Formation of oxygen complexes in controlled atmosphere at surface of doped glassy carbon

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Abstract. The effects of boron and phosphorus incorporation in phenolic resin precursor to the oxidation resistance of glassy carbon have been studied. In order to reveal the nature and composition of the oxygen complexes formed at the surface of doped glassy carbon, under controlled atmosphere, the surface of the samples was cleaned under vacuum up to 1273 K. Specific functional groups, subsequently formed under dry CO_2 or O_2 atmosphere on the surface of boron-doped and phosphorus-doped glassy carbon samples, were examined using the temperature-programmed desorption method combined with mass spectrometric analysis. Characterization of surface properties of undoped and doped samples has shown that in the presence of either boron or phosphorus heteroatoms, a lower amount of oxygen complexes formed after CO_2 exposure, while, typically, higher amount of oxygen complexes formed after O_2 exposure. It has been concluded that the surface of undoped glassy carbon has a greater affinity towards CO_2, while in the presence of either boron or phosphorus heteroatoms, the glassy carbon surface affinity becomes greater towards O_2, under experimental conditions.

Keywords. Glass-like carbon; doping; mass spectroscopy; temperature programmed desorption; surface properties.

1. Introduction

It is well known that the incorporation of heteroatoms into the carbon materials affects the surface properties and oxidation resistance. A number of studies have been focused on carbon surface modification by introducing boron or phosphorus heteroatoms into different carbon materials. Boron is thought to be capable of blocking active sites at the edges of graphene layer. There are three important characteristic effects of substitutional boron: graphitization enhancement, formation of boron oxide layer and redistribution of π-electrons in the graphene layer, lowering the Fermi level of carbon and inhibiting the desorption of CO and CO_2. Electron distribution in the graphene layer in the presence of substitutional boron is suggested to be a balance between three potentially competing effects: (i) reduced total electron density, (ii) decreased contribution of delocalized π-electrons to the electron density on the remaining carbon atoms and (iii) σ-electron localization on C atoms due to higher electronegativity of C with respect to B (Radovic *et al* 1998). Boron as a substitutional element

in pristine carbons creates an electron acceptor level in a lower energy region (Kurita 2000). Boron can replace C in the graphene layer, resulting in altering the electronic structure and providing oxidation inhibition of carbon fibre (Jones and Thrower 1987). Substitutional boron has shown both a catalytic and an inhibiting effect on carbon oxidation (McKee *et al* 1984; Zhong *et al* 2000; Lee *et al* 2004). Conflicting results on the effects of B doping are a consequence of dual action of substitutional B, being an inhibitor at high temperature, but a catalyst at low temperature (McKee *et al* 1984). The dominant factor actually depends on boron content and distribution, carbon nature and reaction conditions.

Phosphorus as a doping element was thought to block active sites at graphene edges to inhibit graphite oxidation (McKee *et al* 1984; Oh and Rodriguez 1993). The oxidation inhibition mechanism in P-doped carbon fabrics appears to be the blockage of active sites resulting in the proportional increase of oxidation inhibition with increasing P loading (Lee and Radovic 2003).

Moreover, after the exposure of carbon materials to different gases, their surface characteristics change as well (Chen *et al* 1993; Fu *et al* 1994; Zhuang *et al* 1994; Perić-Grujić *et al* 2002). The reaction with oxygen-containing gases and its influence to the surface characteristics of

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glassy carbon can be explained by semiempirical molecular orbital calculations (Chen *et al* 1993).

The modification of glassy carbon through introduction of boron and phosphorus heteroatoms in the carbon precursor has been reported (Laušević *et al* 1990; Perić *et al* 1996a,b; Đurkić *et al* 1997). Characterization of the surface properties using X-ray photoelectron spectroscopy (XPS) has shown that phenol, alcohol, ether, carbonyl, semiquinone, carboxyl, acid anhydride and lactone functional groups exist on glassy carbon surface (Sundberg *et al* 1989; Đurkić *et al* 1997). Structures of some functional groups on glassy carbon surface, relevant to this paper, are presented in figure 1.

Previous mass-analysed temperature programmed desorption (TPD) experiments have shown that the main desorption products, CO and CO_2, result from the decomposition of different surface oxygen complexes (Roman-Martinez *et al* 1993; Zhuang *et al* 1994; Đurkić *et al* 1997). Two CO desorption maxima (900 K and 1100 K) are suggested to be the result of decomposition of less stable carbonyl and/or ether and more stable quinone and/or phenol species, respectively, while two CO_2 desorption maxima (600 K and 900 K) correspond to the decomposition of less stable carboxyl and more stable acid anhydride and/or lactone species.

Elucidation of glassy carbon surface is important for understanding the processes leading to the stabilization or activation of the surface. The possibility of preparing glassy carbon with controlled surface properties becomes very important. Since our previous results refer to previously air-exposed glassy carbon samples (Đurkić *et al* 1997), in this work, the influence of different gases to the surface characteristics has been examined. Boron and phosphorus doped glassy carbon samples previously exposed to either pure CO_2 or pure O_2 atmosphere were studied. Mass-analysed TPD experiments were performed in order to investigate the nature and thermal stability of doped glassy

carbon surface oxygen groups. The apparatus consisting of temperature-programmed furnace and quadrupole mass spectrometer (MS) has been constructed in our laboratory (Perić *et al* 1996a,b; Perić-Grujić *et al* 1998).

2. Experimental

2.1 *Sample preparation*

Glassy carbon was produced by the carbonization of a commercial phenol–formaldehyde resin. Two types of precursor resin samples were prepared: (i) phenol–formaldehyde resin mixed with boric acid, to obtain 2 wt% of boron in GCB precursor before polymerization and (ii) phenol–formaldehyde resin mixed with phosphorus pentoxide, to obtain 2 wt% of phosphorus in GCP precursor before polymerization.

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 Kh^{-1}. Carbonized samples were exposed to air at room temperature for more than a week. Therefore, the surface oxide complexes were cleaned by heating the samples in vacuum (10^{-6} torr) up to 1273 K. Samples were cooled down to room temperature in vacuum and TPD–MS analyses showed the absence of oxide functional groups at the surface of cleaned samples. Further, TPD–MS analyses under the following conditions were performed: (i) cleaned samples were exposed to CO_2, at 1033 mbar, for 24 h, at 373 K and (ii) they were then exposed to O_2, at 1033 mbar, for 24 h, at 373 K. In each TPD experiment, 50 mg of powdered sample was used.

2.2 *TPD–MS*

The 20 cm^3 desorption chamber, constructed from stainless steel, was pumped down to the 10^{-7} mbar range. The desorption chamber was placed in a temperature-programmed furnace 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 was used for temperature measurements. To perform a TPD scan, after pumping for 30 min at room temperature, samples were 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 heating time was achieved using the channeltron detector, a Gould digital storage oscilloscope (Model 4050) and an IBM PC computer with GPIB/IEE 488 interface so that the ion signals at m/z 28 and 44 (CO and CO_2) were simultaneously recorded as a function of temperature. The laminar flow was achieved from the furnace to the mass spectrometer. The intensity of the m/z 28 signal was corrected for the contribution of background N_2 signal intensity.
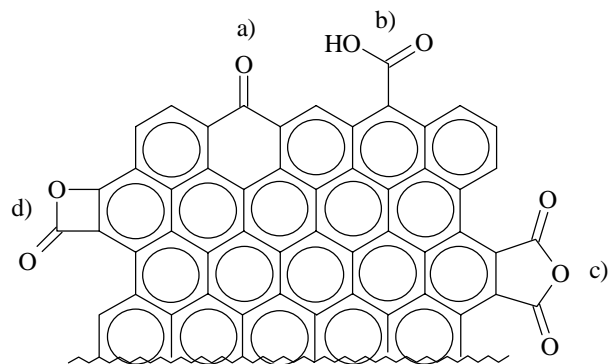

Figure 1. Structures of semiquinone (a), carboxyl (b), acid anhydride (c) and lactone (d) functional groups on glassy carbon surface.

2.3 *Quantitative analysis*

In order to compare all the results quantitatively, the amount of desorbed CO and CO_2 for each sample was calculated. The calibration method included the use of suitable salts, i.e. CaC_2O_4 for CO calibration and $CaCO_3$ for CO_2 calibration (Perić-Grujić 1998). The results were obtained in $\mu mol\,g^{-1}\,K^{-1}$ of each desorbed gas.

3. Results and discussion

In this work, the TPD–MS spectra of CO_2- and O_2-exposed boron (GCB)- and phosphorus (GCP)-doped glassy carbon samples were recorded. The most significant products of TPD obtained were CO (m/z 28) and CO_2 (m/z 44). In order to follow the influence of treatment in CO_2 and O_2 atmospheres to the surface properties of doped samples, the amounts of desorbed CO and CO_2 from unit mass of each samples were calculated and presented as a function of desorption temperature. Corresponding values for undoped glassy carbon samples (GC), obtained in our previous work (Perić-Grujić *et al* 2002), were added to diagrams, as dotted lines.

3.1 *CO₂ exposed samples*

The amounts of desorbed CO (a) and CO_2 (b) as a function of desorption temperature, for CO_2-exposed samples are presented in figure 2.

The CO desorption maxima from the CO_2 exposed samples (figure 2a) at temperature above 1273 K correspond to the decomposition of semiquinone groups (Roman-Martinez *et al* 1993; Zhuang *et al* 1994). Two CO_2 desorption maxima at 800 K and 1100 K indicate the presence
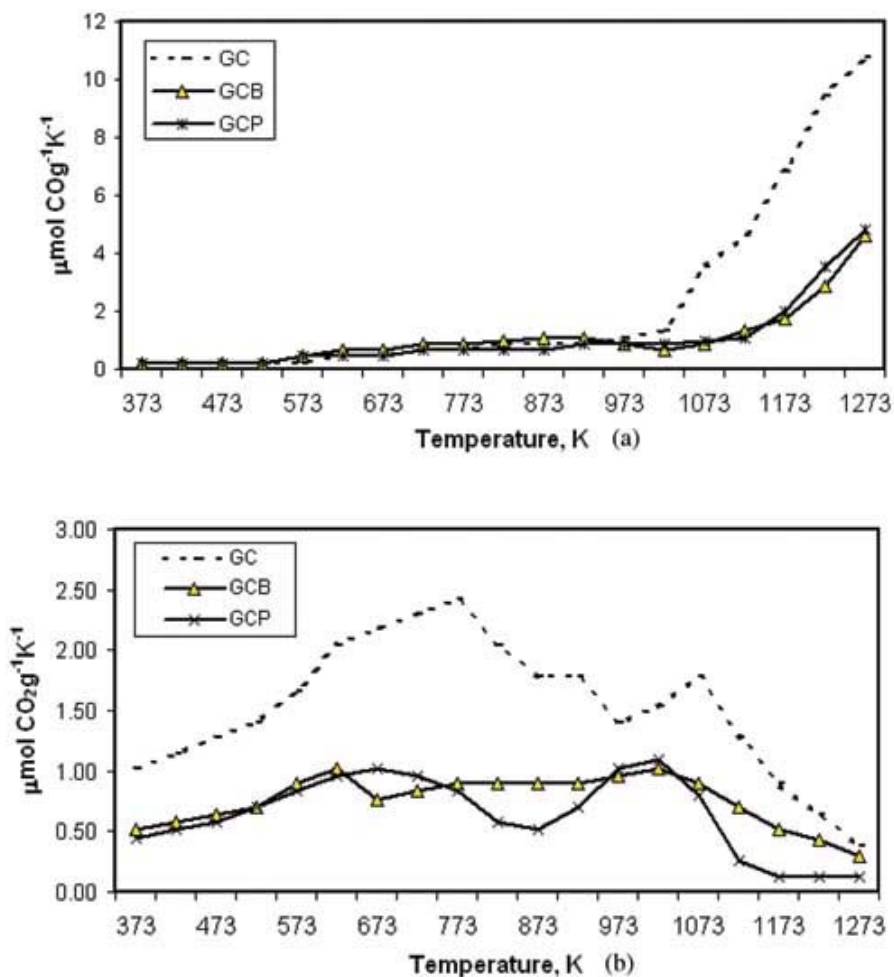

Figure 2. The amount of desorbed CO (a) and CO_2 (b) as a function of desorption temperature for CO_2-exposed GC, GCB and GCP samples.

of carboxyl and acid-anhydride and/or lactone groups, respectively (Zhuang *et al* 1994) in the case of undoped glassy carbon sample (figure 2b). The same type of oxide groups are present at the surface of doped samples, but corresponding desorption maxima shifted towards lower temperatures indicating lower thermal stability of these groups.

It can be noticed that boron and phosphorus have quite similar effects on the CO_2-exposed glassy carbon, under examined conditions. A fewer amounts of all oxide species are present at surfaces of doped samples, indicating that a number of reactive carbon sites on doped samples decreased.

This result is in agreement with conventional wisdom that boron lowers the Fermi level and inhibits chemisorption of CO and CO_2 (Jones and Thrower 1987). Moreover, reduced number of reactive sites on CO_2-exposed boron doped glassy carbon seems to be a consequence of reduced electron density on reactive carbon atoms, reinforcing the oxidation inhibition due to B_2O_3 formation (Radovic *et al* 1998; Lee *et al* 2004). With regard to the phosphorus doped sample, a reduced number of reactive sites seems to be the blockage of active sites due to the formation of C–P–O or C–O–P bonds at graphene edges, in agreement with previous studies (McKee *et al* 1984; Lee and Radovic 2003).
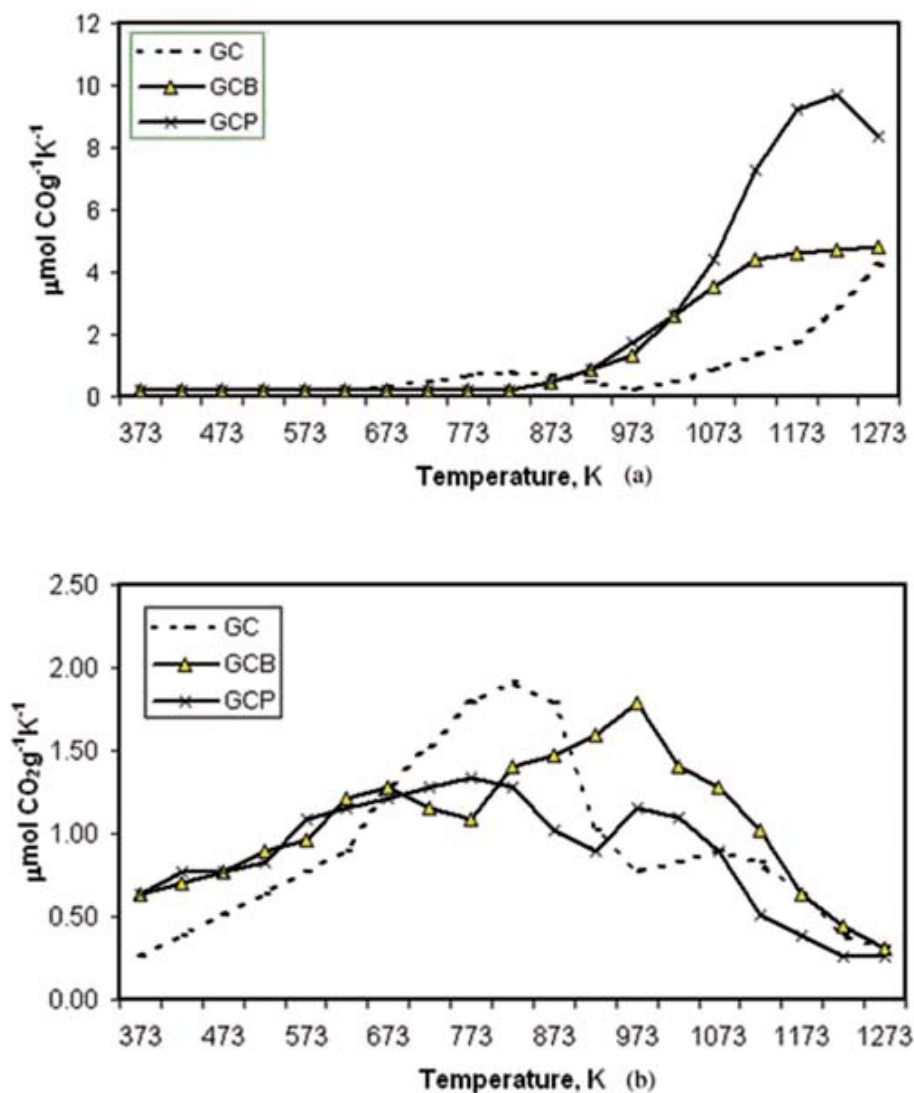

Figure 3. The amount of desorbed CO (a) and CO_2 (b) as a function of desorption temperature for O_2-exposed GC, GCB and GCP samples.

3.2 *O_2 exposed samples*

In figure 3, the amounts of desorbed CO (a) and CO_2 (b) as a function of desorption temperature, for O_2-exposed samples are presented.

The CO desorption maxima above 1200 K indicate the presence of semiquinone groups (figure 3a). The amount of these groups is higher in the case of doped samples. Corresponding desorption maxima are shifted towards lower temperatures, indicating lower stability of oxide species on doped samples. Both doped samples exhibit the presence of carboxyl and acid-anhydride groups (figure 3b). The absence of water, as in our experimental conditions, reduces or prevents the formation of lactone species (Fanning and Vannice 1993). The amount of carboxyl groups is lower on doped sample surfaces, while the amount of acid-anhydride and/or lactone species is higher. The thermal stability of all CO_2 evolving groups is lower on doped samples. Higher amount of semiquinone and anhydride species is in agreement with previous studies (Fanning and Vannice 1993).

On the one hand, in the presence of boron, reduced electron density and formation of oxide surface film which acts as an active site blocker and O_2 diffusion barrier (Jones and Thrower 1987; McKee 1991; Lee *et al* 2004) could explain reduced amount of lower energy desorption oxide groups on B-doped glassy carbon. On the other hand, upon O_2 exposure boron acts as a π electron acceptor and such π electron distribution results in weakened C–C bonds and strengthened C–O bonds (Radovic *et al* 1998). More-
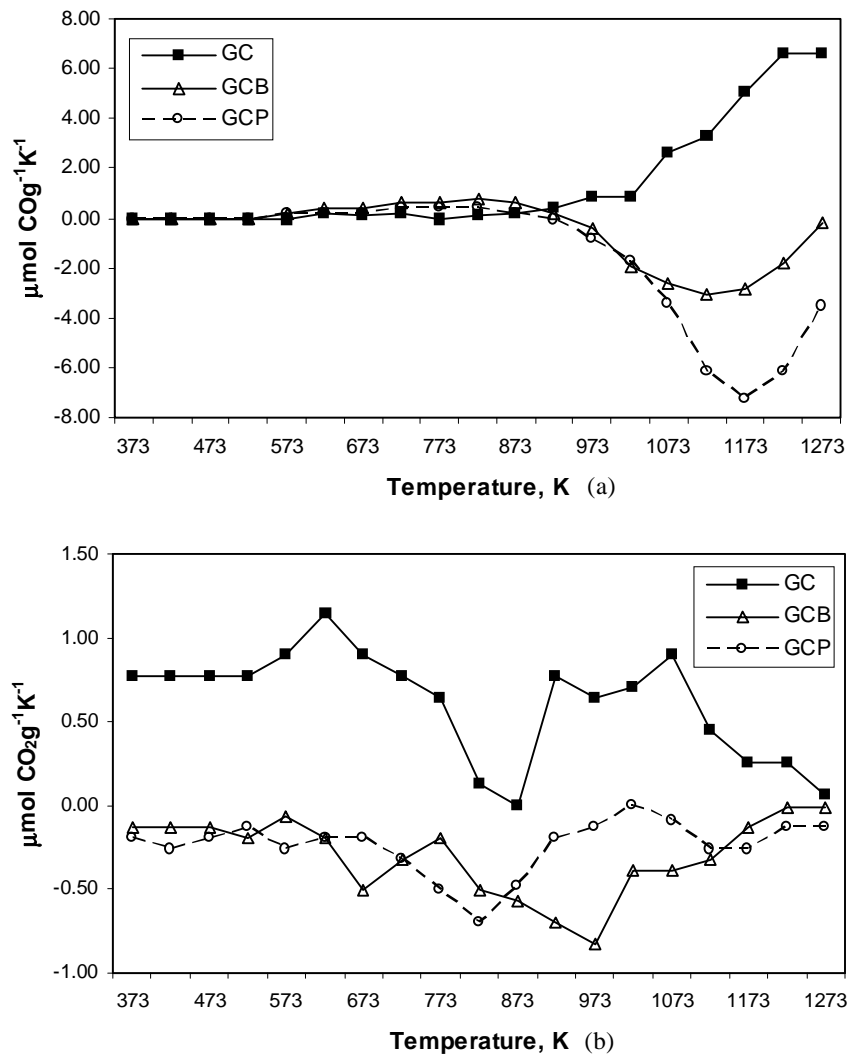

Figure 4. The difference of the amount of desorbed CO (a) and CO_2 (b) between corresponding CO_2- and O_2-exposed GC, GCB and GCP samples as a function of desorption temperature.

over, it has been suggested that boron atom at edge site or close to edge site would have this pronounced effect compared to the one in the centre of graphene layer (Lee *et al* 2004). Carbon oxidation, assumed to be an electrophilic reaction, is inhibited by a lower electron density on reactive sites, but the affinity of O_2 for reactive edge carbon sites becomes greater (Radovic *et al* 1998). This, actually, could explain higher amount of high desorption energy groups on the surface of B-doped glassy carbon.

Reduced CO and CO_2 desorption up to 900 K from phosphorus doped sample is evident. At higher desorption temperatures higher amount of surface oxide groups is observed. It can also be noticed that the amount of semiquinone groups on P-doped sample is twice higher compared with the amount of similar groups on B-doped sample. Concerning previous studies, where it was suggested that the formation of either C–O–P (McKee *et al* 1984) or C–P–O bonds (Oh and Rodriguez 1993) was responsible for blocking active sites at graphene edges, it can be concluded that proposed blockage mechanism becomes inefficient to prevent the reaction with O_2.

3.3 *A comparison of CO_2- and O_2-exposed samples*

Figure 4 provides a basis for comparison of CO_2- and O_2-exposed samples.

Differences between amounts of desorbed CO (figure 4a) and CO_2 (figure 4b), for corresponding CO_2- and O_2-exposed samples were calculated and presented as a function of desorption temperature. From the results presented in figure 4, the difference in surface affinity towards CO_2 and O_2 atmosphere of doped and undoped glassy carbon samples becomes obvious. The formation of the surface oxygen complexes on pure glassy carbon is enhanced in CO_2 atmosphere, while O_2 atmosphere affects doped samples more. In the presence of either boron or phosphorus heteroatoms, proposed active sites blockage mechanisms might be efficient to reduce the surface affinity towards CO_2, so that the amount of all oxide groups is lower on

Table 1. Desorption products and corresponding desorption energies for CO_2- and O_2-exposed boron (GCB) and phosphorus (GCP) doped glassy carbon.

Desorption product	Sample	Desorption energy (kJ mol^{-1})	
CO	GC (CO_2)	/	>336
	GC (O_2)	217	>336
	GCB (CO_2)	/	>336
	GCB (O_2)	/	>336
	GCP (CO_2)	/	>336
	GCP (O_2)	/	323
CO_2	GC (CO_2)	205	283
	GC (O_2)	217	283
	GCB (CO_2)	165	270
	GCB (O_2)	178	257
	GCP (CO_2)	178	270
	GCP (O_2)	204	257

doped samples. On the other hand, higher amount of semiquinone and acid-anhydride groups on doped samples, compared with undoped glassy carbon, after O_2 exposure, indicates that the surface of doped samples has a greater affinity towards O_2 and that the proposed active sites blockage mechanisms are less efficient. It has been suggested (Chen *et al* 1993) that off-plane oxygen atoms from the gas molecules chemisorb on saturated carbon atom next to the reactive site; higher bond strength between the off-plane oxygen atom and the in-plane carbon atoms than C–C diatomic energies indicated that it was easier to break the surface C–C bonds rather than C–O bonds. This type of oxygen bonding leads to the formation of less stable oxide complexes which decompose at lower temperatures, in agreement with our results.

3.4 *Stability of surface oxide complexes*

Assuming that the desorption energy reflects the stability of the chemisorption bond, in order to compare and discuss the stability of differently treated samples, desorption energy, E_d, has been calculated using the peak-position method (Tompkins 1978; Zhou *et al* 1994)

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

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

All calculated desorption energies are higher than 100 kJ mol^{-1}, indicating that chemisorption processes are involved. Desorption energies of corresponding oxide groups are higher for undoped samples, indicating their higher stability compared with doped samples. Values obtained for undoped samples are in very good agreement with the results in literature (Kelemen and Freund 1985). After either CO_2- or O_2-exposure, corresponding desorption energies for doped samples have similar values, suggesting that surface oxide groups of boron and phosphorus doped samples have similar thermal stability. Desorption energies of more stable oxide groups on O_2-exposed doped samples are lower than corresponding desorption energies for the same groups on CO_2-exposed samples. Since the amount of these groups is increased on O_2-exposed doped samples, their lower stability could be a consequence of off-plane oxygen atom bonding and thus, weakening surface C–C bond, so that lower energy is required for its cleavage (Fagan and Kuwana 1989).

4. Conclusions

In order to follow the influence of boron and phosphorus presence in the CO_2- and O_2-exposed glassy carbon, the

surfaces of all samples were previously cleaned in vacuum up to 1273 K. Subsequently formed surface oxide complexes, under dry CO_2 or O_2 atmosphere, were analysed by temperature-programmed desorption method combined with mass spectrometry.

After CO_2-exposure, a lower amount of all surface oxide groups has been formed on doped glassy carbon samples than on the surface of pure glassy carbon. The thermal stability of these surface oxide groups also reduced on doped samples. After O_2-exposure, a smaller amount of lower desorption energy oxide groups and higher amount of high desorption energy groups was established on doped samples. The thermal stability of all oxygen complexes formed is lower, compared with the thermal stability of similar complexes on undoped sample.

On the basis of results obtained, following conclusions can be made:

(I) After CO_2-exposure, due to the electron distribution and B_2O_3 formation, number of reactive sites is lower on boron doped glassy carbon than on the undoped sample. The formation of C–O–P and/or C–P–O bonds is responsible for reduced number of reactive sites on phosphorus doped glassy carbon, compared with the undoped sample.

(II) The affinity of O_2 for the reactive sites on doped samples is greater compared to CO_2, so that sites at graphene edges with high electron density become targets for oxygen bonding. The highest amount of semiquinone groups on P-doped sample and acid-anhydride groups on B-doped sample indicate that these edge sites are most prone to the attack of oxygen.

(III) The surface of undoped glassy carbon has a greater affinity towards CO_2, while in the presence of either boron or phosphorus heteroatoms, the glassy carbon surface affinity becomes greater towards O_2, under examined experimental conditions.

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