

POSTER

TG-MS STUDY OF SEVERAL GRAPHITE OXIDES IN HELIUM AND HYDROGEN

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Introduction

Graphite oxide is a known material since last century, but it is quite difficult to establish its structure. This difficulty is due to the fact that the graphite oxide is a non stoichiometric solid, which has a high hygroscopicity and a low thermal stability.

Several structures have been proposed for graphite oxides [1, 2], all of them including the presence of hydroxyl, carbonyl and ether groups. Thermal decomposition of these groups may produce the formation of H₂O, CO₂, CO and/or O₂.

As it is said above, graphite oxide is a thermolabile compound, which deflagrates spectacularly when it is subjected to a high heating rate. Nevertheless, if a low heating rate is used (1 °C/min), the decomposition is a controlled process, and under these conditions a kinetic study (using TG results) and an analysis of the evolved gas in its decomposition can be obtained.

In previous papers [3, 4], TG and DTA studies were carried out in several atmospheres, using the above conditions. Results showed that evolved heat in nitrogen, carbon dioxide or air as atmosphere during decomposition are similar and much higher than the obtained under hydrogen flow. This difference can be explained considering the results obtained from the evolved gas analysis.

Experimental

Several graphite oxides with different oxidation degree were prepared following the Staudenmaier method. Samples were textural and

chemically characterized and TG and DTA studies were carried out, under inert (nitrogen) and reactive (air, carbon dioxide and hydrogen) atmospheres [3-5].

Simultaneous thermal (TG/DTA) and mass spectrometry (MS) analyses of graphite oxides were carried out. About 10 mg of sample were heated from 30 up to 280 °C under inert (helium) and reactive (hydrogen) flow (60 cm³/min), using a heating rate of 1 °C/min. Thermal analysis was performed in a Seiko TG/DTA 320 system and mass spectrometry in a Balzers, MSC 200 Thermo Cube.

Results and Discussion

Decomposition of graphite oxide samples in helium as well as hydrogen atmosphere was studied in a temperature range of 30-280 °C. TG data indicated us that, in this temperature range, the detected weight loss is independent of the used atmosphere. Results obtained from simultaneous TG and MS analyses are given in Table 1, showing a good agreement.

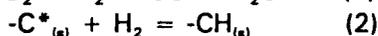
Mass spectra of graphite oxides under helium or hydrogen flow indicated that the major evolved gases were H₂O, CO and CO₂. Two different profiles were observed: one for water, which presents two maxima at 70 and 234 °C; and the other for CO and CO₂, which exhibits only one maximum at 234 °C. Figure 1 shows the profile of the evolution of H₂O and CO₂ with the temperature for G240 sample in helium atmosphere. In all cases, carbon dioxide was the major gas, whereas water and carbon monoxide were minor products, the contribution of both gases being approximately

the same and about a third of the contribution of carbon dioxide.

Mass spectra for water of different samples showed two peaks in all cases. The first one, at around 70-80 °C can be assigned to the adsorbed water in graphite oxide (due to the high hygroscopicity of this material) . The second one, placed at 234 °C, can be attributed to the formation of water from the decomposition of hydroxyl groups.

The production of CO and CO₂ at 234 °C could be due to the decomposition of carbonyl and ether groups. Hydroxyl, carbonyl, and ether groups in samples of graphite oxide were predicted by structural models proposed in the literature. Moreover, all these oxygen-containing groups have been detected and identified in a previous work [5].

As it was mentioned above, in previous works [3, 4], it was observed that heats evolved during decomposition of graphite oxide (150-280 °C) in N₂, He, CO₂ or air flow are essentially the same ($\Delta H = -1.3$ KJ/g); however, if hydrogen is used, the evolved heat was significantly lower ($\Delta H = -0.3$ KJ/g). This fact was explained assuming that in hydrogen atmosphere, other endothermic reactions could take place simultaneously to the exothermic decomposition of graphite oxide. At least two reactions may be considered:



being -C* carbon active atoms.

MS results in hydrogen flow showed a qualitative increase of the detected amount of CO and H₂O with respect to the detected in helium flow, as well as a decrease in the amount of CO₂. This fact indicates that, at least, reaction (1), that is, gas shift reaction, could take place, justifying therefore a decrease of the heat evolved during the process. Moreover, reaction (2) is a solid-gas reaction and this type of reactions are more probable to occur than gas-gas reactions, being possible that reaction (2) also contributes to the global decomposition process.

Table 1.- Weight losses obtained by TG and MS in inert atmosphere (helium)

Sample	% weight loss up to 150 °C		% weight loss up to 280 °C	
	TG	MS	TG	MS
G0	0.0	0.6	0.0	0.1
G24	1.4	1.6	9.0	8.3
G48	2.9	3.4	17.2	16.2
G96	5.3	6.4	29.1	25.7
G240	5.6	10.0	30.5	28.1

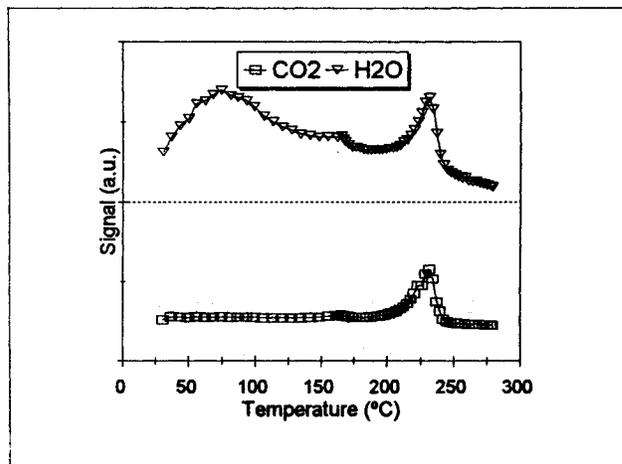


Figure 1.- Evolution of CO₂ and H₂O in sample G240 in helium atmosphere

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