

SYNTHESIS AND THERMAL STABILITY OF GRAPHITE OXIDE-LIKE MATERIALS

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Introduction

In a recent study of the graphite oxide reaction with AlCl_3 , a product was found to have an Al:C atomic ratio as high as 1:4. Heating this material in air resulted in Al_2O_3 with a surface area of $80 \text{ m}^2/\text{gm}$ [1]. This result suggests the possible applications in the areas of batteries, catalysts, and sensors.

Graphite has been used as the reactant for graphite oxide synthesis since its discovery in 1860 [2]. In this research, the possibility of using today's commercially available non-graphite carbon to synthesize graphite oxide was studied. The products were studied by examining their structure, chemical composition, thermal stability and reactivity to AlCl_3 .

Experimental

The method developed by Hummers and Offeman [3] was used to synthesize graphite oxide. This method uses H_2SO_4 , NaNO_3 and KMnO_4 as the reactants. In this research five different kinds of carbon materials were used to react with these chemicals. They were, in the order of decreasing x-ray diffraction (XRD) peak height, crystalline graphite powder (300 mesh, 99%), graphite powder (<1 micron, 99.9995%), graphite sheet (0.254 mm thick, 99.9%), graphitized carbon fiber (Amoco VCB-45, 10 micron diam., 99%), and activated carbon ($1100 \text{ m}^2/\text{gm}$, containing small amounts of Al and Si).

The graphite oxide-like materials thus obtained were heated in nitrogen at 100, 150, and 200°C for 20-24 hours. The heating rates were such that the above three decomposition temperatures were reached in 16, 16, and 180 minutes, respectively. The sample mass before and after such heating was measured. The carbon mass loss during these reactions was estimated by finding the differences between the carbon masses in the reactants and the products, which were calculated from the products of the sample masses and their carbon mass %. These carbon mass losses as fractions of total mass loss, as well as total carbon mass in the reactant, were then calculated.

The bulk compositions were analyzed using a "Leco" process for carbon and sulfur contents, and inductively coupled plasma mass spectrometry (ICPMS) for metal contents, both described elsewhere [4]. The surface compositions were analyzed using x-ray photoelectron spectroscopy (XPS). Their structures were studied using x-ray diffraction (XRD) data. Their microscopic views were obtained from scanning electron microscopy (SEM). Their semi-quantitative chemical analyses were conducted using their energy dispersive spectra (EDS).

The products obtained from the precursors of crystalline graphite powder, sub-micron graphite powder, and activated carbon were exposed to AlCl_3 to test their ability to hold large quantities of aluminum. They are exposed to AlCl_3 at temperature histograms of from 120°C to 193°C for 42 hours, and finally 225°C for 0.2 hour to evaporate the unused AlCl_3 .

Results and discussion

Chemical analysis of the products of the graphite oxide synthesis reactions is described in Table 1. All samples contained large quantities of C and O.

The XRD data indicated that none of these products had graphite peaks. The sample made from graphite sheet had sharp peaks at 5.23 and 2.62 Å. Together with their high sulfur content (Table 1), it is believed to be a H_2SO_4 -graphite intercalated compound with an identity period of 5.23 or 10.46 Å. This sample was not a graphite oxide-like compound and was not studied any further.

The sample made from crystalline graphite was the only one that had the graphite oxide peak at about 8 Å. All other samples has no XRD peaks, suggesting amorphous structures. Since they did not have graphite oxide peaks but are compounds of carbon and oxygen, they are called graphite oxide-like materials.

Table 2 describes the mass loss of the graphite oxide and graphite oxide-like materials during their thermal decomposition. For graphite oxide made from crystalline graphite, most of the mass loss occurred before they reached 150°C . For all other samples, most of the mass loss occurred before they reached 100°C .

Table 1. Chemical Analysis (wt %) of the Products of Graphite Oxide Synthesis Reactions

Precursors	C	S	K	Mn	O* (balance)
Crystalline Graphite	34.3	1.45	1.56	0.07	62.6
Sub-micron Graphite	36.1	2.68	1.63	8.85	50.7
Graphite Sheet	13.8	13.8	1.79	4.61	66.0
Carbon Fiber	58.9	3.09	1.25	1.81	35.0
Activated Carbon	61.1	1.96	0.46	0.04	36.4

* Include water

Table 2. Mass Loss (% of the reactant mass) During 100, 150, and 200° C Decomposition of Graphite Oxide and Graphite Oxide-like Materials

Precursors	100°C	150°C	200°C
Crystalline Graphite	24.4	46.7	41.5
Sub-micron Graphite	22.6	29.2	30.9
Graphite Sheet	41.9	46.1	48.1
Carbon Fiber	21.6	25.7	19.4
Activated Carbon	26.4	29.7	25.2

* The low mass loss for some samples tested at 200°C are believed to be the result of slow heating.

Table 3. Carbon Loss During 200°C Decomposition of the Graphite Oxide and Graphite Oxide-like Materials

Precursors	% of Carbon Mass Before Decomposition	% of Total Mass Loss During Decomposition
Crystalline Graphite	0	0
Sub-micron Graphite	4.2	4.91
Carbon Fibers	8.0	24.3
Activated Carbon	14.1	34.1

The carbon loss as a fraction of carbon mass in the reactant and the carbon loss as the fraction of total mass loss during heating at 200°C were estimated and summarized in Table 3. It is observed that carbon loss began to occur at a temperature below 200°C for the products made from non-graphite carbon, but above 200°C for those made from crystalline graphite. At 200° C, the lower the degree of graphitization, the higher the contribution of carbon loss to total mass loss.

According to EDS data, after the reaction with AlCl₃, the sample using activated carbon as a precursor has an atomic Al : C ratio of about one fourth of that obtained using crystalline graphite as a precursor. On the other hand, the product made from sub-micron graphite contained more aluminum than those made from traditional graphite oxide. This is confirmed by further analysis using Leco and ICPMS. The results of these analyses are summarized in Table 4. Similar compositions were found from XPS analysis on the sample surfaces. The atomic Al:C ratio for the product made from the sub-micron graphite was found to be as high as 2:5.

Conclusions

Sub-micron graphite oxide powder, pitch-based graphitized carbon fibers, and activated carbon were treated with the process of graphite oxide synthesis, resulting in graphite oxide-like material. They were amorphous, but contained oxygen at the concentrations range of the traditional graphite oxide.

These samples began to lose both water and carbon at a temperature below 200°C. During such decomposition, the lower the degree of graphitization, the higher the contribution of carbon loss to total mass loss.

The graphite oxide-like material obtained using activated carbon as the precursor reacted with AlCl₃, but to a lesser extent than that using crystalline graphite as the precursor. However, those made from sub-micron graphite powder reacted with AlCl₃ the most, resulting in a product having an Al:C atomic ratio as high as 2:5.

References

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Table 4. Chemical Analysis (wt %) of the Carbonaceous Products Having High Al:C ratio *

Precursors	C	Al	Cl**	S	K	Mn
Crystalline Graphite	24.8	13.2	52.1	0.52	0.6	0.07
Sub-micron Graphite	15.1	20.4	53.6	1.19	1.3	1.1

* The balance is mostly oxygen

**From the Al:Cl ratio estimated using EDS data