

# XPS study of carbon species at the surface of platinum single crystal planes

R.I. Kvon\*, S.V. Koscheev, A.I. Boronin

*Borskov Institute of Catalysis, SBRAS, Novosibirsk 630090, Russia*

## Abstract

Carbonaceous deposits obtained by ethylene decomposition on the surface of (111), (110) and (100) planes of Pt were studied by X-ray photoelectron spectroscopy (XPS) in the wide temperature range of 570–1470 K. Three different carbon states were found depending on the temperature and Pt plane chosen. At  $T < 770$  K, adsorbed state of carbon is formed at all three planes studied. Higher adsorption temperature results in graphite formation at Pt(111) and diamond-like carbon at two other planes. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Graphite; Diamond; Platinum; XPS; AES

## 1. Introduction

The significant interest to carbon transformations at metal surfaces has been stimulated recently by the prominent advances in the synthesis of the various types of carbon materials (carbon filaments, diamond-like films, fullerenes, etc.). X-ray photoelectron spectroscopy (XPS) has proved then to be rather a powerful and convenient tool both for the identification of the produced carbon species and for the characterisation of carbon–metal interface [1–4]. The extended investigation of carbon states at platinum surface is still necessary. The aggregation of carbon particles is especially interesting, as this process is believed to play an important role in the coke formation at sup-

ported Pt catalysts. Therefore, understanding of the mechanisms of carbon transformations at platinum surface would help to optimise both catalytic and regeneration processes. This work presents a systematic XPS study of elementary carbon species at the surface of Pt single crystal. To explore the effect of electronic and geometric structure on the formation of carbon deposits, all three main planes — (111), (110), and (100) — have been studied. The particular interest was related with the reconstruction properties of (110) and (100) planes.

## 2. Experimental

The experiments were carried out in the electron spectrometer VG ESCALAB HP using  $\text{MgK}_\alpha$  and  $\text{AlK}_\alpha$  excitation. The spectrometer was calibrated against  $\text{Au}4f_{7/2}$  and  $\text{Cu}2p_{3/2}$  lines (84.0 and 932.7 eV, respectively). The

\* Corresponding author. Fax: +7-3832-343056.  
E-mail address: kvonr@catalysis.nsk.su (R.I. Kvon).

binding energy value for Pt4f<sub>7/2</sub> peak ( $E_b = 71.1$  eV) was chosen as the internal standard. To form the saturation carbon layer, Pt single crystal had been exposed to the permanent flow of ethylene at  $P = 2 \times 10^{-7}$  mbar. XPS spectra were acquired in situ in the temperature range of 570–1470 K.

### 3. Results and discussion

One can distinguish three regions in Fig. 1, where the values of  $E_b$  (C1s) peak vs. ethylene adsorption temperature are plotted. At lower temperature ( $T < 770$  K), carbon state is the same for all three Pt planes studied. With the elevation of sample temperature, C1s binding energy rises, indicating carbon adlayer to transform drastically. However, the magnitude of BE shift for each plane strongly differs from the other ones. At last, at  $T > 1170$  K the binding energy sets in the new level, again different for each crystal plane. Fig. 2 presents the saturation coverage by carbon ( $\theta_C$ ) plotted against sample temperature. With carbon coverage being close

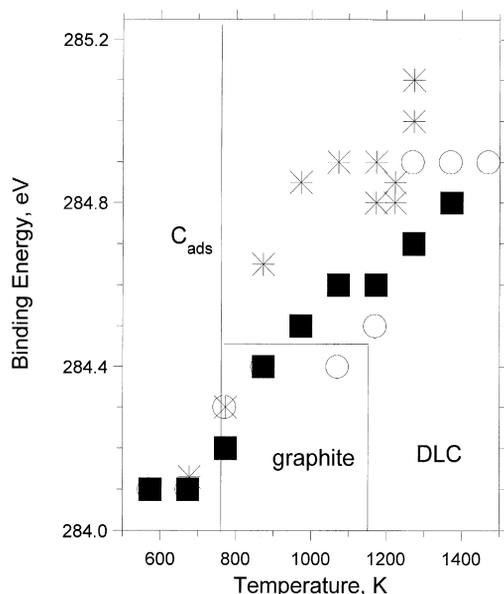


Fig. 1. The dependence of  $E_b$  (C1s) on adsorption temperature for carbon layer formed in the flow of ethylene at:  $\circ$  — Pt(111),  $\blacksquare$  — Pt(110),  $*$  — Pt(100).

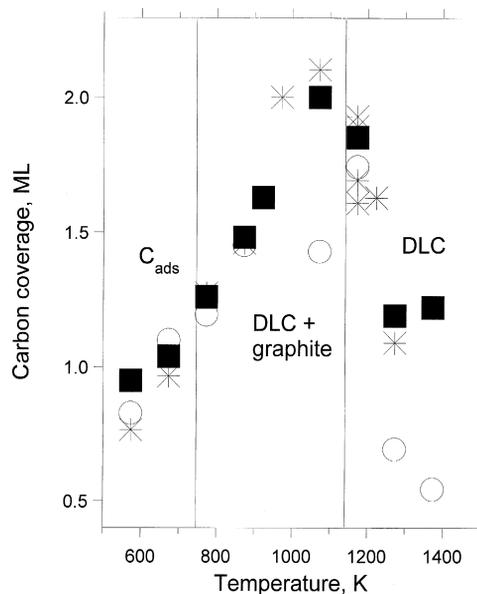


Fig. 2. The dependence of  $\theta_C$  on adsorption temperature for carbon layer formed in the flow of ethylene at:  $\circ$  — Pt(111),  $\blacksquare$  — Pt(110),  $*$  — Pt(100).

to 1 ML at  $T < 770$  K,  $\theta_C$  increases with temperature rise and drops to former level at  $T > 1170$  K.

The comparative analysis of  $E_b$ (C1s) and  $\theta_C$  plots shows that a low temperature carbon state ( $T < 770$  K) is the same for all single crystal planes studied. This carbon state is exactly chemisorbed one. The detailed identification of such species, based on the spectroscopic analysis of C1s and C-KLL lines and the data on its thermal stability, reactivity towards hydrogen and oxygen, and kinetics of the deposition, was reported for Pt(110) earlier [5–8]. At elevated temperatures ( $770 \text{ K} < T < 1170 \text{ K}$ ) the denser packed carbon adsorbed layer is formed. However, both C1s binding energy and carbon coverage values are different for each plane. To determine the nature of carbonaceous deposits obtained, the precise comparison of C1s and C-KLL spectra with the ones for highly oriented pyro-graphite (HOPG) and ultra dispersed diamond samples has been performed (see Fig. 3 and Fig. 4, respectively). One could see the aggregation of carbon atoms on the surface of

Pt(111) results in the graphite structure formation, which is proved by “carbon rings” in LEED [9]. On the contrary, neither LEED nor STM pictures [5,6] reveal graphite structures to form at Pt(110) and Pt(100). The comparison of C1s (Fig. 3) and C-KLL (Fig. 4) spectra for these adsorbed layers to those ones for diamond materials demonstrates their strong similarity. Indeed, the estimation of the so-called  $D$  parameter (i.e., difference between maximum and minimum in derivative C-KLL peak [4]) gives  $D = 13.4$  eV for diamond sample and  $D = 22.7$  eV for HOPG (compare with 13.5–14.5 and 22.8 eV, respectively, in Ref. [4]). For carbon adsorbed layer at Pt(111), this value is 23.9 eV and for C/Pt(110), it is 11.7 eV. Thus, the formation of diamond-like species (DLC) at the reconstructing planes of Pt could be reliably concluded.

One could see that the thermal stability of carbon deposits at Pt(111) is substantially lower than at the other studied Pt planes (see Figs. 1 and 2). Diamond-like carbon at Pt(110) is stable at least up to 1670 K, whereas carbon coverage on Pt(111) drops at  $T > 1170$  K. At the same time C1s binding energy value of  $E_b$  (C1s) rises

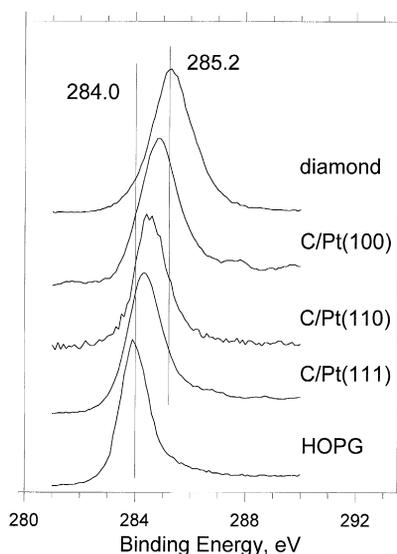


Fig. 3. Comparison of C1s spectra of carbonaceous deposits produced at 1070 K with reference samples of HOPG and diamond.

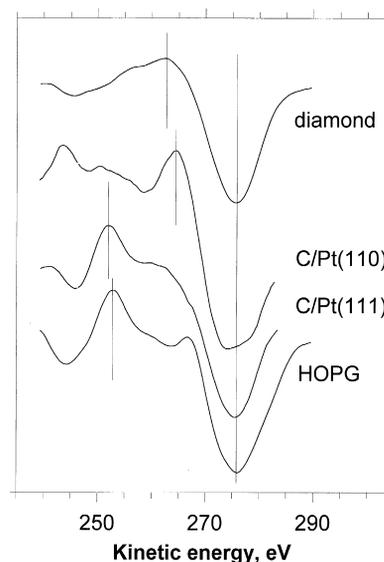


Fig. 4. Comparison of C-KLL spectra of carbonaceous deposits produced at 1070 K with reference samples of HOPG and diamond. Dashed patches of the curve correspond to region where Pt Auger line interferes. Short vertical lines mark maxima of C-KLL peaks.

up to 284.9 eV, indicating that transition to another carbon state at the surface of Pt(111) (most likely, DLC) occurs. Still, additional investigations are necessary to identify this carbon state exactly.

#### 4. Conclusions

Systematic XPS study of ethylene decomposition at Pt(111), Pt(110), and Pt(100) reveals the strong effect of the surface structure on the nature of carbonaceous deposits formed. Either graphite or diamond-like carbon was observed, depending on the temperature and the plane of platinum examined. Both structural mismatching and easiness of reconstruction are responsible for DLC rather than graphite formation at (110) and (100) planes.

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