceptor behavior is more significant on the external surface due to the greater concentration of oxygenated groups outside the porosity.

Acknowledgements

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