Carbonization of Some Organic Polymers Previously Impregnated with $Fe(NO_3)_3$

J.D. López-González[1], A. Guerrero-Ruiz[*], F. Rodríguez-Reinoso[2] and I. Rodríguez-Ramos[2].

1.- Dpto. de Química Inorgánica. UNED. Madrid. Spain.
2.- Dpto. de Química Inorgánica. Universidad de Alicante. Alicante. Spain.

Introduction

Carbons prepared by the carbonization of polymers have physical and structural characteristics imposed by the conditions of carbonization and by the precursor used. These carbons may find applications as catalyst supports[1,2]. Furthermore, sometimes, they present molecular sieve properties and high adsorption capacity.

It was the purpose of this work to investigate the carbonization process of some polymers with and without previous impregnation with solution of iron nitrate. In this paper it is studied the thermal analysis data of the carbonization reaction and the textural characteristics of the obtained carbons.

Materials

Three polymers were investigated: a) copolymer Saran, with 88% PVDC, 12% PVC and 1.5% matrix (supplied by Dow Chemical Co.); b) polyacrylonitrile (prepared by polymerization of acrylonitrile in aqueous solution); c) polyvinyl alcohol (supplied by Merck).

These polymers were impregnated by an incipient wetness technique with $Fe(NO_3)_3 \cdot 6H_2O$ in ethanolic solution. The carbonization process was studied on the original polymers as well as on the impregnated polymers.

Procedure

The T.G.A. was carried out on a Mettler Thermal Balance (TA 3000), in nitrogen stream (100 ml.min^{-1}). A 20 mg sample and a heating rate of 5 K.min^{-1} were used.

Samples carbonized (at a heating rate of 2 K.min^{-1}) up to 973K for 4 h were studied by gas adsorption methods to know the textural characteristics of the carbons obtained. Adsorption isotherms of N_2 at 77K and CO_2 at 298K were made using a conventional gravimetric system.

Iron content of the carbonized samples was analyzed gravimetrically after burning-off the carbon content at 973K in air. X-ray diffraction on the impregnated and carbonized

* Present address: Centre de Thermodynamique et de Microcalorimetrie du CNRS. Marseille. France.

polymers confirmed that iron was present as α-Fe.

Results and Discussion

The T.G.A. data for the carbonization processes are presented in Table 1. In general, there is an agreement of these results and those reported by Dollimore and Heal[3] for the degradation of these polymers. It can be seen that there is not significant differences in the results determined on PAN and on PVA when they are or not impregnated with iron nitrate. On the other hand, the carbonization of Saran copolymer is affected by the adition of iron. In this case, the cake formation, which appears when Saran is carbonized, do not appear when samples are previously impregnated with $Fe(NO_3)_3$. We have observed the formation of Cl_3Fe, which is volatilized at carbonization temperature. The starting decomposition temperature for the Saran impregnated is smaller than the corresponding to the original Saran.

Surface areas and micropore volumes for the different carbonized products are included in Table 2. The BET method was applied to the N_2 adsorption and the Dubinin-Radushkevich-Kaganer equation to the CO_2 adsorption in order to obtain the specific surface areas. The latter method also provided the micropore volume. The N_2 adsorption isotherms obtained were of type I of the BDDT classification for the samples S and S-Fe, which means that these carbons were essentially microporous. On the other hand, the N_2 adsorption isotherms corresponding to the sample PVA-Fe was of type II.

From data shown in Table 2, we can observe that S_{CO_2} is always higher than S_{N_2} ($S_{CO_2}/S_{N_2} > 1$). This might be attributed to the better penetration of CO_2 in the smaller micropores (activated adsorption?). This effect is greater for the samples PAN, PAN-Fe and PVA, which means that these carbons have smaller micropores. Moreover, it can be seen in Table 2 that adition of iron nitrate to the polymers before the carbonization produces changes in the surface areas and porous structure of the carbons obtained from them. This effect can be attributed to the catalytic effect of the metal during the reaction of carbonization.

Chemisorption (H_2 and CO) experiments

and activity measurements (in CO+H_2 reaction) were made on the carbon obtained from the impregnated samples. The results show that they have not noticeable chemisorption capacity neither catalytic activity. Then, we suppose that the metal was in the bulk of the carbons.

References

1. F. Rodríguez-Reinoso, J.D. López-González, C. Moreno-Castilla, A. Guerrero-Ruiz and I. Rodríguez-Ramos, Fuel, 63, 1089 (1984).

2. I. Fernández-Morales, A. Guerrero-Ruiz, F.J. López-Garzón, I. Rodríguez-Ramos and C. Moreno-Castilla, Appl. Catal., in press.

3. D. Dollimore and G.R. Heal, Carbon 5, 65 (1967).

4. I. Fernández-Morales, A. Guerrero-Ruiz, F.J. López-Garzón, I. Rodríguez-Ramos and C. Moreno-Castilla, Carbon 22, 301 (1984).

Table 1. DTG Carbonization data.

Sample	Peak temp. (K)	%Wt loss	Comment	%Fe in the carbon
Saran copolymer (S)	533	58	"cake"	
	793	17	formation	—
Saran copolymer + Fe(NO$_3$)$_3$ (S-Fe)	383	3.		
	423	23	Not "cake"	
	493	47	formation	2.4
	773	6		
Polyacrylonitrile (PAN)	623	33	Big peak	—
Polyacrylonitrile + Fe(NO$_3$)$_3$(PAN-Fe)	623	35	starting at 533K	5.9
Polyvinyl alcohol (PVA)	558	71		
	683	12	—	—
Polyvinyl alcohol + Fe(NO$_3$)$_3$(PVA-Fe)	558	60		
	688	11	—	8.1

Table 2. Textural characterization of the carbons.

Sample	S_{N_2} $m^2 \cdot g^{-1}$	S_{CO_2} $m^2 \cdot g^{-1}$	$V_{micropores}$ $cm^3 \cdot g^{-1}$	S_{CO_2}/S_{N_2}
S*	977	1325	0.54	1.55
S-Fe	794	1155	0.47	1.45
PAN	4	260	0.11	65.0
PAN-Fe	18	775	0.32	43.0
PVA	5	170	0.07	34,0
PVA-Fe	126	145	0.06	1.15

* From ref. (4).