Surface characterization of silver and palladium modified glassy carbon

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Abstract. In this work, the influence of silver and palladium on the surface of undoped, boron doped and phosphorus doped glassy carbon has been studied. The silver and palladium concentrations in solution, after metal deposition, were measured by atomic absorption spectrophotometer. The morphology of metal coatings was characterized by scanning electron microscopy. In order to investigate the nature and thermal stability of surface oxygen groups, temperature-programmed desorption method combined with mass spectrometric analyses, was performed. The results obtained have shown that silver and palladium spontaneously deposit from their salt solutions at the surface of glassy carbon samples. Silver deposits have dendrite structure, whilst palladium forms separate clusters. The highest amount of both silver and palladium deposits at the surface of sample containing the highest quantity of surface oxide complexes. It has been concluded that carboxyl groups and structure defects are responsible for metal reduction. Calculated desorption energies have shown that the surface modification by metal deposition leads to the formation of more stable surface of undoped and doped glassy carbon samples.

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

1. Introduction

The possibility of preparing carbon materials with controlled surface properties is very important due to the wide range of carbon materials application. There are two major approaches to influence the surface of carbon materials. The first approach is the incorporation of heteroatoms, which affects the surface activity and oxidation resistance. A number of studies have been focused on the surface modification of carbon materials by introducing boron or phosphorus heteroatoms. Substitutional boron has shown both catalytic and inhibiting effect on carbon oxidation. The dominant factor depends on boron content and distribution, carbon nature and reaction conditions (McKee *et al* 1984; Zhong *et al* 2000; Lee *et al* 2004). The oxidation inhibition mechanism in phosphorus doped carbon fabrics appears to block active sites resulting in the proportional increase of oxidation inhibition with increasing phosphorus loading (Lee and Radovic 2003).

The modification of glassy carbon through the 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; Perić-Grujić *et al* 2006). 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). 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).

The other approach to influence the surface of carbon materials is to prepare superficially modified materials by spreading coatings with deposits or thin films. Previous studies have shown that some metals, like silver, copper and palladium, can be deposited spontaneously at the surface of carbon materials from their salt solutions (Dentzer *et al* 1986; Ehrburger *et al* 1987; Dekanski *et al* 1990). Glassy carbon modified by silver deposition has electrocatalytic properties. Such prepared material can be used as an indicator electrode in potentiometric titrations (Dekanski *et al* 2001), as well as in commercial applications with regard to the separation of precious metals from ores (Konova *et al* 2005).

Since previous results refer to either doped or surface modified glassy carbon, in this work, the influence of

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silver and palladium surface modification on the surface properties of doped glassy carbon has been studied. In order to compare doped and undoped samples, undoped surface modified samples were examined, as well. Mass-analysed TPD experiments were performed in order to investigate the nature and thermal stability of 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. Three types of precursor resin samples were prepared: (i) phenol-formaldehyde resin without any additions in order to obtain pure glassy carbon precursor before polymerization, (ii) phenol-formaldehyde resin mixed with boric acid, to obtain 2 wt% of boron in glassy carbon precursor before polymerization and (iii) phenol-formaldehyde resin mixed with phosphorus pentoxide, to obtain 2 wt% of phosphorus in glassy carbon 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}. Prepared undoped, boron doped and phosphorus doped glassy carbon samples were further treated: (i) all three samples were immersed in $AgNO_3$ solution (50 mg dm^{-3}) for 7 days and (ii) all three samples were immersed in $PdCl_2$ solution (50 mg dm^{-3}) for 7 days. Samples were then removed from salt solutions and rinsed in water until a negative reaction to Ag^+ or Pd^{2+} ions was achieved. After metal deposition, the concentration of silver and palladium in solution was measured by atomic absorption spectrophotometer, PYU UNICAM SP9, Philips. The morphology of silver and palladium deposits at the glassy carbon surface was characterized by scanning electron microscopy (SEM JEOL-T20). Further, TPD–MS analyses were performed. In each TPD–MS 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.

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 influence of surface modification on the surface properties of undoped and doped glassy carbon has been studied. In figure 1, the amounts of silver and palladium metal deposits on undoped (GC), boron doped (GCB) and phosphorus doped (GCP) glassy carbon samples are presented.

It can be noticed that the highest amount of metals has been deposited at the surface of GCP sample, while the lowest has been observed at the surface of GC sample. The amounts of deposited silver are always higher than the corresponding amounts of deposited palladium.

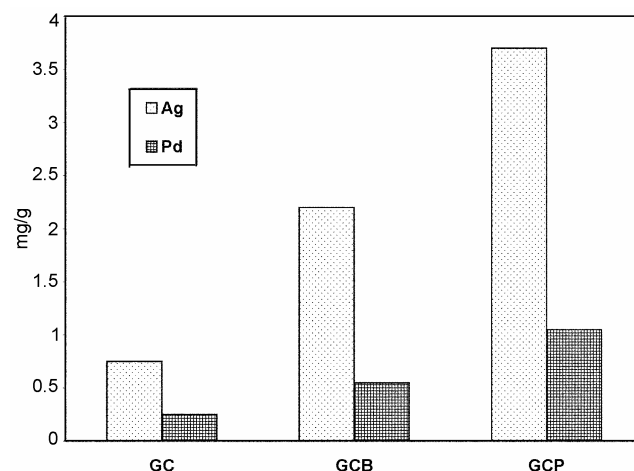The morphology of silver and palladium deposits at the glassy carbon surface was characterized by scanning elec-

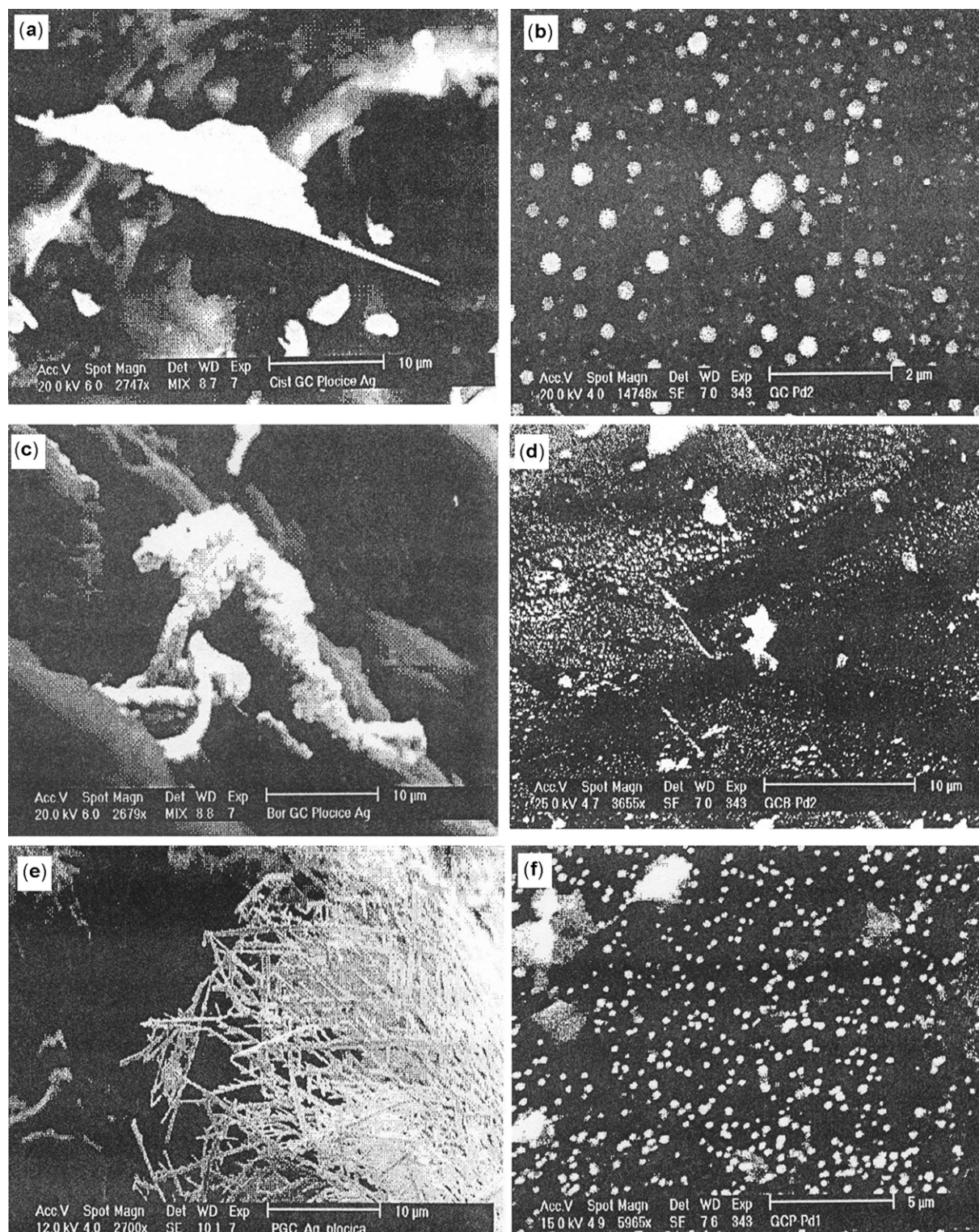**Figure 1.** The amounts of deposited silver and palladium on GC, GCB and GCP samples.

Figure 2. Morphology of metal deposits: (**a**) GC–Ag, (**b**) GC–Pd, (**c**) GCB–Ag, (**d**) GCB–Pd, (**e**) GCP–Ag and (**f**) GCP–Pd.

tron microscopy (SEM). The SEM results (figure 2) have shown that silver on glassy carbon has dendrite structure, whilst palladium forms separate clusters.

In order to follow the influence of surface modification on the surface properties of undoped and doped samples,

the TPD–MS spectra of silver or palladium surface modified GC, GCB and GCP samples were recorded. The most significant products of TPD obtained were CO (m/z 28) and CO_2 (m/z 44). The amounts of desorbed CO and CO_2 from unit mass of each sample were calculated and pre-

sented as a function of desorption temperature. Corresponding values for GC, GCB and GCP samples which were not superficially modified, obtained in our previous work (Ðurkić *et al* 1997; Perić-Grujić 1998), were added in the diagrams, as dotted lines.

3.1 *GC samples*

The amounts of desorbed CO (a) and CO_2 (b) as a function of desorption temperature, for undoped, glassy carbon (GC) samples, before and after surface modification, are presented in figure 3.

Two CO desorption maxima (573 K and 1073 K) in the case of GC sample before surface modification indicate the presence of less stable carbonyl and/or ether and more stable semiquinone groups, respectively (Roman-Martinez *et al* 1993; Zhuang *et al* 1994). After surface modification, the same types of oxide groups are present, but corresponding CO desorption maxima are shifted towards higher temperatures indicating higher thermal stability of these groups. Higher amount of semiquinone groups after surface modification is evident. Two CO_2 desorption maxima (723 K and 923 K) correspond to the decomposition of less stable carboxyl and more stable acid anhydride and/or lactone species, respectively (Zhuang *et al* 1994). After surface modification, corresponding CO_2
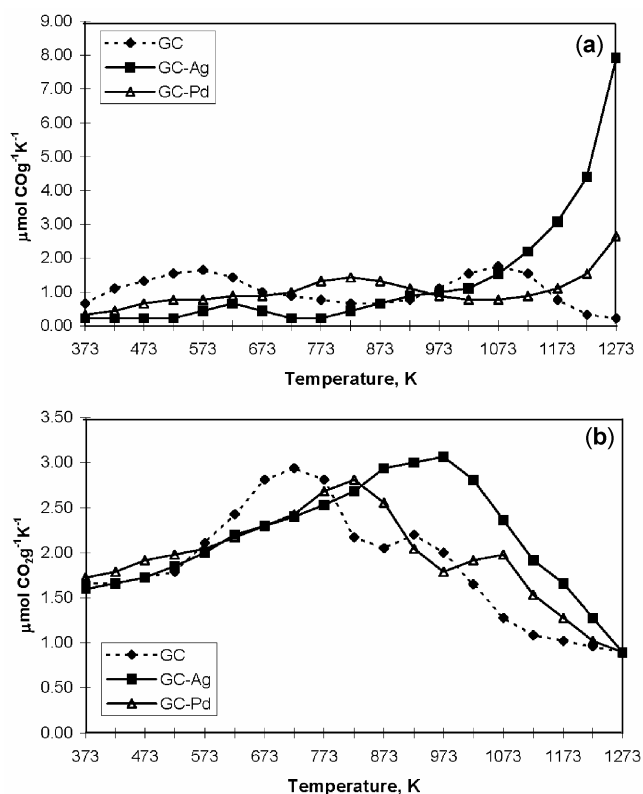
desorption maxima are shifted towards higher temperatures. In the case of silver modified sample, it can be noticed that there is no temperature maximum around 700 K, thus indicating the absence of carboxyl groups. Both silver and palladium modified samples contain higher amounts of acid anhydride and/or lactone groups, than the GC sample before modification.

From the results presented, it can be assumed that surface modification of pure glassy carbon leads to the formation of more stable surface with higher amount of semiquinone, acid anhydride and/or lactone groups. The highest amount of these thermally stable species has been established at the surface of silver modified GC sample. Moreover, the absence of carboxyl groups on silver modified sample indicates that silver deposition leads to the conversion of these groups into more stable surface species and thus, enhanced bonding energy of the surface oxide complexes. The differences between silver and palladium modified samples can be explained by the differences in morphology of metal deposits.

3.2 *GCB samples*

In figure 4, the amounts of desorbed CO (a) and CO_2 (b) as a function of desorption temperature, for GCB samples, before and after surface modification are presented.

Figure 3. The amounts of desorbed (**a**) CO and (**b**) CO_2 as a function of desorption temperature, for GC samples, before and after surface modification.

Figure 4. The amounts of desorbed (**a**) CO and (**b**) CO_2 as a function of desorption temperature, for GCB samples, before and after surface modification.

Before surface modification, at the surface of GCB sample, the presence of carbonyl and/or ether and semiquinone groups result in CO desorption (figure 4a). After surface modification, higher amounts of more stable semiquinone groups have been observed. Carboxyl, acid anhydride and/or lactone groups (figure 4b), which decompose resulting in CO_2 desorption, are present at the surfaces of GCB samples, before and after surface modification. Nevertheless, the amount of these groups is lower and their stability is higher after surface modification.

Our previous results (Đurkić *et al* 1997) have shown that boron, which incorporates into the carbon lattice substitutionally, typically enhances the amount of surface oxide groups. After surface modification, the amount of all oxide species has been typically reduced, except the amount of very stable semiquinone groups. The higher amounts of semiquinone groups could be a consequence of conversion of some less stable groups into more stable semiquinone species during metal reduction. This indicates that groups with lower stability are responsible for silver and palladium reduction and their deposition in metallic form (Baćić-Vukčević *et al* 2006). On the other hand, deposits of silver and palladium at the surface of GCB sample could block reactive carbon sites, thus resulting in reduced number of oxide groups.

3.3 *GCP samples*

The amounts of desorbed CO (a) and CO_2 (b) as a function of desorption temperature, for GCP samples, before and after surface modification are presented in figure 5.
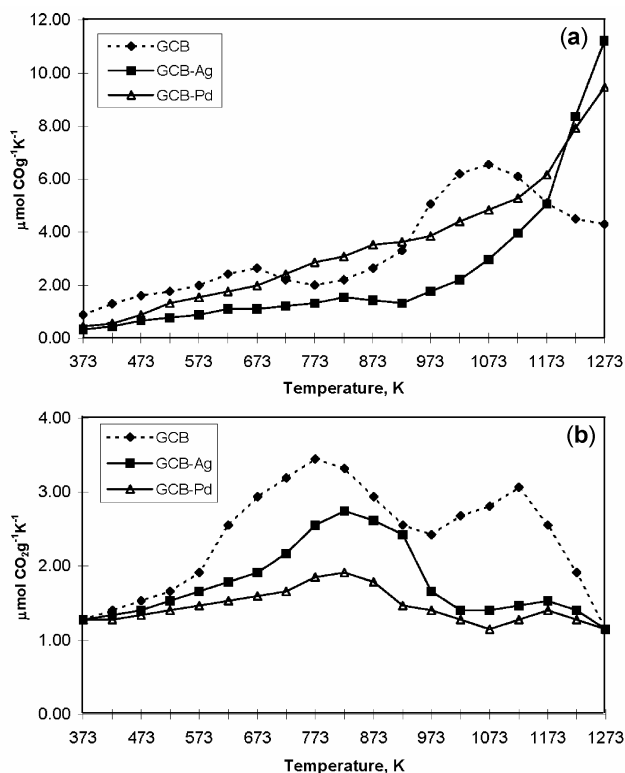
Three CO desorption maxima (figure 5a) at the surface of GCP sample before surface modification indicate the presence of carbonyl and/or ether, acid-anhydride and semiquinone groups, respectively (Roman-Martinez *et al* 1993; Zhuang *et al* 1994). After surface modification, the presence of very stable semiquinone groups is evident. The amount of all groups is lower after surface modification. CO_2 desorption maxima (figure 5b) indicate the presence of acid-anhydride species, before and after surface modification. The amount of these groups is lower and their stability is higher after surface modification. The presence of carboxyl groups has been observed neither before nor after surface modification.

Our previous results (Đurkić *et al* 1997) have shown that the presence of phosphorus in glassy carbon contributes to the typically increased amount of surface oxide groups. An increased quantity of chemisorbed oxygen complexes on GCP surface has been related to the increased disorder of glassy carbon structure caused by the presence of a second phosphorus phase observed by X-ray diffraction (Đurkić *et al* 1997). Calculated amounts of deposited metals have shown that the highest amount of silver and palladium has been deposited at the surface of GCP sample which, actually, contains the highest total

amount of surface oxide groups, compared with GC and GCB samples. After surface modification of GCP sample, the amount of all oxide species has been reduced, while the presence of carboxyl groups has been observed neither before nor after surface modification. It has been noticed that when carboxyl groups are present (GC and GCB samples), the amounts of acid-anhydride and semiquinone groups, on GC sample, and semiquinone groups on GCB sample, increase after surface modification, indicating that carboxyl groups convert into more stable species. In agreement with previous studies (Baćić-Vukčević *et al* 2006), it can be concluded that carboxyl groups are responsible for metal reduction. On the other hand, assuming that the presence of a second phosphorus phase increases disorder of glassy carbon structure, structure defects could be responsible for silver and palladium reduction. Lower quantity of all oxide groups on GCP sample after surface modification could be a consequence of blockage of reactive sites, due to the high amount of metal deposits.

3.4 *Relation between amounts of surface oxide groups and metal deposits*

On the basis of TPD–MS graphs, the amounts of CO- and CO_2-evolving groups, before surface modification, were
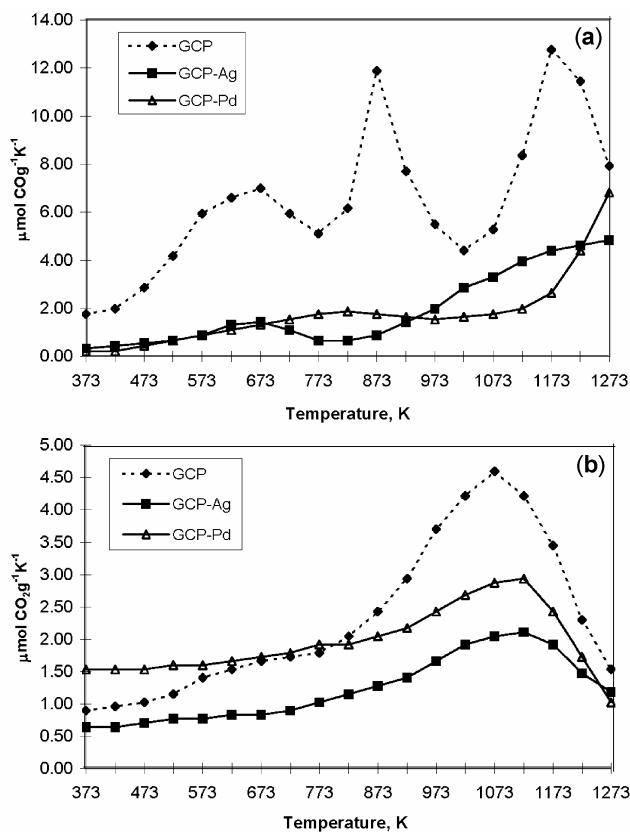

Figure 5. The amounts of desorbed (**a**) CO and (**b**) CO_2 as a function of desorption temperature, for GCP samples, before and after surface modification.

Table 1. Total amounts of CO- and CO_2-evolving groups before surface modification and amounts of metal deposits.

Sample	CO-evolving group (mmolg^{-1})	CO_2-evolving group (mmolg^{-1})	Ag (µmolg^{-1})	Pd (µmolg^{-1})
GC	0·90	1·98	6·95	2·35
GCB	3·96	2·07	20·39	5·17
GCP	13·50	2·52	34·29	9·87

Table 2. Desorption products and corresponding desorption energies for GC, GCB and GCP samples before and after surface modification.

Desorption product	Sample	Desorption energy (kJmol^{-1})		
CO	GC	151		238
	GC–Ag	164		>336
	GC–Pd	217		>336
	GCB	178		>336
	GCB–Ag	/		>336
	GCB–Pd	/		>336
	GCP	178	230	310
	GCP–Ag	178		>336
	GCP–Pd	217		>336
CO_2	GC	191		244
	GC–Ag	/		257
	GC–Pd	217		283
	GCB	204		296
	GCB–Ag	217		310
	GCB–Pd	217		310
	GCP	/		283
	GCP–Ag	/		296
	GCP–Pd	/		296

calculated. In table 1, the amounts of CO- and CO_2-evolving groups and amounts of metal deposits on corresponding samples are presented.

It can be noticed that higher amounts of metals are deposited on sample surfaces with higher content of surface oxide groups. On the other hand, the enhancement of amounts of metal deposits is not proportional to the enhancement of surface oxide group content. This indicates that not only surface oxide complexes are responsible for metal reduction and deposition, but also structure defects, as possible electron donors, could be responsible for silver and palladium reduction.

3.5 *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 samples before and after surface modification, desorption energy, E_d, has been calculated using the peak-position method (Tompkins 1978; Zhou *et al* 1994):

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

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 ν a frequency factor of the chemisorption bond ($\nu = 10^{13}$ s^{-1}). The desorption energies calculated from the position of peak maxima are listed in table 2.

All calculated desorption energies are higher than 100 kJ mol^{-1}, indicating that the chemisorption processes are involved. Desorption energies of corresponding oxide groups are typically higher after surface modification, indicating their higher stability compared with not superficially modified samples. If the difference between the influence of silver and palladium deposition is considered, it can be noticed that palladium deposition leads to the formation of more stable carbonyl and/or ether groups on GC and GCP samples and acid–anhydride groups on GC sample. The other corresponding desorption energy values for silver and palladium modified samples are the same, indicating similar effect of silver and palladium deposition to the surface stability. From the results obtained, it can be concluded that metal deposition leads to the formation of more stable surface of undoped and doped samples.

4. Conclusions

Silver and palladium spontaneously deposit from their salt solutions at the surface of undoped, boron doped and phosphorus doped glassy carbon. The highest amount of both silver and palladium has been deposited at the surface of GCP sample which contains the highest quantity of surface oxide complexes. The lowest amount of metal has been deposited on GC sample which contains the lowest quantity of surface oxide complexes. The amounts of deposited silver are always higher than corresponding amounts of deposited palladium.

The SEM results have shown that silver on glassy carbon has dendrite structure, whilst palladium forms separate clusters.

TPD–MS analyses have shown that surface modification of GC and GCB samples leads to the conversion of less stable carboxyl into more stable species. After surface modification of GCP sample, the surface with lower content of all oxide groups has been obtained. On the basis of

results obtained, it has been concluded that carboxyl groups as well as structure defects, are responsible for metal reduction.

Calculated desorption energies have shown that after surface modification more stable surfaces of undoped, boron doped and phosphorus doped samples have been obtained.

Acknowledgements

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