

SURFACE PROPERTIES OF EXTREMELY THIN GRAPHITE LAMELLAE

H. P. BOEHM, A. CLAUSS, G. FISCHER and U. HOFMANN

Anorganisch-Chemisches Institut der Universität, Heidelberg, Germany

(Manuscript received September 15, 1961)

Extremely thin lamellae of carbon were obtained either by deflagration of graphitic oxide on heating or by reduction of graphitic oxide in alkaline suspension. These lamellae consist of very few carbon layers as was estimated from the absorbance in the electron microscope. The crystallite dimensions and the specific surface area also show the existence of very thin carbon sheets. The adsorption of nitrogen, phenol and methylene blue was measured as well as the catalytic efficiency in the hydrogen bromide synthesis. The reduction product had the maximum surface area while still in aqueous suspension. On drying the lamellae showed a tendency to stick together with a corresponding decrease of the specific surface area. Higher surface areas were measured by the "wet" methods in comparison to the "dry" methods (e.g. N₂ adsorption) because of partial redispersion of the lamellae. With the deflagration product, in contrast, roughly identical surface values were obtained by all methods, independent of heat treatment. This is probably due to the existence of holes in the carbon layers caused by the loss of carbon in the form of oxides upon deflagration of graphitic oxide. The carbon sheets of the reduction product are not perforated.

I. INTRODUCTION

The thin lamellae or foils of graphite or, rather, carbon described herein were prepared by reduction of graphite oxide suspended in alkaline medium. In order to facilitate understanding the method of preparation and the properties of the reduction product, the most important characteristics of graphite oxide (G.O.) are discussed first.

II. PROPERTIES OF GRAPHITE OXIDE

G.O. is a lamellar compound containing the carbon layers of the graphite lattice. Even though G.O. has been known for 100 years,¹ its structure is not yet understood in all details. However, the properties and the general principles of the G.O. structure have been described in numerous publications, mainly by U. Hofmann and his school,²⁻⁸ H. Thiele⁹ and de Boer.¹⁰

G.O. is prepared from graphite or graphite salts by oxidation with strong oxidizing agents such as potassium chlorate¹¹ or potassium permanganate¹² dissolved in concentrated sulfuric acid.

If the samples are oxidized thoroughly, the resulting G.O. is almost white with a slight yellowish tinge.⁶ It turns dark brown during

¹ B. Brodie, *Phil. Trans. Roy. Soc. London*, **149**, 249 (1859); B. Brodie, *Ann. Chem., Liebigs*, **114**, 6 (1860).

² U. Hofmann and A. Frenzel, *Ber. deut. chem. Ges.*, **63**, 1248 (1930); U. Hofmann, A. Frenzel and E. Csalan, *Ann. Chem., Liebigs*, **510**, 1 (1934).

³ U. Hofmann and E. König, *Z. anorg. u. allg. Chem.*, **234**, 311 (1937).

⁴ U. Hofmann and R. Holst, *Ber. deut. chem. Ges.*, **72**, 754 (1939).

⁵ A. Clauss and U. Hofmann, *Angew. Chem.*, **68**, 522 (1956).

⁶ A. Clauss, R. Plass, H. P. Boehm and U. Hofmann, *Z. anorg. u. allg. Chem.*, **291**, 205 (1957); A. Clauss, *Proc. Third Carbon Conf.* Pergamon Press (1959) p. 321.

⁷ A. Clauss, U. Hofmann and Ar. Weiss, *Z. Elektrochem.*, **61**, 1284 (1957).

⁸ H. P. Boehm, A. Clauss and U. Hofmann, *J. Chim. Phys.*, **141** (1961).

⁹ H. Thiele, *Kolloid-Z.*, **80**, 1 (1937).

¹⁰ J. H. de Boer and A. B. C. van Doorn, *Proc. Koninkl. Ned. Akad. Wetenschap. Ser. B*, **57**, 181 (1954); *ibid.*, **B**, **61**, 12 (1958); *ibid.*, **B**, **61**, 17 (1958); *ibid.*, **B**, **61**, 160 (1958); *ibid.*, **B**, **61**, 242 (1958).

¹¹ L. Staudenmaier, *Ber. deut. chem. Ges.*, **31**, 1481 (1898).

¹² W. S. Hummers and R. E. Offeman, *J. Amer. Chem. Soc.*, **80**, 1339 (1958).

the washing and drying procedures, however, if no special precautions are taken. Since there is no detectable difference in composition between light-coloured G.O. and the dark compound, this colour transition very probably is due to some sort of isomerism. There is some evidence that this might be a keto-enol transition.

Upon oxidation to G.O., the shape of the graphite particles is preserved. There is only a very large swelling in the direction of the *c*-axis. The oxidation has a nearly theoretical yield, in so far as no carbon is lost in the form of volatile or soluble compounds. From this observation it is concluded that the carbon layers as such remain intact.

An idealized formula for G.O. can be written $C_8O_2(OH)_2$.⁶ Its structure preserves the hexagon network of the carbon layers as present in the graphite structure. However, it is generally thought that these carbon layers are puckered as in hydroaromatic compounds. The structure is in principle aliphatic, the carbon atoms being bonded to oxygen by their fourth valencies. This oxygen is bound above and below the carbon layers. The oxygen is present in the form of hydroxyl groups and—very probably—ether bridges connecting carbon atoms of the same layer. Since the number of hydroxyl groups and ether groups is not equivalent to the number of carbon atoms, double bonds must be inherent in the structure. There is some evidence for

the presence of enol groups and—as one might expect—keto groups, too. Furthermore, the existence of carboxyl groups has been established by various methods. The carboxyl groups are bound to the peripheral carbon atoms of the layers and their number increases with decreasing particle size. The hydroxyl groups of G.O. react more or less acidic. Therefore, G.O. often is called graphitic acid.

Table I presents a brief summary of the various functional groups that were observed in G.O. The analytical methods by which these groups were estimated are also indicated.

G.O. has rather strong oxidizing properties. It is reduced to black elementary carbon by reducing agents such as hydroxyl amine, hydrazine, hydrogen sulfide, iodide or iron(II)-ions. Our carbon lamellae were prepared in this way. Like the oxidation, this reduction also has a 100% yield. That means no carbon is lost. Therefore, the carbon layers should be recovered intact after oxidation of graphite to G.O. and subsequent reduction.

G.O. also shows thermal instability. When heated quickly to about 180°C it deflagrates with production of a very voluminous fluffy carbon. This so-called G.O. soot consists of very thin carbon sheets. An electron microscopic picture of this deflagration product is shown in Fig. 1. The carbon sheets are extremely crumpled and remind one of crumpled paper tissue.

TABLE I
Functional Groups in Graphite Oxide

Functional group	Method of estimation	Number in mMol/100g
Carboxyl groups	Reaction with PCl_5 , Neutralization of $NaHCO_3$, Esterification with CH_3OH	80–130
Hydroxyl groups, total	Neutralization of C_2H_5ONa , Hydrogen content after careful drying	1000
Enol groups	Neutralization of $NaOH$, Reaction with CH_2N_2	450
Ether groups	Difference in oxygen content	1100
Double bonds	Difference between functional groups and carbon atoms	700

FIG. 1.

The ox
deflagrat
monoxide
clusion is
contain
the carb

G.O. so
calculated
after heat

A very
capability
—or any
between

increase
content a
the parti
surroundi
omenon,
character
observed
means of

One-di

anhydrous
 H_2O vap
 H_2O (liq
NaOH, 2
NaOH, 0
NaOH, 0

¹³ K. H.
Kolloid-Z.,

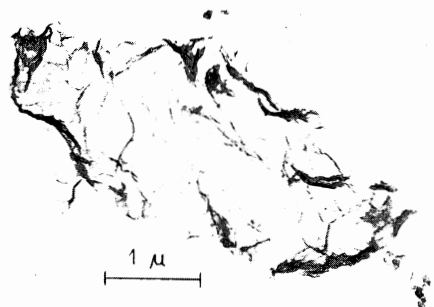


FIG. 1. Soot obtained by deflagration of graphite oxide. (No. 106/60).

The oxygen contained in G.O. is released on deflagration in the form of water, carbon monoxide and carbon dioxide. The conclusion is that the sheets of the G.O. soot must contain many small holes in the network of the carbon layers.

G.O. soot has a carbon content of *ca.* 80%, calculated on an ash-free basis and of 98% after heat treatment at 1100°C.

A very interesting feature of G.O. is its capability of intracrystalline swelling. Water—or any other polar liquid—can penetrate between the layers with a corresponding increase of the interlayer spacing. The water content and the interlayer spacing depend on the partial pressure of water vapor in the surrounding atmosphere. Actually this phenomenon, which is also a very important characteristic of many clay minerals, was observed for the first time with G.O.² By means of this property membranes of G.O. can

be used for determinations of partial pressures of water vapor,^{5,8} of osmotic pressures^{8,13} and of membrane potentials.^{7,8}

In Table II the interlayer spacing of G.O. under various conditions is given as determined by X-ray diffraction. The specimens were sealed under atmospheres of a given relative humidity or under various immersion liquids. Under water, the spacing increases from 6.35 to 11.6 Å. Still larger swelling occurs under very dilute sodium hydroxide solutions. Under 0.01 N sodium hydroxide the swelling continues to complete separation of the layers and the G.O. layers are dispersed in the resulting colloidal sol as individual macromolecules. This is indicated by the sign ∞ for the interlayer spacing.

Complete dispersion into individual layers under dilute sodium hydroxide solutions also has been observed with many clay minerals. As Weiss¹⁴ demonstrated, this phenomenon always occurs when the charge density on the layers has a value of about 0.7–2 charges per 100 Å². With G.O., the charge obviously results from the dissociation of the sodium ions bound by neutralization of the acidic groups.

III. PREPARATION OF EXTREMELY THIN LAMELLAE OF CARBON

It was thought that it should be possible to obtain single layers of the graphite structure by reduction of G.O. that has been dispersed into individual layers. The question remained, how fast these carbon layers would agglomerate forming the structure of microcrystalline carbon with the layers ordered parallel to each other.

G.O. dispersed by agitation in *ca.* 0.01 N NaOH (*ca.* 5 g in 2 l.) was reduced by heating with an excess of hydrazine hydrate or of hydroxyl ammonium chloride plus the equivalent amount of NaOH. The suspension turned black during this treatment. After

TABLE II
One-dimensional Intracrystalline Swelling of Graphite Oxide

Swelling medium	Interlayer spacing
anhydrous	6.35 Å
H ₂ O vapor, $p/p_0 = 0.5$	7.7
H ₂ O (liquid, vapor $p/p_0 = 1$)	11.6
NaOH, 2N	11.2
NaOH, 0.05N	12.4
NaOH, 0.01N	∞

¹³ K. H. Hellwege, W. Knappe and G. Müh, *Kolloid-Z.*, **174**, 46 (1961).

¹⁴ Ar. Weiss, *Chem. Ber.* **91**, 487 (1958).

cooling the alkali and the excess reducing agent were removed by dialysis.

A part of this suspension was filtered and the residue was analyzed after drying. The reduction product contained *ca.* 90% carbon, calculated on an ash-free basis. Also present were about 1.5% of nitrogen and 1.5% of hydrogen, the rest being oxygen.

Preliminary results of a detailed investigation of the functional groups in this reduction product indicate that the carboxyl groups bound at the edges of the carbon layers of G.O. remain in the reduction product as well. This would be expected.

Figure 2 shows an electron microphotograph

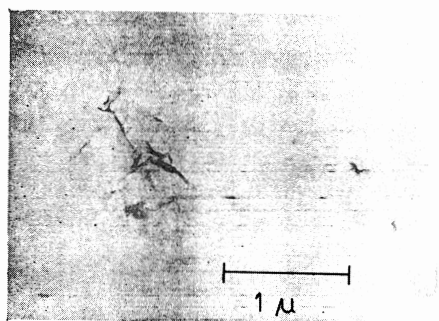


FIG. 2. Thin lamellae of the reduction product of graphite oxide. (No. 1027/61).

of the reduction product. The specimen was prepared directly from the suspension. As can be seen, the foils of the reduction product are distinctly thinner in comparison to the G.O. soot obtained by deflagration. Moreover, they are less crumpled than the foils of the G.O. soot. (The sheets are so thin that they can be distinguished in the reproduction only by their wrinkles.)

IV. ESTIMATION OF THE THICKNESS OF THE LAMELLAE OF THE REDUCTION PRODUCT

An attempt was made to estimate the thickness of the lamellae of the G.O. reduction product. For this purpose thin films of collodion (nitro cellulose) of known thickness were prepared by spreading a drop of a solution

in amyl acetate on a water surface of known area. From the volume and the concentration of the drop the thickness of the collodion films was calculated. These films were used as supporting films for the lamellae of the G.O. reduction product and at the same time as standard of mass thickness. It is known that collodion films are decomposed by electron irradiation and that about 75% of their mass is lost.¹⁵ Therefore, the mass thicknesses of the supporting films after irradiation were known.

The optical density of the electron microphotographs (negatives) was measured using a microdensitometer. From the optical densities the ratio of the electron absorption in the supporting film and in the lamellae of the reduction product was determined. This is illustrated in Fig. 3. The density of the photo

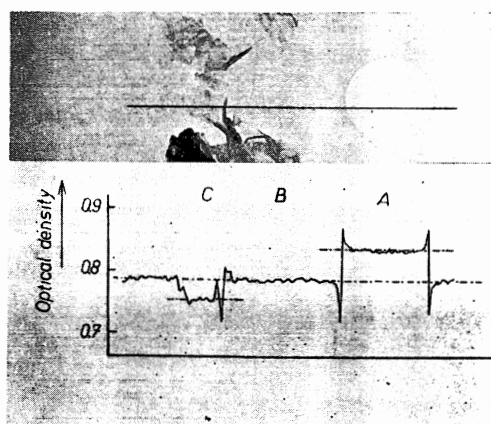


FIG. 3. Photometry of the electron microphotograph No. 623/56. The photometer curve is drawn to the same scale. The thickness of the supporting film was 113 Å; the estimated thickness of the lamella of the reduction product is 12.6 Å.

plate was measured following the black line first at the site of a hole in the supporting film (A), then in the supporting film (B) and through the image of the reduction product lamellae (C). The resulting photometer curve, drawn to the same scale, is shown in the lower

¹⁵ A. Brockes, *Physik. Verhandl. Folge 2*, 6, 27 (1951); A. Brockes, *Angew. Chem.* 67, 331 (1955).

part
was
radi
The
mike
cont
to us
of the
60 kV
obtai
ratio
the t
using

S is th
(.4).
pond
supp
prod
The
0.35
and 2.1
latter
spacing
All
presen

Thick

3.0 Å
3.3
3.3
3.8
3.9
4.0
4.5
4.5
4.6
4.6
4.9
5.2
6.0
6.1
6.1
6.3

Average:
4.6 Å

part of Fig. 3. The density of the photo plate was proportional to the incident electron radiation up to an optical density of $S = 0.9$. The instrument used was a Siemens Uebermikroskop 100 e. In order to get a better contrast on the photo plates, it is expedient to use rather low energy electrons. For most of the electron microphotographs a voltage of 60 kV was used. The results agreed with those obtained with 80 kV electrons. From the ratio of the optical absorbance at (B) and (C) the thickness of the lamella was calculated using the relation

$$\frac{\ln S_A/S_B}{\ln S_A/S_C} = \frac{D_{BPB}}{D_{BPB} + D_{x\rho x}}$$

S is the density of the photo plate; the places (A), (B) and (C) are designated by the corresponding subscripts. D is the thickness of the supporting film (subscript B) or reduction product (subscript x), and ρ is the density. The density values used were $0.25 \times 1.4 = 0.35 \text{ g}\cdot\text{cm}^{-3}$ for the irradiated collodion film and $2.1 \text{ g}\cdot\text{cm}^{-3}$ for the reduction product. The latter value was calculated from the interlayer spacing as determined by X-ray diffraction.

All the results obtained in this way are presented in Table III. The spectrum of the

thickness values gives the impression that values scattered around 4.6 \AA and multiples thereof are more frequent. With the higher values the scattering becomes very broad. In microcrystalline disordered carbon a layer has a thickness of 3.6 \AA . The conclusion is that the thinnest lamellae of the reduction product consist of—to express it cautiously—only a very few carbon layers. The figures around 4.6 \AA are so much more frequent than the higher values mainly because only the very thinnest of the lamellae were measured.

There is some doubt whether really single layers of graphite or carbon were observed. The distinction between graphite and carbon based on the perfection of the stacking order of the layers becomes meaningless with lamellae of only one or two layers. Theoretically, with 60 kV even a 1.5 \AA layer of carbon should give a distinct contrast in the electron microscope.¹⁶ The value of 4.6 \AA contains all errors in the determination of the thickness of the original collodion film and the extent of its decomposition and of photometry. In quite a few lamellae steps of about this height were observed with an average height of 3.7 \AA . This observation confirms the assumption that the thinnest of the lamellae really consisted of single carbon layers.

A possible source of error in this method could be the fact that thin coatings of carbon are deposited on all surfaces within the electron microscope. This carbon is formed by decomposition of organic vapors coming, for instance, from rubber gaskets and vacuum grease. Obviously, the extent of this contamination is very uncertain. If such carbon coatings were deposited on the specimens, the values of Table III should be too low. However, this error cannot have been very significant since small values for the average thickness of the lamellae of the reduction product were found by other, independent methods.

For instance, an average thickness of 14.5 \AA in the direction of the c -axis was estimated

¹⁶ B. v. Borries, *Die Uebermikroskopie*, Verlag Saenger, Berlin (1949) pp. 194–195.

TABLE III
Thicknesses of Extremely Thin Carbon Lamellae

3.0 Å	7.6 Å	12.4 Å	16.7 Å	22.8 Å
3.3	8.3	12.4	19.9	23.6
3.3	8.7	12.6		
3.8	9.1	13.1		
3.9	9.2	13.5		
4.0	9.8	13.9		
4.5	10.9	14.6		
4.5	11.5	15.1		
4.6		15.3		
4.6				
4.9				
5.2				
6.0				
6.1				
6.1				
6.3				
Average: 4.6 Å	9.5 Å	13.7 Å	18.3 Å	23.2 Å

own
tion
dion
d as
(G.O.
e as
that
tron
ass is
f the
own.
icro-
ing a
sities
the
f the
his is
photo

hoto-
ve is
f the
ated
duct

k line
orting
B) and
roduct
curve,
e lower

2, 6, 27
955).

from the broadening of the (002) reflection in the X-ray diffraction diagram. The X-ray diagram of the G.O. reduction product shows only the (002) reflection and the two-dimensional (10) and (11) bands. From the latter the diameter of the crystallites was estimated as about 150 Å and higher. Obviously, this is not the actual size of the lamellae but the average distance between wrinkles or other defects in the carbon planes.

V. SURFACE AREA MEASUREMENTS

Surface area measurements were conducted with the G.O. reduction product as well as with the G.O. soot obtained by deflagration. A few techniques were used which had given good results in earlier investigations of other carbon materials, such as carbon blacks.¹⁷ In detail, these were the adsorption of nitrogen at 77° K (B.E.T. method), the adsorption of phenol and of methylene blue from aqueous solution and the determination of the catalytic efficiency in the synthesis of hydrogen bromide from the elements at 150°C. All these methods usually agree quite well with each other. The surface area conversion factors from the adsorption

¹⁷ A. Clauss, H. P. Boehm and U. Hofmann, *Z. anorg. u. allg. Chem.* **290**, 35 (1957).

data or the catalytic efficiency were obtained by using the BET surface areas of non-porous carbons as a standard.

The results of the surface area measurements are presented in Table IV. With the reduction product of G.O., they are influenced considerably by the method of isolation from the suspension and by the drying temperatures. After filtration and drying at 105° a lower surface area was found than after careful vacuum drying at 20°C. The dispersion of the carbon lamellae was still better preserved by freeze-drying. However, subsequent heat treatment resulted in a decrease of the surface area in this case as well. This is shown best by the methylene blue adsorption data.

It appears that the carbon lamellae tend to stick together once they are in close contact. When the surface area was measured directly in the suspension by methylene blue adsorption, a surface area of 820 m²/g was found. This value is in very good agreement with the surface area that was calculated from the crystallite thickness as determined by X-ray diffraction. With another sample, when a very dilute suspension of G.O. was reduced, a surface area of ca. 1200 m²/g was found. A single carbon layer would have a specific surface area of 2600 m²/g. Consequently, the average

TABLE IV
Specific Surface Areas of the G.O. Reduction Product and of G.O. Soot

Sample and treatment	Specific surface areas in m ² /g from				
	meth. blue	adsorption of phenol	N ₂ (BET)	catalytic efficiency in HBr synthesis	crystallite dimensions (X-ray)
<i>Reduction product</i>					
Suspension	820				
freeze-dried, 20°	580	430	113		740
freeze-dried, 105°	440		120		
freeze-dried, 150°	400	400	123	210	750
freeze-dried, 1100°	235		310		
filtered, 20°	410				
filtered, 105°	270				
<i>G.O. soot</i>					
20°	600				560
150°	610	470	510	570	
1100°	650	630	520	550	390
activated with CO ₂ at 750°	690	730	670	660	470

thickness product

With surface method methylene "dry" this might special group would a some c foils. T for all s treatme decrease treatme is mad treatme howeve some e remova content arrange imperfe

Surface soot pre a quite practical by all m little int might b soot are above, c as CO an carbon network of a few with ho foils wo perforat cules of bromine to all in agglomerate contact treated in

thickness of the lamellae of the reduction product was 3.2 or 2.2. layers, respectively.

With the reduction product of G.O., higher surface areas were measured by the "wet" methods, that is by adsorption of phenol or methylene blue from solution, than by the "dry" methods using gases. The reason for this might be that the molecules of phenol, and, especially, of methylene blue—having a polar group on an otherwise unpolar molecule—would act as detergents and would, at least to some extent, redisperse the agglomerated foils. The B.E.T. surface areas were the same for all samples independent of moderate heat treatment while the methylene blue adsorption decreased with increasing temperature of heat treatment. The sticking together of the foils is made increasingly irreversible by heat treatment. After heat treatment at 1100°, however, the BET surface area increased to some extent. This is probably due to the removal of the residual oxygen and hydrogen content and the beginning crystallite rearrangement with creation of holes and imperfections in the layers.

Surface area measurements with the G.O. soot prepared by deflagration of G.O. showed a quite different behavior. With this material, practically the same surface areas were found by all methods. Heat treatment also had very little influence. The reason for this difference might be the fact that the foils of the G.O. soot are perforated. As has been mentioned above, on deflagration of G.O. carbon is lost as CO and CO₂. As a consequence the resulting carbon must contain many small holes in the network of the layers. In thin foils consisting of a few layers some of the holes would overlap with holes in the adjacent layers so that the foils would be perforated, too. When such perforated foils are stuck together, the molecules of the adsorbates or of hydrogen and bromine could penetrate through these holes to all inner surfaces formed in the course of agglomeration. Naturally, the places of actual contact would be inaccessible. This is illustrated in a schematic diagram (Fig. 4). The

thick black lines symbolize thin carbon foils consisting of a few layers.

The foils of the G.O. soot are very strongly crumpled as was shown in Fig. 1. Therefore, it is very unlikely that extended areas would come into close contact and stick together. The specific surface area would then be large. All pockets formed in the agglomeration of the carbon foils would be accessible through the holes in the layers. This assumption would explain the experimental results.

No carbon losses were observed, however, when G.O. was reduced with hydroxyl amine or hydrazine. The layers of the reduction product are *not* perforated, therefore. Consequently, the pores occluded between the lamellae or foils would *not* be accessible to gases, e.g. nitrogen. Furthermore, since the



FIG. 4. Schematic representation of the structures of agglomerated G.O. soot and G.O. reduction product.

(a) *G.O. Soot*

Foils strongly crumpled,
Few places of contact;
Foils perforated.
Pores accessible.

(b) *Reduction Product*

Foils less crumpled,
Many extended places of contact;
Foils not perforated,
Pores inaccessible.

lamellae are smoother and flatter than those of the deflagration product, more extended areas could come into close contact and stick together. The result would be that with "dry" methods, e.g. nitrogen adsorption, rather small surface areas would be measured. This has been observed experimentally. The real surface area is measured only when surface active compounds are adsorbed from solution and the lamellae are redispersed.

The surface of G.O. soot and, to a still larger extent, of the reduction product is formed practically totally by the basal planes of the

graphite structure, that is by the hexagon layers. With all other microcrystalline carbons having less extended layer planes a significant part of the surface is formed also by prism planes, that is the cut off edges of the carbon layers. Therefore, G.O. soot and the reduction product are very interesting materials for studying the surface properties and phenomena of carbon. For instance, the agreement of the surface areas measured by nitrogen adsorption and estimated from the catalytic efficiency shows that the HBr synthesis is catalyzed at the basis planes of the graphite crystals. Using the conversion factor (0.0067 m Mol HBr per hour and m² at 150°C), it was calculated

that 100 carbon atoms in the layer plane will catalyze the formation of 10 HBr molecules per hour. Likewise, we found evidence that the surface oxides which are formed as the first step in combustion are bound only at the peripheral carbon atoms of the layers.¹⁸ Further studies with these promising materials certainly will bring interesting results.

The authors gratefully acknowledge valuable support by the Fonds der Chemie, Düsseldorf, by the European Research Associates, Brussels, and by the National Carbon Comp., Cleveland, Ohio. Thanks are due to the Deutsche Forschungsgemeinschaft for the loan of an electron microscope.

¹⁸ cf. G. R. Hennig, this volume, p. 143.

In
form
tion
sma
suer
of ca
(act
X-r
alde
up t
in tl
of v
theo
150
and
of a
the
of tl

PORO
venier
studie
result
specin
micro
invest
by act
a rota
produ
about
carbon
chloric
110°C
chloric
decom
inrea
furthe
750°C
This f