

# XPS Study of Carbon Films on the Pt(111) Surface Obtained by High Temperature Decomposition of Methane and Ethylene

E. M. PAZHETNOV and A. I. BORONIN

*Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,  
Pr. Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)*

*E-mail: gosha@catalysis.nsk.su; boronin@catalysis.nsk.su*

## Abstract

The carbon films grown on Pt(111) surface by the high temperature catalytic decomposition of methane and ethylene were investigated with aid of X-ray photoelectron spectroscopy (XPS). It was observed that photoelectron spectra of carbon films depend on the hydrocarbon used as a reagent. It was shown that in case of methane used as the reagent the flat graphite films are deposited on the Pt(111) surface while ethylene or ethylene/methane mixture stimulates the carbon films distortion resulting in curved fullerites/like structures. The formation of curved carbon films occurs through the formation of flat graphenes as the intermediate structures. It was determined that this topographic transition is reversible and has dynamic character depending on the crystal temperature and ethylene presence in the gas phase. The role of the diffusion-segregation phenomenon of carbon atoms in the formation of the curved films was established.

## INTRODUCTION

The investigation of electronic and geometric structures of carbon materials and films is one of the important parts in carbon chemistry, which is developing very rapidly now. The structure and properties of carbon films on the surface of metals are of great importance to gain a better understanding of catalysts deactivation processes and the mechanisms of carbon materials growth [1]. Application of platinum single crystals for the carbon films investigation is defensible due to the fact that platinum as a catalyst is very perspective for the formation of pure carbon materials such as filaments, single-wall and multiwall nanotubes, *etc.*, which possess different electronic properties. As it is well known, the combination of the geometry and the conductivity properties can lead to construction of the materials that will be used as electron emitters [2].

Recently [3] it was reported that depending on the conditions of high temperature treatment of platinum surface (111) in the flow of ethylene the carbon films are characterized by different features of C1s photoelectron spectra. It was proposed that this phenomenon is connected with the film geometry properties. In paper [3] it was proposed that flat graphene structures under certain conditions can bend and form the hill-like or fullerite-like structures. In the paper [4] this idea was evidenced by means of scanning tunnel microscopy (STM). The revealed phenomenon of the graphenes bending on smoothed closely packed Pt(111) surface was very important to understand what mechanisms are in charge of the formation of nanotubes or carbon filaments in hydrocarbon catalysis.

Thus, in this paper we carry out further investigations of the C/Pt(111) system by means of X-ray photoelectron spectroscopy (XPS). For carbon film deposition, we use the reaction of pure methane or methane/ethylene gas mixture

at high temperature under the conditions of catalytic hydrocarbon cracking.

## EXPERIMENTAL

All experiments were performed using VG ESCALAB HP spectrometer equipped with aluminum anode for Alka X-ray emission ( $h\nu = 1486.6$  eV). XP spectra were recorded in the regime of retarding voltage at the constant analyzer pass energy (HV). For recording the survey spectra, the HV value was equal to 50 eV while for recording the separated regions, a high-resolution regime with HV = 20 eV was used. Before measurements, the spectrometer was calibrated using the  $Au4f_{7/2}$  binding energy (BE) of 84.00 eV and the  $Cu2p_{3/2}$  BE of 932.7 eV taken as referenced values for clean gold and copper foils [5].

The sample was cut from Pt monocrystal as a disk with diameter  $\varnothing = 9$  mm and thickness 1 mm. The misorientation of the disk surface from (111) plane was not more than  $1^\circ$ . The disk was spot welded to the holder through the tungsten wires, which served as the heaters. The main residual gases in the chambers of the spectrometer were CO, CO<sub>2</sub>, H<sub>2</sub>O on the level less than  $10^{-9}$  mbar. The surface cleanliness was obtained by ion etching in the preparation chamber. After this procedure the surface ordering was performed by the crystal annealing during 20 min at 1100 °C.

Quantitative analysis was performed using the integrated intensities of the XPS peaks corrected by the atomic sensitivity factors of the corresponding elements [5]. For estimation of carbon coverage, the surface concentration unit  $\Theta = 1.5 \times 10^{15}$  at./cm<sup>2</sup> was taken as one monolayer (ML). The XPS analysis can be performed in hydrocarbon atmosphere with  $P < 10^{-6}$  mbar at the crystal temperature up to 1100 °C in the regime *in situ*.

## RESULTS AND DISCUSSION

In Fig. 1, the spectra of carbon films formed on the surface Pt(111) as a result of catalytic cracking of ethylene or methane are shown for comparison. The procedure of hydrocarbon cracking consisted of two main steps as follows:

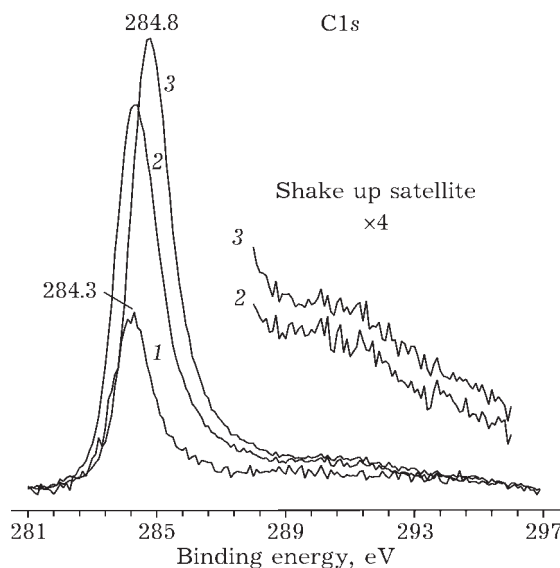


Fig. 1. C1s spectra of the carbon films formed as a result of catalytic decomposition of methane and ethylene (for all the details, see in the experimental part): 1 – the spectrum of the film after Pt(111) exposure in the flow of methane (pressure  $P(\text{CH}_4) = 10^{-2}$  mbar, treatment time, 30 min, carbon coverage  $\theta = 2.1$ ); 2 – the spectrum of the film after Pt(111) exposure in the flow of methane (pressure  $P(\text{CH}_4) = 10$  mbar, treatment time, 30 min, carbon coverage  $\theta = 3.9$ ); 3 – the spectrum of the film after Pt(111) exposure in the flow of ethylene (pressure  $P(\text{C}_2\text{H}_4) = 10^{-5}$  mbar, treatment time, 30 min, carbon coverage  $\theta = 4.2$ ). The value  $\Theta = 1$  is attributed to the surface concentration of carbon atoms to be equal to  $1.5 \times 10^{15}$  at./cm<sup>2</sup>, which corresponds to 1 ML of platinum atoms on the Pt(111) surface.

– The step of Pt(111) bulk saturation with carbon. On this step, the sample was treated in the flow of the gas (ethylene or methane or their mixture) at temperature 1100 °C for a long time. At this temperature methane and ethylene decompose completely giving carbon atoms which diffuse into the bulk of the sample.

– The step of immediate formation of carbon films. On this step, the monocrystal was cooled quickly at a rate of  $\sim 20$  °C/s in the hydrocarbon flow at the same pressure. The sample was cooled to  $T = 600$  °C, then there was evacuation of the gas from the chamber, and the photoelectron spectra were taken. As it was determined earlier [3, 4], in the process of sample cooling the segregation of carbon atoms from platinum bulk to the surface takes place.

Thus, the films obtained by this double-step procedure were composed of both the carbon atoms segregated to the surface and carbon residues (C or C–C fragments) due to hydrocarbon cracking.

As it can be seen from comparison of the C1s spectra presented in Fig. 1, the carbon films obtained by ethylene cracking are characterized by  $E_b(\text{C1s}) = 284.7$  eV while the films obtained when methane was used as the reagent are shifted to lower BE on 0.4–0.5 eV. The line intensity after methane interaction is much lower than after ethylene interaction at the same exposure. In order to form the same carbon coverage on the surface, the pressure of methane was increased to  $P = 10$  mbar that is six orders of magnitude more than in case of ethylene. In spite of the fact that we obtained practically the same coverage (spectra 2 and 3), the line position in C1s spectra taken for films originated from methane and ethylene treatments differ significantly. At the same time, the C1s line positions for both films obtained from methane (spectra 1 and 2) coincide in spite of the difference in coverage. Thus, the effect of hydrocarbon nature (methane or ethylene) plays an important role in specificity of deposited carbon films.

The presence of a broad line in all the spectra in the region 290–292 eV (shake up satellite) points to carbon structure having extensive  $\pi$ -bonds, *i.e.* carbon atoms are in  $sp^2$  hybridization state. In all cases the presence of shake-up feature gives a good evidence that any films on the Pt(111) surface consist of carbon atoms in the same  $sp^2$  hybridization.

According to conclusions made in works [3, 4], the differences in the C1s line position in the films 2 and 3 (see Fig. 1) are connected with the specificity of their morphology. The C1s line position in films 1 and 2 coincide with one from HOPG, so they should be attributed to flat graphite-like films. In the case of film 3, the shift of the maximum of C1s to the position 284.7 eV is related to hill-like or fullerite-like species (“full of bubbles” carbon film) in accordance with [3, 4].

The experiments with the gas mixtures were undertaken to clarify peculiarities in the film growth and to consider the reason for their bending under certain conditions. We vary the composition of reagents in the course of the experiments to find the conditions of the appearance of curved carbon films and their disappearance as well.

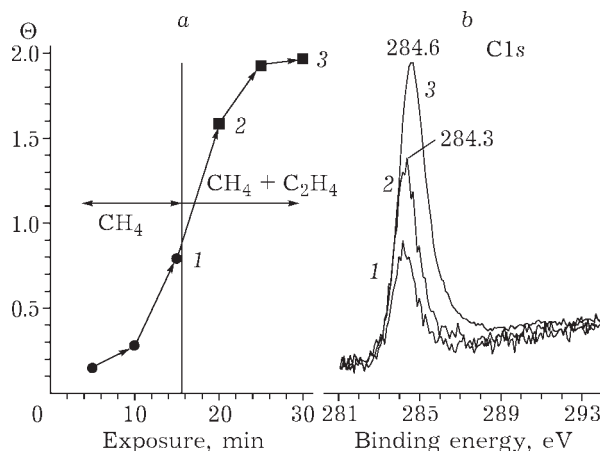


Fig. 2. The kinetics of the carbon film growth on the Pt(111) surface (a), and carbon electronic state of carbon (C1s spectra) (b). The initial step of the film growth occurs in the flow of methane ( $P(\text{CH}_4) = 5 \times 10^{-7}$  mbar); the second step occurs in the flow of gas mixture (partial pressures of ethylene and methane  $P(\text{CH}_4) = P(\text{C}_2\text{H}_4) = 5 \times 10^{-7}$  mbar). C1s spectra taken at the points marked in (a) are shown in (b).

In Fig. 2, the coverage of carbon layers (a) and C1s spectra (b) depending on hydrocarbon exposure at 1100 °C are presented. The initial step of the carbon film growth is bound with the interaction of methane at  $P = 5 \times 10^{-7}$  mbar during 15 min with subsequent cooling to 600 °C (two-step standard procedure). This treatment with methane results in submonolayer coverage characterized by  $E_b(\text{C1s}) = 284.3$  eV that is related to graphite-like structures. After the admission of ethylene to gas phase during 15 min the sharp increase in carbon coverage occurs (see Fig. 2, a). Also, the C1s line shifts to higher BE indicating the topographic transition of carbon adsorbed layer from flat graphitic structure to the curved one. These experiments give direct evidence of important participation of ethylene residues, most likely C–C fragments, which play a crucial role for graphite sheets bending.

The next step was connected with the investigation of the reversibility of the topographic transition in the carbon films, *i.e.* flat graphene sheets – curved carbon sheets. These results are presented in Fig. 3. They should be discussed together with the data presented in Fig. 2. In Fig. 3, the C1s spectra recorded from the carbon films formed by standard procedure are shown. In this case, ethylene was evacuated from the gas phase and

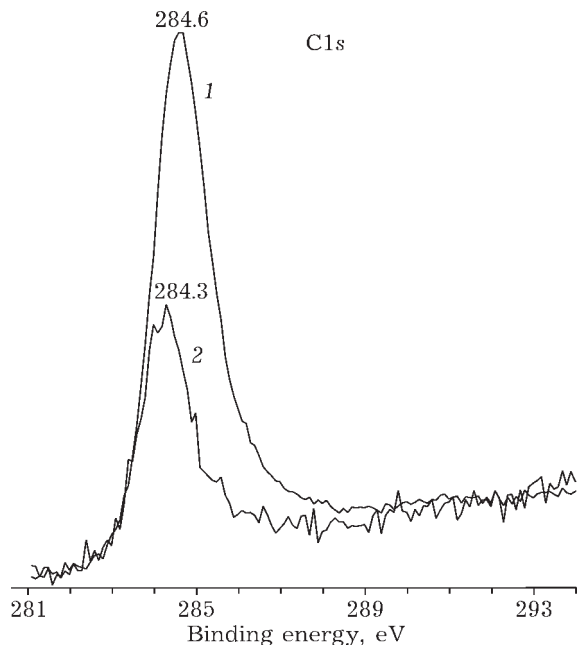


Fig. 3. The changes in the electron states of the carbon film after ethylene evacuation and exposure in the flow of methane ( $P(\text{CH}_4) = 5 \times 10^{-7}$  mbar) during 15 min at the temperature  $1100^\circ\text{C}$ . The spectrum 2 shown in this figure is identical to the spectrum 3 in the Fig. 2, b. The carbon coverage  $\Theta$  is, for the spectrum 1,  $\Theta = 0.8$ , and for the spectrum 2,  $\Theta = 2.8$ .

the crystal was treated in the presence of methane only. The  $\text{C1s}$  spectra show a sharp decrease in carbon coverage and the line shift to the lower BE value characterizing flat sheet graphite. It implies that the observed topographic transition is a reversible one. This transition is determined by carbon coverage on the  $\text{Pt}(111)$  surface and other parameters of the process like the presence of ethylene in gas phase, its pressure, the crystal temperature, etc. Obviously the heating/cooling conditions are also important for this transition.

The temperature of the hydrocarbon treatment is another crucial parameter that determines coverage and topography of the carbon films. In Fig. 4, the results on thermal stability of flat graphite structures at  $T = 1100^\circ\text{C}$  are presented. After the formation of carbon film ( $E_b(\text{C1s}) = 284.3$  eV) with coverage of 1.3 ML, methane was pumped down and the sharp heating to  $1100^\circ\text{C}$  was made. All presented  $\text{C1s}$  spectra were recorded at this temperature, so Fig. 4, a represents the kinetics of the graphite layer dissolution in the Pt bulk. The presented kinetic data show that

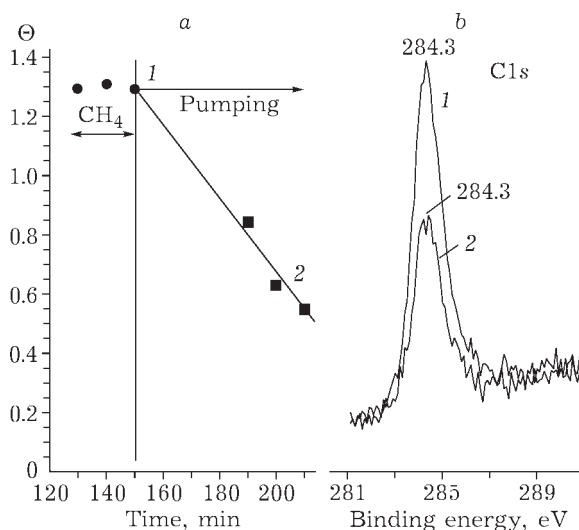


Fig. 4. The kinetics of the carbon film dissolution in the bulk of the  $\text{Pt}(111)$  monocrystal at  $T = 1100^\circ\text{C}$ . The initial step (a) – carbon saturation  $\text{Pt}(111)$  surface in methane flow ( $P(\text{CH}_4) = 5 \times 10^{-7}$  Torr). The three measurements were taken. The total time of treatment was 150 min. The second step (b) shows the kinetics of the carbon film dissolution after methane evacuation to the residual pressure  $P_{\text{res}} = 10^{-9}$  mbar. The right part of the figure demonstrates  $\text{C1s}$  spectra taken at the points marked. The spectra were recorded at the temperature  $T = 1100^\circ\text{C}$ .

about 0.8 ML of graphite layer dissolves during 1 h. The  $\text{C1s}$  spectra presented in Fig. 2, b demonstrate the constant line position and spectral shape indicating the stability of carbon layer as graphite species. The observation of linear dependence of coverage on time allows to propose that the limiting stage in the dissolution process is the cleavage of carbon atoms from the edges of graphite islands.

## CONCLUSIONS

By means of X-ray photoelectron spectroscopy, the properties of carbon films obtained by hydrocarbon cracking on the surface of  $\text{Pt}(111)$  were investigated. It was shown that in case of methane used as the reagent the flat graphite films are deposited on the  $\text{Pt}(111)$  surface while ethylene or ethylene/methane mixture stimulate the carbon films distortion resulting in curved fullerite-like structures. The formation of curved carbon films occurs through the formation of flat graphenes as the intermediate structures. It was

determined that this topographic transition is reversible and has dynamic character depending on the crystal temperature and ethylene presence in the gas phase. The kinetics of carbon dissolution from the graphitic state was investigated by recording XP spectra in the regime *in situ* at 1100 °C. The cleavage of carbon atoms from the graphite island edges is proposed to be the limiting stage for the carbon dissolution process.

#### REFERENCES

- 1 K. Shaikhutdinov, V. I. Zaikovskii, L. B. Avdeeva, *Appl. Catal. A: Gen.*, 148 (1996) 123.
- 2 N. S. Lee, D. S. Chung, I. T. Han *et al.*, *Diamond Related Materials*, 10 (2001) 265.
- 3 E. M. Pazhetnov, S. V. Koshcheev, A. I. Boronin, *Kinetika i Kataliz*, 44, 3 (2003) 1.
- 4 D. E. Starr, E. M. Pazhetnov, A. I. Stadnichenko *et al.*, *Surf. Sci.*, 600 (2006) 2688.
- 5 J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer, Eden Prairie, MN, 1992, 261 p.