

## A TPD-MS study of glassy carbon surfaces oxidized by CO<sub>2</sub> and O<sub>2</sub>

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*Abstract:* The temperature-programmed desorption (TPD) method combined with mass spectrometric (MS) analysis has been applied to investigate the surface properties of carbon materials. The apparatus consisting of a temperature-programmed furnace and a quadrupole mass spectrometer was constructed in order to characterize the surface of differently treated glassy carbon samples. In this work, samples of glassy carbon exposed to air, CO<sub>2</sub> and O<sub>2</sub> were examined. The desorption of H<sub>2</sub>O, CO and CO<sub>2</sub>, as major products, indicated the presence of different oxide groups. The amount of these groups for all samples was calculated. It is concluded that oxidation affects the nature and the amount of the surface oxide groups and contributes to their increased stability.

*Keywords:* glassy carbon, oxidation, mass spectra, temperature-programmed desorption.

### INTRODUCTION

Glassy carbon is a synthetic carbon material, obtained by controlled heating of a thermostable resin. Elucidation of the properties of a glassy carbon surface is important for understanding the processes leading to the stabilization or activation of the surface. Numerous studies have been focused on the surface properties and the nature of the surface species on various carbon materials, such as graphite,<sup>1</sup> carbon black,<sup>2</sup> glassy carbon<sup>3–5</sup> and carbon fibres.<sup>6–8</sup> Glassy carbon has a unique combination of properties, including chemical and thermal stability, hardness, impermeability to gases and liquids and high electrical conductivity. These properties result in a wide range of glassy carbon applications, such as medical implants,<sup>9,10</sup> high performance materials for the aerospace industry,<sup>11</sup> electrodes<sup>12</sup> and supports for metal catalysts.<sup>13</sup> Therefore, the preparation of glassy carbon with controlled surface properties has become very important. In this work, the influence of oxidation on the properties of glassy carbon surfaces has been examined. Samples of glassy carbon previously exposed to air, CO<sub>2</sub> and O<sub>2</sub> were analysed to TPD-MS.

Temperature-programmed desorption (TPD) is a technique in which the sample is heated at a programmed rate in an inert atmosphere or under vacuum. In this way, information about

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the nature of chemisorbed species and the decomposition of surface oxide complexes can be obtained. The TPD technique has previously been employed in surface studies of different carbon materials.<sup>5,14-17</sup> In order to investigate the surface properties of carbon materials, an apparatus consisting of a temperature-programmed furnace and a quadrupole mass spectrometer was constructed in our laboratory.<sup>18-21</sup> In this work, the TPD method combined with mass spectrometric (MS) analysis has been applied to the characterization of the surface of glassy carbon samples previously exposed to air, CO<sub>2</sub> and O<sub>2</sub>.

#### EXPERIMENTAL

##### TPD-MS apparatus

The experiments were carried out using the apparatus presented in Fig.1.

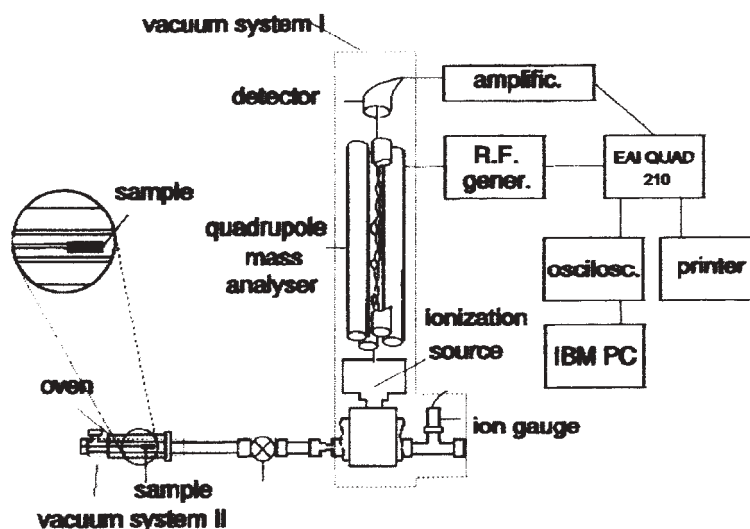


Fig. 1. TPD-MS apparatus.

The 20 cm<sup>3</sup> desorption chamber, constructed from stainless steel, is pumped down to the 10<sup>-7</sup> mbar range. The desorption chamber is placed in a temperature-programmed furnace (home made), connected to the gas-inlet system of an EAI QUAD 210 quadrupole mass spectrometer (Electronic Associates, Inc., CA, USA) *via* a stainless steel tube (50 cm long). A platinum/platinum-rhodium thermocouple in direct contact with the sample was used for temperature measurements. After introduction into the TPD system, the physisorbed moisture and air constituents from the sample surface were removed by pumping for 30 min at 298 K, before commencing the TPD run. To perform a TPD scan, the sample was heated by linearly increasing the temperature, 2 K/min. A Transitrol 12-90B temperature controller was used to program the temperature between 373 K and 1273 K. Data acquisition during the heating time was achieved using a channeltron detector, a Gould digital storage oscilloscope (Model 4050) and an IBM PC computer with a GPIB/IEE 488 interface so that the ion signals at *m/z* 18, 28 and 44 (H<sub>2</sub>O, CO and CO<sub>2</sub>) and the sample temperature were simultaneously recorded. Laminar flow was achieved from the furnace to the mass spectrometer and there were no dead volume products in the connection lines. The intensity of the *m/z* 28 signal was corrected for the contribution of the background N<sub>2</sub> signal intensity.

##### Sample preparation

Glassy carbon was produced by carbonization of a commercial resol type of phenol-formaldehyde resin. Polymerization of resin was carried out at 363 K for 24 h. The polymer was carbonized in argon up to 1273 K with a heating rate of 12 K/h. The carbonized sample was exposed to air at room temperature for more

than a week before surface characterization. Three types of samples were prepared:

1. glassy carbon which had been exposed to air;
2. glassy carbon which had been exposed to CO<sub>2</sub>, at 1033 mbar, for 24 h, at room temperature and
3. glassy carbon which had been exposed to O<sub>2</sub>, at 1033 mbar, for 24 h, at 373 K.

For each TPD experiment, 1.00 g of powdered sample was used.

#### *Quantitative analysis*

In order to compare all the results quantitatively, the amount of desorbed CO and CO<sub>2</sub> for each sample was calculated.<sup>22</sup> The calibration method included the use of suitable salts, *i.e.*, CaC<sub>2</sub>O<sub>4</sub> for CO calibration and CaCO<sub>3</sub> for CO<sub>2</sub> calibration. The results were obtained in  $\mu\text{mol/K}$  of each gas desorbed from 1.00 g of powdered sample.

### RESULTS AND DISCUSSION

It is well known that after the exposition of carbon materials to different gases their surface characteristics change.<sup>23–26</sup> The modification of glassy carbon surfaces in contact with air has been reported, as well.<sup>18–22</sup> In this work the influence of CO<sub>2</sub> and O<sub>2</sub> on the surface properties of glassy carbon has been studied. The TPD-MS spectra of glassy carbon (a), glassy carbon that had been exposed to CO<sub>2</sub> (b) and glassy carbon that had been exposed to O<sub>2</sub> (c) are presented in Fig. 2.

The most significant products obtained by TPD were H<sub>2</sub>O ( $m/z$  18), CO ( $m/z$  28) and CO<sub>2</sub> ( $m/z$  44). The relative intensities of the corresponding peaks are presented as a function of TPD temperature.

#### *CO<sub>2</sub> exposed sample*

The H<sub>2</sub>O desorption maxima of the sample exposed to CO<sub>2</sub> can be detected at temperatures below 373 K, where physisorbed water is desorbed. This indicates that, in the case of CO<sub>2</sub> exposed samples, water is not a product of the decomposition of surface oxide groups, as is the case of air-exposed samples.

The CO desorption from the CO<sub>2</sub> exposed sample (Fig. 2b) at temperatures above 1273 K indicates the decomposition of semiquinone groups. The presence of these groups as well as carbonyl and/or ether groups, has been established on the surface of air-exposed samples. The CO<sub>2</sub> desorption has two desorption maxima, at 773 K and 1073 K. The first desorption maximum indicates the presence of carboxylic groups and the second is due to the decomposition of acid-anhydride and/or lactone groups. The same type of oxide groups were found on the surface of air-exposed glassy carbon, but their stability was changed. After oxidation of graphite with CO<sub>2</sub>, the temperatures of the corresponding CO and CO<sub>2</sub> desorption maxima were lowered.<sup>16</sup> This indicates that the surface oxide groups of CO<sub>2</sub> oxidized glassy carbon are more stable than the surface oxide groups of CO<sub>2</sub> oxidized graphite.

#### *O<sub>2</sub> exposed sample*

In the case of O<sub>2</sub> oxidized glassy carbon (Fig. 2c), H<sub>2</sub>O desorption occurs in a similar manner as for the CO<sub>2</sub> oxidized sample. The CO desorption has two desorption maxima, at 823 K and above 1273 K. The first maximum is due to the decomposition of

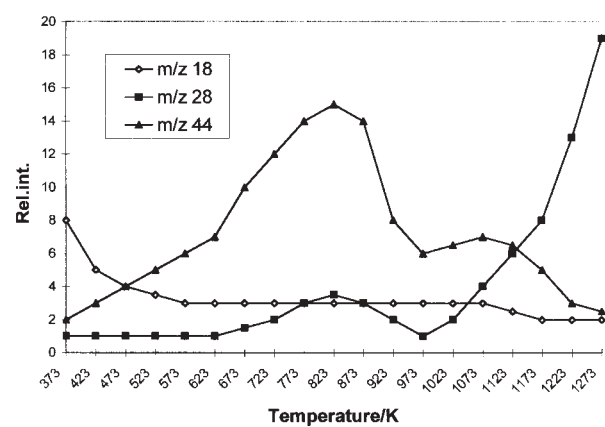
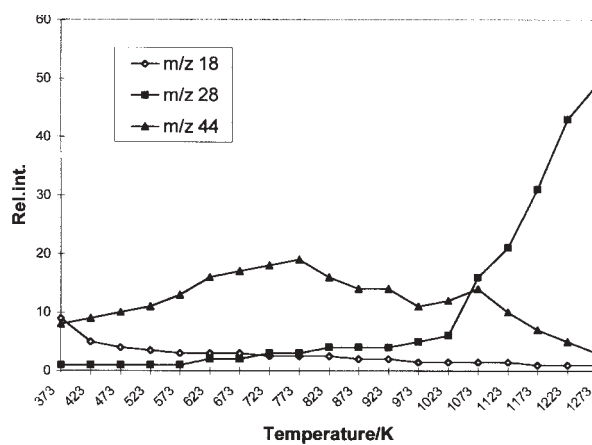
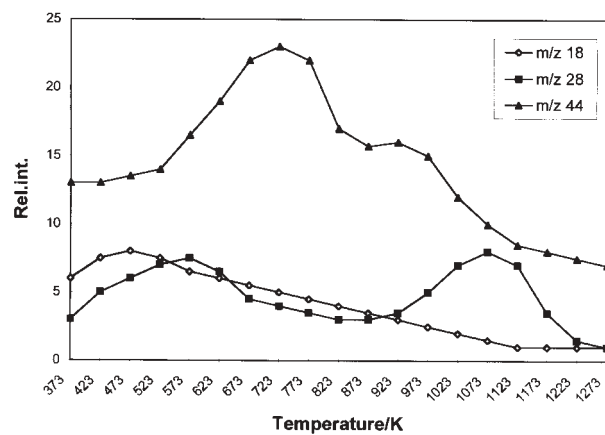


Fig. 2. TPD-MS spectra of air exposed– (a) CO<sub>2</sub> exposed– (b) and O<sub>2</sub> exposed (c) glassy carbon samples.

acid-anhydride groups. In comparison with the air-exposed sample, it can be noticed that in this case there are no less stable carbonyl and/or ether groups and that more stable acid-anhydride groups are formed. The second CO maximum occurs in the same way as in the case of CO<sub>2</sub> oxidized glassy carbon. The CO<sub>2</sub> also has two desorption maxima. The first at 823 K, corresponding to the decomposition of carboxylic groups and the second, at 1073 K, is due to the decomposition of acid-anhydride and/or lactone groups. The same type of oxide groups were detected on the surface of air-exposed glassy carbon, but changes in their stability can be noticed.

*Stability of surface oxide complexes and quantitative analysis*

Assuming that the desorption energy reflects the stability of the chemisorption bond, in order to compare and discuss the stability of differently treated samples, the desorption energy,  $E_d$ , was calculated using the peak-position method:<sup>27</sup>

$$E_d = RT_m \ln(v/\beta)$$

where  $R$  is gas constant,  $T_m$  – the peak temperature, *i.e.*, the temperature at which the desorption rate has maximal value,  $\beta$  is the linear heating rate ( $\beta = 2$  K/min) and  $v$  is a frequency factor of the chemisorption bond ( $v = 10^{13} \text{ s}^{-1}$ ). The desorption energies calculated from the position of the peak maxima are listed in Table I.

TABLE I. Desorption products and corresponding desorption energies for air-, CO<sub>2</sub>- and O<sub>2</sub>, exposed glassy carbon (GC)

Desorption product	Sample	Desorption energy / kJ mol <sup>-1</sup>	
H <sub>2</sub> O	GC (air)	125	
	GC (CO <sub>2</sub> )	< 98	
	GC (O <sub>2</sub> )	< 98	
CO	GC (air)	151	283
	GC (CO <sub>2</sub> )		> 336
	GC (O <sub>2</sub> )	217	> 336
CO <sub>2</sub>	GC (air)	217	243
	GC (CO <sub>2</sub> )	204	283
	GC (O <sub>2</sub> )	217	283

All the calculated desorption energies are higher than 100 kJ/mol, indicating that chemisorption processes are involved. The higher desorption energies observed for the CO<sub>2</sub> and O<sub>2</sub> oxidized samples show that oxidation under the described conditions typically stabilizes the surface oxide structures.

In order to compare the surfaces of air-exposed glassy carbon, CO<sub>2</sub> oxidized glassy carbon and O<sub>2</sub> oxidized glassy carbon, the amounts of desorbed gases from a unit mass of each samples was calculated.<sup>22</sup> The calculated amounts of CO (a) and CO<sub>2</sub> (b) are presented as a function of desorption temperature in Fig. 3.

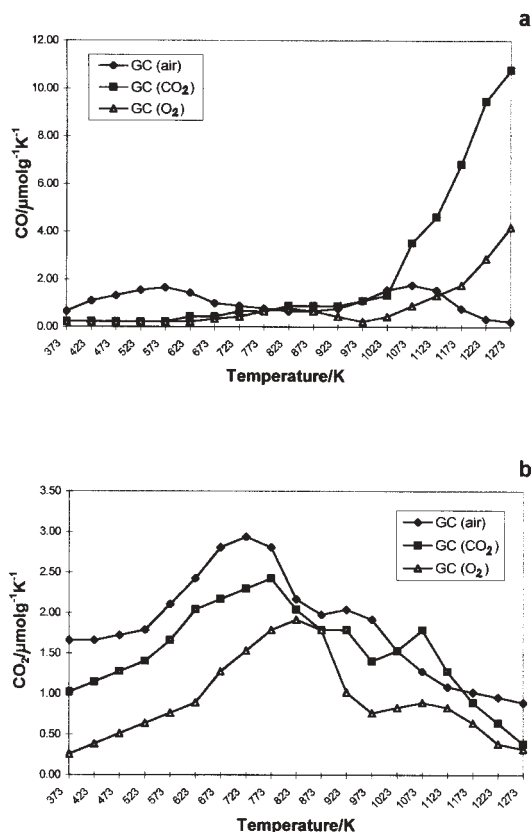


Fig. 3. The amount of desorbed CO (a) and CO<sub>2</sub> (b) as a function of temperature for air exposed-, CO<sub>2</sub> exposed- and O<sub>2</sub> exposed glassy carbon samples.

It can be noticed that both the CO<sub>2</sub> and O<sub>2</sub> oxidized samples contain more oxide groups which desorb as CO at temperatures above 1000 K. This indicates that in contact with CO<sub>2</sub> and O<sub>2</sub> semiquinone groups are formed, in amounts much higher than in the air-exposed sample. The amounts of oxide groups which decompose at temperature below 1000 K are lower for the CO<sub>2</sub> and O<sub>2</sub> oxidized samples. The amount of oxide groups whose decomposition results in CO<sub>2</sub> desorption is lower over the whole temperature range except at 1073 K. The desorption maximum at this temperature indicates the presence of acid-anhydride and/or lactone groups. The amount of these groups is higher for the CO<sub>2</sub> oxidized sample. The corresponding desorption maxima appear at higher temperatures, indicating that more stable acid-anhydride and/or lactone groups are formed.

The reaction of glassy carbon with oxygen-containing gases and its influence on the surface characteristics of the glassy carbon can be explained by semi-empirical molecular orbital calculations.<sup>26</sup> Due to the large electronegativity of oxygen, the carbon atoms with the highest negative charges should be the targets for bonding oxygen atom. Thus, it seems reasonable to assume that two main groups of active oxygen-containing structures can be formed on the edge sites. One is the in-plane group, which contains oxygen atoms in the plane of the graphite basal plane. The another contains both in-plane and off-plane oxygen

atoms. The former groups decompose at higher temperatures and in the latter group, the C–C bonds are weakened and they decompose at lower temperatures. This can be caused by changes in the local electron density of carbon atoms when off-plane oxygen atoms are chemisorbed on saturated carbon atoms. However, in the case of air-exposed glassy carbon both types of active oxygen-containing structures exist. This results in the decomposition of both less stable (carboxyl, carbonyl and/or ether) and more stable (semiquinone, acid-anhydride and/or lactone) groups. In the case of oxidized samples, the higher amounts of the more stable and the lower amounts of the less stable groups have been typically observed. This means that oxidized samples contain higher amounts of less active oxygen-containing complexes which decompose at higher temperature. The conversion of more active to less active groups could explain the lower amount of less stable and the higher amount of more stable groups in the oxidized samples. This result is in agreement with the results published in the literature.<sup>26</sup> Actually, the more active complex converts to the less active complex which is always more abundant than the more active one. Comparing the CO<sub>2</sub> and O<sub>2</sub> oxidized samples, the reason for the lower amount of all groups desorbed from the O<sub>2</sub> oxidized sample could be the possible conversion of all groups to more stable ones. These new-formed groups would decompose at very high temperatures, which could not be examined under the available conditions. Under the oxidation conditions described in this work, glassy carbon surfaces with higher amounts of more stable groups were formed. This was even more significant for the CO<sub>2</sub> oxidized sample than for the O<sub>2</sub> oxidized sample.

#### CONCLUSION

The temperature-programmed desorption method combined with mass spectrometric analysis has been employed for the characterization the surfaces of air, CO<sub>2</sub> and O<sub>2</sub> exposed glassy carbon samples. In this way, information about the nature, quantity and stability of the surface oxide species was obtained. The results showed that the chemisorption of CO<sub>2</sub> or O<sub>2</sub> on glassy carbon, under the conditions in this work, leads to a reduction of the amount of surface oxide groups which decompose below 1000 K and to the formation of more stable oxide groups which decompose at higher temperatures.

#### ИЗВОД

#### МАСЕНОСПЕКТРОМЕТРИЈСКО ИСПИТИВАЊЕ СТАБИЛНОСТИ ПОВРШИНЕ СТАКЛАСТОГ КАРБОНА ОКСИДОВАНОГ УГЉЕН-ДИОКСИДОМ ИЛИ КИСЕОНИКОМ

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За испитивања површинских карактеристика угљеничних материјала, конструисан је уређај за температурски програмирану десорпцију са масеноспектрометријским детектором

помоћу кога се прате десорпциони производи разлагања површинских оксидних комплекса. При томе је могуће вршити њихову квалитативну и квантитативну анализу. У оквиру овог рада испитан је утицај оксидације угљен-диоксида, односно кисеоником, на површинске особине стакластог карбона, јер је он синтетички угљенични материјал чија примена у великој мери зависи од његових површинских особина. Десорпција воде, угљен-моноксида и угљен-диоксида, као главних десорпционих производа, указала је на присуство различитих количина, различитих оксидних група на површини испитаних узорка. Резултати су показали да оксидација угљен-диоксида, односно кисеоником доводи до смањења броја оксидних група које се разлажу на температурама испод 1000 К, као и до формирања стабилнијих група које се разлажу на вишим температурама.

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