X-RAY PHOTOELECTRON SPECTROSCOPIC STUDIES OF PALLADIUM DISPERSED ON CARBON SURFACES MODIFIED BY ION BEAMS AND PLASMATIC OXIDATION*

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The effects of ion bombardment and r.f. plasma oxidation of graphite surfaces on subsequent growth and electronic properties of vacuum deposited palladium clusters have been investigated by methods of X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy with X-ray excitation (XAES). Due to the significantly increased density of surface defects on which the nucleation process occurs the bulk value of the Pd 3*d* core level binding energy is achieved at higher surface coverage by palladium on bombarded surfaces than on ordered graphite. Angle resolved photoelectron spectra of oxidized graphite surfaces reveal significant embedding of oxygen in graphite surface layers. The C 1*s* and O 1*s* photoelectron spectra are consistent with presence of two major oxygen species involving ≡C–O and >C=O type linkages which are not homogeneously distributed within the graphite surface layers. Two effects were observed on oxidized surfaces: an increase of palladium dispersion and interaction of the metal clusters with surface oxygen groups. Using the simple interpretation of the modified Auger parameter the relaxation and chemical shift contributions to the measured Pd core level shifts are estimated. In the region of low surface coverage by palladium the effect of palladium–oxygen interaction on Pd core level binding energy exceeds the effects of increased dispersity.

Metals supported on carbon are widely used as catalysts in industrial chemical processes including many organic syntheses. These catalysts exhibit behaviour which is quite different from that of alumina supported catalysts. Various authors have demonstrated that chemical composition of a support can affect the catalytic activity of the supported metal. This work has received little attention until recently when we could see an increased interest in metal–support interactions, stimulated by reports that metals supported on some supports could have unusual properties which were ascribed to metal–support interactions[1].

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The nature of metal–carbon interactions and the influence of carbon surface properties on these interactions are far from being understood. It is frequently assumed[2] that carbon is a typical example of weakly interacting support. The weak metal–support interaction leads to high mobility of metal atoms and small clusters on the carbon surface and formation of a large metal aggregates. It is now widely accepted that surface defects and oxygen-containing functional groups are the most probable nucleation centers on which the metal particles grow[3–5]. In recent studies of carbon supported platinum both dispersion and resistance to sintering were found to be influenced by concentration of surface oxygen-containing groups[6,7]. Significant influence of the nature of the carbon surface and the presence of oxygen functional groups on catalytic properties of other carbon-supported metals were reported in the literature[5,8,9]. For example, preoxidation of the surface of carbon support was found to increase the degree of dispersion of Pd prepared by reduction of Pd acetate and activity of Pd/C catalysts in hydrogenation of olefines[10]. The detailed study of these effects is frequently complicated by the presence of various impurities in ordinary carbons which can have also marked influence on catalytic properties.

There are at least two effects which may be responsible for the observed changes of catalytic properties of metals deposited on physically and chemically modified carbon surfaces: (i) change of the mean particle size and/or morphology which in turn modifies their electronic structure and (ii) modifications of the electronic structure of particles by their interaction with surface defects and functional groups. The question arises whether it is possible to separate these effects and determine which of them has more important role in changing the electronic structure of dispersed metal.

One of the most productive techniques in this area of research is electron spectroscopy. It has been applied with considerable success to practical catalysts[11,12], however, most of the basic understanding of the electronic properties of deposited metal particles has come from studies of well-defined model systems.

In this contribution we present the results obtained by using X-ray photoelectron spectroscopy (XPS) and X-ray excited Auger spectroscopy (XAES) techniques to study Pd clusters supported on ordered graphite, quasi-amorphous carbon produced by an Ar ion beam treatment of graphite and plasmatically oxidized graphite. In addition, the results obtained with Pd deposited on fullerene surface are given for comparison.

EXPERIMENTAL

The experiments were performed in a VG ESCA 3 Mk II electron spectrometer with pressure of residual gases better than 10^{-10} mbar*. Electron spectra were recorded using AlKα radiation as an ex-

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* 1 mbar = 1 . 10^2 Pa.

citation source (11 kV and 20 mA). The hemispherical electron analyzer was operated in the fixed transmission mode with a pass energy of 20 eV, giving the widths of 1.1 eV for the Au $4f_{7/2}$ spectral line. The Fermi level of the spectrometer was used as an energy reference. Unless stated otherwise the angle of photoelectron detection with respect to sample surface normal was 45°. Spectra of C 1*s* and Pd 3*d* photoelectrons and Pd $M_{45}N_{45}N_{45}$ Auger electrons were measured at room temperature. Core level binding energies (E_B) and peak widths (W) were determined with an accuracy of ±0.1 eV.

The carbon substrates were graphite foils with flat surface (Goodfellow Metals Ltd., 99.9% pure), graphite samples the surface of which was modified either by sputtering with argon ions (energy 4 – 5 keV, dose 150 – 300 μA min) or by r.f. oxygen plasma ($f \approx 40$ kHz, $p(O_2) \approx 10^{-1}$mbar). Graphite samples were placed in vacuum immediately after cleavage to ensure the surface cleanliness[4]. Fullerene substrates were prepared by vacuum deposition of the C_{60} (containing about 7% of C_{70}) layers the thickness of which was ≥10 nm onto gold substrate cleaned by Ar ion sputtering. Controlled amounts of palladium were deposited on the substrates using a doser, consisting of a resistively heated tungsten filament wrapped with high purity (Goodfellow Metal Ltd.) Pd wire of 0.2 mm diameter. The substrates were placed in a position such that macroscopically uniform coverage of the metal deposition could be obtained. The samples were transferred into analyzer chamber of the spectrometer under ultrahigh vacuum.

The amount of deposited palladium was estimated from the measured integral intensities of the metal and support photoemission peaks using the methods described in our previous publication[13] and the values of electron inelastic mean free paths recommended by Tanuma[14]. Using these values we obtained that the density of palladium atoms in a complete monolayer amounts $1.67 \cdot 10^{15}$ atoms/cm^2 which is close to the density of atoms on the most densely packed (111) plane of the bulk Pd crystal ($1.53 \cdot 10^{15}$ atoms/cm^2).

RESULTS AND DISCUSSION

Characterization of Carbon Substrates

Prior to deposition of palladium the surfaces were characterized by the XPS method. In Fig. 1 the C 1*s* core level spectra of the substrates used throughout this work are shown. The C 1*s* spectra of unmodified graphite surface show satellite ≈6 eV apart from the parent C 1*s* line (E_B = 284.4 eV, W = 1.25 eV), characteristic of the well ordered graphite structure[15]. The satellite almost disappears after argon ion sputtering. Besides, the C 1*s* line shifts by 0.2 eV towards higher binding energies and considerably broadens (W = 2.1 eV). The values obtained are characteristic of quasi-amorphous carbon[16,17]. These results agree with the well known fact that ion sputtering produces significant amount of surface defects, destroying thus the ordered graphite structure[18]. Rather intensive satellites are observed in the C 1*s* spectra of fullerene.

Plasmatic oxidation leads to rather small shift and broadening of the graphite C 1*s* line (E_B = 284.45 eV, W = 1.55 eV). This result is in agreement with assumption that the graphite surface is predominantly chemically modified, i.e. that r.f. plasmatic oxidation does not create significant concentration of surface defects of the type produced by argon ions. The surface concentration of oxygen, estimated from the ratio of intensities of O 1*s* and C 1*s* lines was only weakly dependent on whether the sample was oxidized 1 or 5 min and amounted 1.8 . 10^{15} and 2.2 10^{15} atoms/cm^2, respectively. In Fig. 2 the curve fit to C 1*s* difference spectrum obtained after subtracting graphite C 1*s* spectrum from the spectrum of oxidized surface is shown. The binding energies of the two peaks obtained by fitting the spectrum (286.6 and 288.2 eV) as well as binding energies of the O 1*s* components obtained by curve fitting the spectrum (vide infra) indicate presence of the two different oxygen containing groups on the surface most likely[16,19] with ≡C–O and >C=O type linkages, respectively. Rather large surface concentration of oxygen suggests that it may be present not only on the graphite surface but also incorporated within the superficial layers. In order to obtain some information on the depth distribution of oxygen in oxidized graphite we have measured O 1*s* and C 1*s* spectra at several different take-off angles. Figure 3 shows the obtained dependence of the O 1*s*/C 1*s* intensity ratio on the collection angle. Using the regularization method[20] we have attempted to extract from the angle dependent intensity ratios an information on the concentration depth profile of oxygen. The resulting profile, shown in Fig. 4 is consistent with incorporation of oxygen into graphite. However, it should be noted that because of several reasons, including the neglect of the influence of sample surface roughness and elastic scattering of photoelectrons it is usually difficult to assess the accuracy of the concentration profiles obtained from angle dependent XPS intensities.

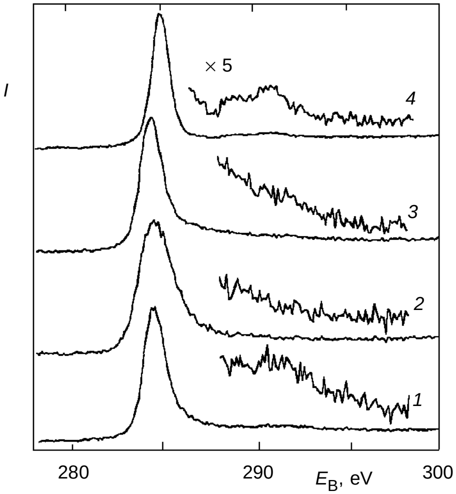

FIG. 1
C 1*s* core level spectra of: *1* graphite, *2* graphite sputtered by Ar ions, *3* graphite oxidized by r.f. plasma for 5 min, and *4* fullerene

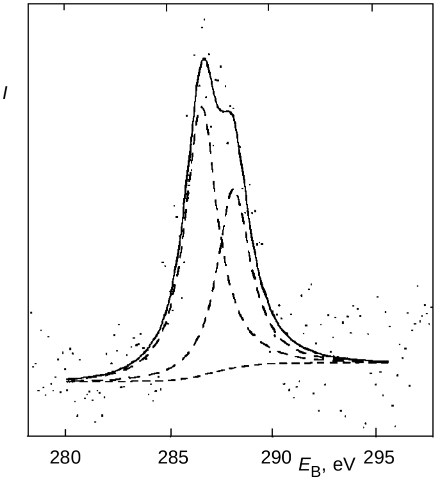

FIG. 2
Fitted C 1*s* difference spectrum obtained by subtracting clean graphite spectrum from that of 5 min oxidized graphite

Effects of the Nature of the Support Surface on Pd Dispersion and Its Electronic Properties

In the region of the surface coverage 0.02 – 1 monolayer (ML) the Pd core level binding energies (and linewidths) decrease with increasing coverage (Fig. 5). By extrapolating this dependence to higher coverage we find that the bulk value of the Pd 3*d* core level binding energy is achieved at a lower surface coverage (≈ 3 ML) on ordered graphite than on an amorphous surface (≈ 6 ML). This difference can be explained by the increased density of surface defects on disordered carbon surfaces which serve as nucleation centers and consequently Pd metal remains highly dispersed at comparatively high surface coverage[21].

The core level binding energies of small Pd particles present on the surface differ from the bulk metal value (Table I). In spite of a large number of studies devoted to the investigation of Pd clusters deposited on carbon surfaces the interpretation of the observed E_B shifts is still controversial (see review article by Mason[22]). Some authors prefer explanation in terms of a changed electronic structure due to the size effects and/or due to interaction with the substrate while others emphasize the role of the final state effects, related to photoemission process.

In our previous paper[13] on this subject we have attempted to estimate contributions of initial state charge distribution, ΔE_c, and of extraatomic relaxation energy change,

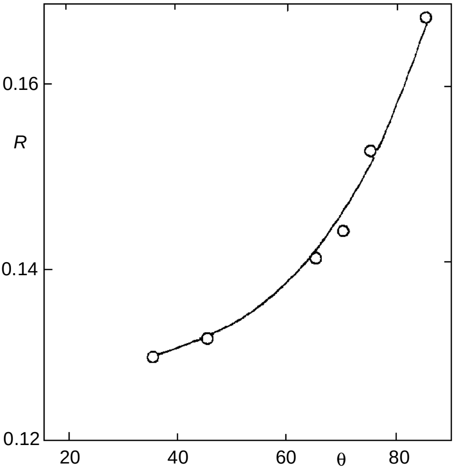

FIG. 3
The dependence of the photoemission line intensity ratio $R = I(\text{O } 1s)/I(\text{C}1s)$ on the photoelectron detection angle, θ (deg), for a graphite sample plasmatically oxidized for 5 min

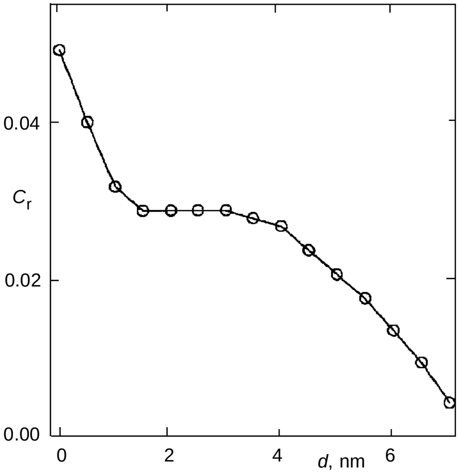

FIG. 4
Depth–concentration profile of oxygen obtained from the angle-resolved XPS intensities shown in Fig. 3. C_r is relative concentration of oxygen (volume fraction)

ΔR_e, to the measured core level binding energy shifts using the simple interpretation of the modified Auger parameter, α, defined as:

$$\alpha = E_B(3d_{5/2} + E_K(M_5N_{45}N_{45}) \qquad (1)$$

$$\Delta\alpha = 2\ \Delta R_e \qquad (2)$$

$$\Delta E_B = \Delta E_c - \Delta R_e\ , \qquad (3)$$

where E_K is the kinetic energy of Auger electrons, $\Delta\alpha$ the difference of Auger parameter between bulk and dispersed metal and ΔE_B the change of core level binding energy. The calculated chemical shift, ΔE_c, for the low coverage of Pd on amorphous carbon was consistent with Pd → C charge transfer the magnitude of which corresponded to the fractional charge on Pd atoms $q = 0.15$. Figure 6 shows that the work function of amorphous carbon (determined from the shifts of the XP spectra cut-off) decreases in the region of submonolayer Pd surface concentrations with increasing surface coverage. This result may again be explained by the presence of positive charge on Pd atoms, provided that they are located on the carbon surface (i.e. not embedded in or

TABLE I

Core level binding energies E_B, kinetic energies of Auger electrons E_K, full width at half maxima of the $3d_{5/2}$ spectra (W), Auger parameters (α), changes of extaatomic relaxation energy (ΔR_e) and chemical shifts (ΔE_c) of Pd deposited on different substarates at surface coverage of 0.05 monolayer (all data are in eV)

Quantity	Pd (bulk)	Ordered graphite	Amorphous carbon	Oxidized graphite[a]	Fullerene	Pd (ox)[b]
E_B ($3d_{5/2}$)	335.1	335.5	336.0	336.6	336.7	336.7
W ($3d_{5/2}$)	1.6	1.9	2.2	3.1	1.4	–
E_K (M_5NN)	327.7	327.0	325.6	325.2	326.1	326.5
α	662.8	662.5	661.6	661.8	662.8	663.2
ΔR_e	0	–0.15	–0.6	–0.5	≈0	0.2
ΔE_c	0	0.25	0.3	1.0	1.6	1.8
X[c]	0.88 ± 0.1	1.72	1.47	1.63	1.6	–

[a] Graphite plasmatically oxidized at room temperature for 5 min; [b] Pd deposited on amorphous carbon (Pd coverage 0.5 ML) and oxidized at 250 °C; [c] X is the ratio of intensity of Auger to core level line, $X = I(M_5NN)/I(3d_{5/2})$.

below the surface carbon atoms) and thus supports our previous interpretation of the observed positive core level shifts.

Two effects may take place when Pd is deposited on carbon surfaces oxidized by r.f. oxygen plasma: an increase of the Pd dispersion due to creation of additional nucleation sites and interaction of metal atoms and/or clusters with the surface oxygen groups. Both effects result in an increased metal core level binding energies. In Table I the Pd $3d_{5/2}$ core level binding energies, peak widths, M_5NN Auger kinetic energies, Auger parameters and the calculated relaxation and chemical shifts are listed for low coverage (≈0.05 ML) of Pd on the studied substrates. At this low coverage most of the Pd atoms should be either atomically dispersed or present in clusters containing rather low number of atoms. It is instructive to compare the core level binding energies and calculated relaxation and chemical shifts obtained for Pd on oxidized graphite with those for Pd dispersed on fullerene surface and with values obtained for oxidized Pd. While the binding energies are within the experimental error identical with these three systems and their dependence on surface coverage coincides in the case of Pd/fullerene and Pd/oxidized graphite (Fig. 5) the relaxation shifts clearly differ. Because of rather high electron affinity of fullerene we would expect its interaction with Pd to be accompanied by the decrease of electron density on Pd atoms[23]. In agreement with this hypothesis the data for Pd/fullerene are very similar to those for oxidized Pd/C (see Table I). It

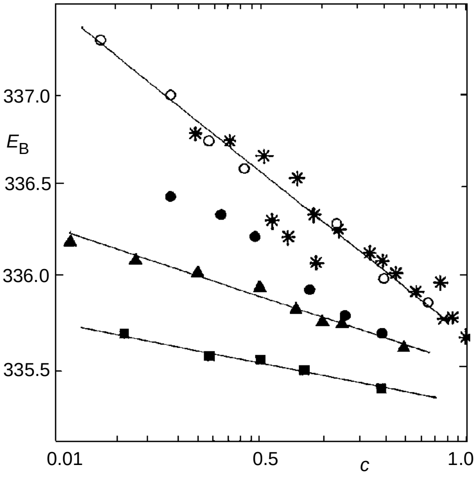

FIG. 5

Dependence of the Pd $3d_{5/2}$ binding energy E_B (eV) on the amount of palladium, *c* (effective monolayers), deposited on the surface of: ■ graphite, ▲ amorphous carbon, ● graphite oxidized for 1 min, ❍ graphite oxidized for 5 min, * fullerene

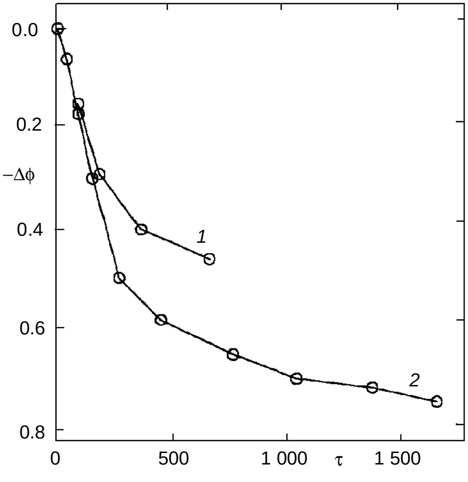

FIG. 6

Dependence of the work function change, Δϕ (eV), of the two different samples of amorphous carbon on the time, τ (s), of palladium deposition. *1* Sample 1, *2* sample 2 follows from the comparison of the chemical and relaxation shifts given in Table I that not only the higher metal dispersion but also the interaction with oxygen functionalities participates considerably to the increased core level binding energy of Pd on an oxidized graphite. (Similar values of relaxation shifts indicate that dispersion is probably comparable for Pd/amorphous C and Pd/oxidized C.)

The difference in Pd $3d_{5/2}$ binding energy observed for 0.05 ML of Pd on surface oxidized 1 and 5 min (0.7 eV) is higher than one would expect on the basis of oxygen surface concentrations which are practically the same. The composite O 1*s* peak (Fig. 7) consists of at least of two oxygen signals corresponding to singly bound (531.9 eV) and double bound (533.1 eV) oxygen, respectively. Note that this assignment is in accord with the interpretation of C 1*s* difference spectra (Fig. 2) of the oxidized substrate (vide supra). The dependence of the relative peak intensities on the measuring angle (Fig. 7) suggests that the higher binding energy state of oxygen is more abundant at the surface. The above mentioned difference of the Pd $3d_{5/2}$ core level binding energy between samples oxidized 1 min and 5 min might thus be accounted for by (i) differences in populations of chemically nonequivalent oxygen functionalities, (ii) creation of some other surface defects the concentration of which increases with time of oxidation. High surface heterogeneity of the substrate oxidized for 5 min is also apparent from the large width of the $3\ d_{5/2}$ line of the Pd deposited (Table I). Oxidation of graphite thus affects electronic structure of supported metal by both, a change of nucleation process and a modification of metal–support interaction leading to the decreased electron density on Pd. The role of palladium interaction with surface oxygen groups increases with decreasing metal cluster size. It should be noted at this place that the interpretation of the change of Auger parameter used in this work is based on some approximations which

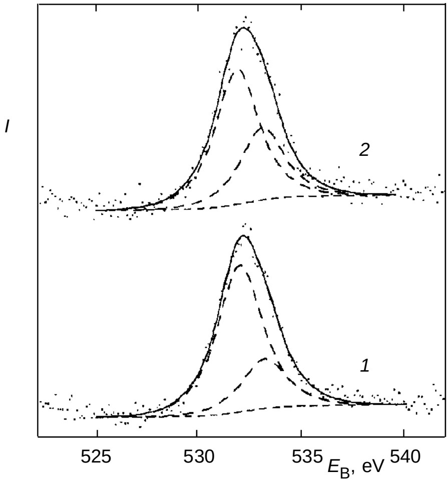

FIG. 7
O 1*s* core level spectra of graphite oxidized 5 min measured at collection angle: *1* 35°, *2* 65°

include neglect of contributions due to the higher order terms[24]. However, it is usually assumed that these contributions are small except when comparison is made between atoms in very dissimilar environments[25].

Due to the substantially lower kinetic energy of Pd MNN Auger electrons their inelastic mean free paths[14] and consequently the sampling depth are nearly two times lower than that of Pd 3*d* electrons. The ratio of intensity of Auger $M_{45}N_{45}N_{45}$ line to intensity of photoelectron 3*d* peak, *X*, (see Table I) is thus a measure of the change of the metal concentration in the direction perpendicular to sample surface. The greater value of this ratio found in the case of Pd/quasi-amorphous carbon indicates that the surface damage produced by ion sputtering facilitates diffusion of palladium atoms into deeper layers of the quasi-amorphous carbon substrate.

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