ELSEVIER

Catalysis Today 42 (1998) 353–355

CATALYSIS TODAY

High-temperature carbon states at Pt(1 1 0) surface and their reactivity towards H_2 and O_2

R.I. Kvon*, A.I. Boronin

Boreskov Institute of Catalysis, SB RAS, Novosibirsk 630090, Russian Federation

Abstract

Ethylene decomposition on Pt(1 1 0) surface at 670–870 K was found to result in the formation of "chemisorbed" carbon. At T>870 K the other carbon state of sp^3 hybridisation was revealed by XPS and AES. This carbon state is rather inert towards both oxygen and hydrogen. We conclude it has diamond-like nature.

Keywords: Ethylene; Carbon; Diamond; Platinum; XPS

1. Introduction

The coke (carbonaceous deposits) formation at catalyst surface is probably the main thing to poison the supported Pt catalysts for oil cracking [1]. Thus, it is rather important to investigate the nature and the properties of the coke. The study of the model system with Pt single crystal samples is a promising way to solve this problem, as it allows to use the modern methods of surface analysis. It is accepted commonly that the carbonaceous deposits at Pt surface consist of disordered graphite structures [2]. Still it is not established completely, especially for more "opened" faces of Pt, such as (1 1 0) and (1 0 0) ones. Furthermore, Belton and Shmieg [3] have reported thin diamond layer to form at the surface of polycrystalline Pt in the flow of activated CH_4/H_2 mixture.

We have explored the formation of carbon species at Pt(1 1 0) surface due to ethylene decomposition in the temperature range 670–1170 K by using X-ray photoelectron spectroscopy (XPS). The state of carbon adsorbed layer as well as the kinetics of carbon deposition and carbon reaction with oxygen have been studied at various temperatures. The reactivity of the different states of carbon towards hydrogen was examined as well.

2. Experimental

XPS experiments were carried out in photoelectron spectrometer VG ESCALAB HP. XPS spectra were recorded using Al K_α irradiation and calibrated against $Au4f_{7/2}$ (BE=84.0 eV) and $Cu2p_{3/2}$ (BE=932.7 eV) lines. The kinetic measurements were performed by using XPS technique as well. The changes of carbon coverage θ_C were registered by monitoring C1s/Pt4f intensity ratio in situ, i.e. under ethylene/oxygen flow through the analyser chamber. Both C1s and Pt4f peak heights were recorded in the same experiment run, to minimise the systematic experimental error for C1s/Pt4f intensity ratio.

---

*Corresponding author.

0920-5861/98/$32.00 © 1998 Elsevier Science B.V. All rights reserved.
PII S0920-5861(98)00114-X

Carbon deposition was carried out in the 5×10^{-8} mbar flow of C_2H_4. The reaction with oxygen was performed in the oxygen flow with $P=10^{-7}$ mbar and the kinetics of carbon removal was registered in situ. As we have forced to admit as high as $P(H_2)=10$ mbar to run the hydrogenation of carbon adlayer, the preparation chamber was used for these experiments.

3. Results and discussion

Ethylene adsorption on Pt(1 1 0) at T>670 K was established previously [4] to result in hydrogen-free "chemisorbed" carbon adlayer. Thorough XPS investigation (see Fig. 1) found no changes of carbon state in the temperature range 670–870 K. But at T>900 K C1s spectrum changed drastically indicating the other carbon state to appear. C1s binding energy shift (from 284.2 to 284.6 eV) was accompanied with C coverage increase (by a factor of 1.4) revealing the denser packed carbon adlayer to form. The detailed analysis of the shapes of both C1s peak and C-KLL X-ray excited Auger spectrum revealed this new state to be mainly sp^3 hybridised carbon [5]. Thus we assumed that this carbon is of diamond-like nature.

The presence of ethylene was found to be critical for diamond-like carbon (DLC) formation, since no DLC has been observed when "chemisorbed" C adlayer was annealed at $T=1070$ K in vacuum. Instead, θ_C considerably decreased indicating that carbon atoms diffused into the bulk, whereas DLC state was found to be thermally stable up to 1170 K.

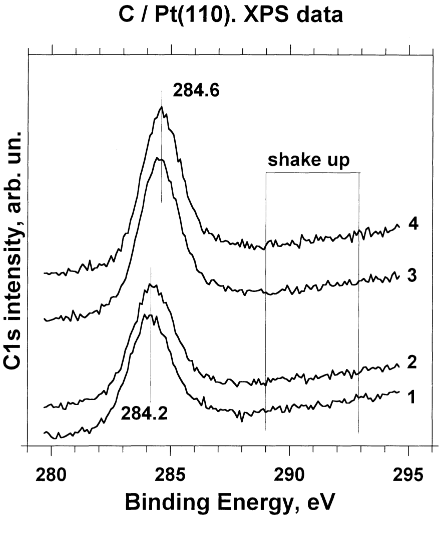

Fig. 1. C1s spectra for carbon adlayers formed at various temperatures of ethylene adsorption. Curve 1 – 770 K; curve 2 – 870 K; curve 3 – 970 K; curve 4 – 1170 K.

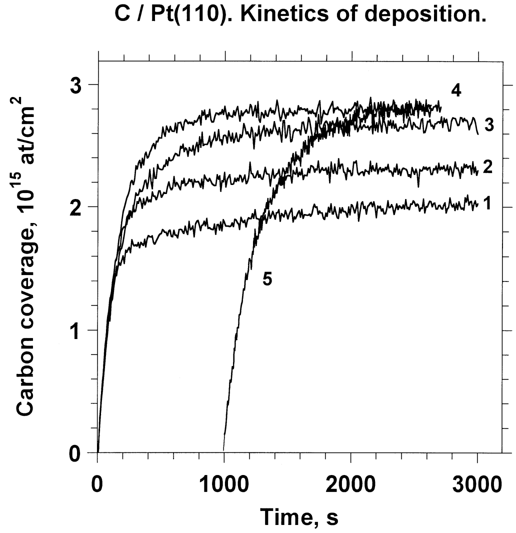

Fig. 2. The kinetics of carbon deposition due to ethylene decomposition on Pt(1 1 0) surface. Curve 1 – at 770 K; curve 2 – at 870 K; curve 3 – at 900 K; curve 4 – at 920 K; curve 5 – 970 K; please note that curve 5 is shifted toward X-axis for 1000 s – just to make the drawing more clear.

The kinetic curves of carbon deposition at different temperatures are presented in Fig. 2. One could see two main peculiarities: first, the slope of initial patches (up to ~15 L) is just the same for all the curves, and second, after mean time the growth of carbon adlayer ceases, indicating that Pt surface is covered fully by carbon. The higher the adsorption temperature, the higher saturation coverage value (θ_C^0). However, at T=920–1170 K when DLC adlayer is formed, θ_C^0 value is constant (see curves 4 and 5 in Fig. 2). Again, in agreement with XPS data θ_C^0 for DLC state (T_{ads}= 920–970 K) is 40% higher than for "chemisorbed" carbon (T_{ads}=770 K), $\approx 2.8\times 10^{15}$ and $\approx 2.0\times 10^{15}$ at/cm^2, respectively, as estimated from XPS data.

It is interesting that at intermediate temperatures the value of θ_C^0 ranges between these limiting values. Our explanation is that at T<920 K the nucleation of the DLC state goes slowly, while the growth of the diamond-like carbon nuclei is rapid enough. As a result, the fewer DLC islands of larger size cover Pt

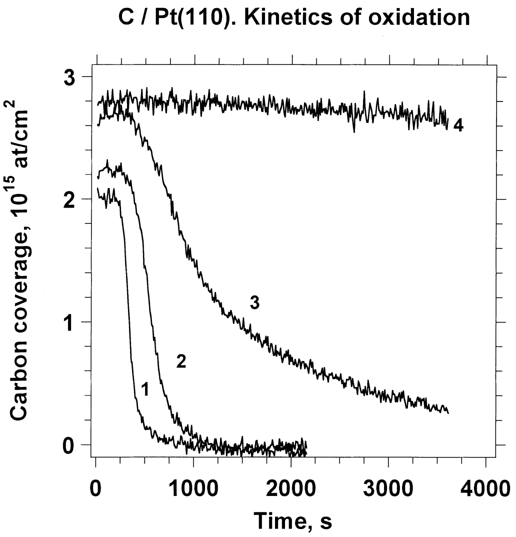

Fig. 3. The kinetics of the reaction with oxygen at T=770 K for carbon adlayer formed: curve 1 – at 770 K; curve 2 – at 870 K; curve 3 – at 900 K; curve 4 – at 970 K.

surface, "chemisorbed" carbon filling the interim between them. At higher temperatures, when both the nucleation and the growth of islands are rapid, the surface is denser packed by (smaller) DLC islands. In this case the total coverage by carbon rises up close to the θ_C^0 value for DLC adlayer.

The kinetics of the reaction of carbon adlayer with oxygen just confirmed our assumption. We have found that at T=770 K "chemisorbed" carbon reacts with oxygen at a high rate, whereas DLC species remains almost inert towards oxygen (Fig. 3, curve 4). The kinetic curve for the intermediate ("mixed") adlayer (T_{ads}=900 K) reveals two profound patches: at first, the "chemisorbed" fraction burns readily, and then the slow oxidation of DLC islands occurs.

"Chemisorbed" C was found to react with hydrogen as well. However, we have forced to admit $P(H_2)$=10 mbar at T=970 K to perform hydrogenation. At last, we have failed to remove DLC layer by hydrogen in any experimental conditions we had tried (i.e. H_2 pressure up to 20 mbar and $T\approx$1070 K).

4. Summary

Thus, the kinetics study of the reactivity of both carbon species observed at Pt(1 1 0) surface towards oxygen and hydrogen confirms the assumption on their nature we made on the basis of spectroscopic data. Ethylene decomposition at 650–850 K produces "chemisorbed" carbon adlayer consisting of isolated carbon atoms with no C–C bonds. At higher temperatures the islands of diamond-like carbon species is formed where C atoms are bonded to each other.

It is known from practice [1] that high pressure hydrogen treatment could regenerate Pt catalysts deactivated by coke. Still some part of catalytic activity could not be restored. We believe it is just DLC state to be responsible for this.

Acknowledgements

This work was kindly supported by Russian Foundation of Base Research under Grant No. 95-03-09676.

References

[1] R.A. Buyanov, Coke Formation on the Catalysts (in Russian), Nauka, Novosibirsk, 1983, p. 207.
[2] K. Baron, D.W. Blakely, G.A. Somorjai, Surf. Sci. 41 (1974) 45.
[3] D.N. Belton, S.J. Shmieg, Surf. Sci. 233 (1990) 131.
[4] A.I. Boronin, V.I. Bukhtiyarov, R.I. Kvon, V.V. Chesnokov, R.A. Buyanov, Surf. Sci. 258 (1991) 289.
[5] R.I. Kvon, A.I. Boronin, Sh.K. Shaikhutdinov, R.A. Buyanov, Appl. Surf. Sci. 120 (1997) 239.