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HREELS STUDY AND CATALYTIC SIGNIFICANCE OF LOW-TEMPERATURE INTERACTION OF ISOLATED CARBON ATOMS WITH HYDROGEN ON Pt(111)

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Isolated atoms of carbon evaporated on to Pt(111) react with hydrogen at $T \geqslant 170$ K to form methine species, characterized with vibrational modes ν(CH) at 2960 and δ(CH) at 800 cm^{-1}. The high reactivity of C_{ads} is in line with their ability to take part as intermediates in the metanation reaction. CH_{ads} species are stable up to $T \approx 500$ K; further heating leads to their dissociation accompanied by H_2 desorption and formation of unreactive graphite-like islands.

1. Introduction

Elucidation of the nature of surface, responsible for the processes of methanation and Fischer-Tropsch synthesis, is of a considerable interest for the fundamental study of the catalytic action of the platinum group metals. Highly reactive carbon atoms, which may be easily hydrogenated, are allegedly formed in the $CO + H_2$ reaction [1]. However, the difficulty of their detection, *in situ*, does not permit one to determine exactly the reaction mechanism. To understand the nature of the active carbon state, attempts have previously been made to study directly the $C_{ads} + H_2$ step by means of hydrogenation of the carbon layer produced by the decomposition of hydrocarbons [2,3]. It was not however, successful, probably because of the clustering of adsorbed carbon to form graphite-like carbon aggregates of low reactivity towards H_2. An appearance of the active carbon state, reacting with H_2 as low as 250 K, was found after electron-induced dissociation of CO on Ru(001), but the nature of the surface carbon was not determined [4]. In this paper we studied the low-temperature reaction between C and H atoms on Pt(111) with High Resolution Electron Energy Loss Spectroscopy (HREEELS) and thermodesorption.

The C_{ads} layer was produced by means of a special source capable of creating the flow of isolated carbon atoms quite free from the impurities and carbon clusters [5]. HREELS spectra of CO_{ads} were applied to characterize the carbon layer adsorbed (isolated C atoms or graphitic islands).

2. Experimental

Experiments were performed in a VG ADES-400 spectrometer (residual pressure of $\approx 5 \cdot 10^{-11}$ Torr). The HREELS method uses an electron gun equipped with an EMU 50 monochromator and a 150°-hemispherical rotatable analyser. Monochromatic electron beams with a kinetic energy of 2.3 eV, a primary current of $5 \cdot 10^{-11}$ A and an incident angle of 45° with respect to the surface normal were used. Energy resolution of elastically reflected beam was ca. 10 meV (80 cm^{-1}) at an intensity of 10^5 cps. Spectra were recorded in the specular direction. Thermodesorption spectra were acquired by means of a quadrupole mass-spectrometer VG QXK-400, a heating rate of 10 K/s (DC) being used. Characteristics of the Pt(111) crystal and the procedure of the surface cleaning have been described elswhere [6].

3. Results and discussion

Fig. 1 shows a sequence of the energy loss spectra obtained after the gradual covering of Pt(111) surface at 300 K with atomic carbon followed by saturation with CO at 300 K. HREELS spectrum (a) reveals two bands in the region of C-O stretchings with υ(CO) at 1870 and 2100 cm^{-1} for bridge and on-top states, respectively, as well as the band at $\not\approx$ (PtC) = 465 cm^{-1} in a low frequency region [7]. Carbon atoms predeposited on the Pt surface reduce the ν(CO) band intensities, but their positions remain unchanged. CO adsorption into the bridge state is seen to be mostly diminished. The ratio of the on-top state band intensity to the bridge one is $\eta = L_t/I_b = 2.7$ for the CO saturated clean Pt(111), whereas the same ratio obtained for the C_{ads}/Pt(111) surface enhances up to $\eta = 15$.

Previously we have studied the NO/O/Pt(111) system and shown that oxygen atoms preadsorbed in the $p(2 \times 2)$ structure suppress the subsequent NO adsorption into the bridge state and do not sufficiently influence the on-top one [6]. The same results obtained for the present CO/C/Pt(111) system show that even low C_{ads} coverage changes the adsorption properties of all the platinum surface; probably this indicates that carbon evaporated adsorbs predominantly as the isolated atoms.

Heating of the deposited carbon layer up to 800 K in vacuum restores η to its previous value of 2.8. It gives evidence for gathering of C_{ads} atoms into islands setting free the considerable part of platinum surface, which can adsorb CO like the clean Pt(111). Energy losses in the 1200–1600 cm^{-1} region can be observed after CO desorption upon heating of Pt up to 1000 K (fig. 1). According to refs. [8,9], similar spectra are typical for carbon films with the graphite-like structure. The quantity of carbon deposited was estimated with the test CO adsorption on the annealed C_{ads} layer followed by adoption of the known dependence of the

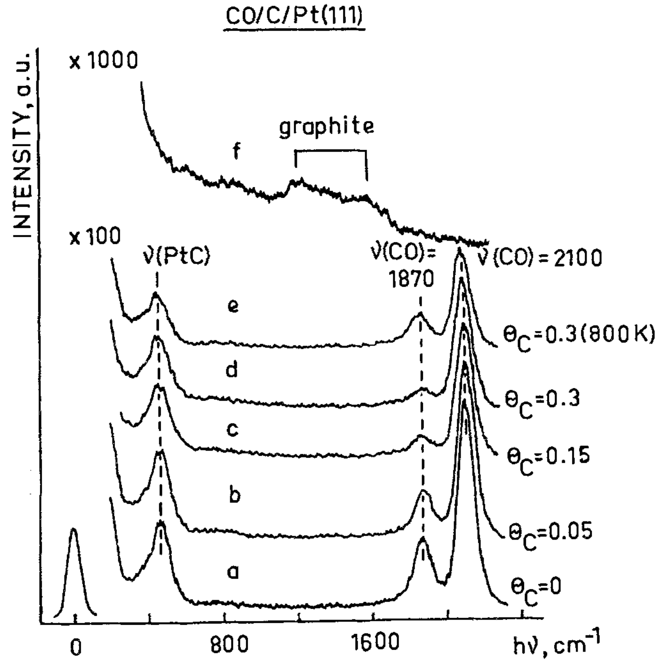

Fig. 1. HREEL spectra obtained after the following treatments of Pt(111):
a–d–CO adsorption up to saturation on the surface predosed with a different quantity of carbon atoms; carbon evaporation and CO adsorption are performed at the crystal temperature of 300 K; CO exposure is 3 L;
e–carbon layer heating at 800 K for 5 min followed by CO exposure of 3 L at 300 K;
f–graphite islands formation after heating at $T = 1000$ K and $\tau = 5$ min of the carbon deposited ($\theta_C \approx 0.7$).

saturated CO coverage, θ_{CO}^{sat}, on the graphitic carbon coverage [2]. The value of θ_{CO}^{sat} was determined from the thermodesorption data.

The reaction of C + H on Pt(111) was studied in the temperature range of 115–300 K (fig. 2). The clean surface was initially exposed to H_2 at 115 K to form a dissociative hydrogen state ($\theta_H \approx 1$ monolayer, ML) characterized with the modes of $\nu(\mathrm{PtH}) = 500$ and $\nu(\mathrm{PtH}) = 1200$ cm^{-1} [10]. Then carbon atoms were deposited on the H/Pt surface at the same temperature up to $\theta_C \approx 0.15$ ML. A monolayer of the surface carbon corresponds to the atomic density in the graphite layer of $3.86 \cdot 10^{15}$ atoms/cm^2. Residual gas pressure increase, when the carbon source is functioning, gives rise to the adsorption of a small amount of CO up to ca. 0.01 ML coverage.

The absence of this C-H bond stretchings in the corresponding loss spectrum made it possible to conclude that carbon and hydrogen atoms do not react with each other at 115 K. Temperature increase up to 170 K results in the appearance of $\nu(\mathrm{CH})$ loss at 2960 cm^{-1} which indicates that the reaction leads to the formation of hydrocarbon species. Further heating up to 250 K increases the

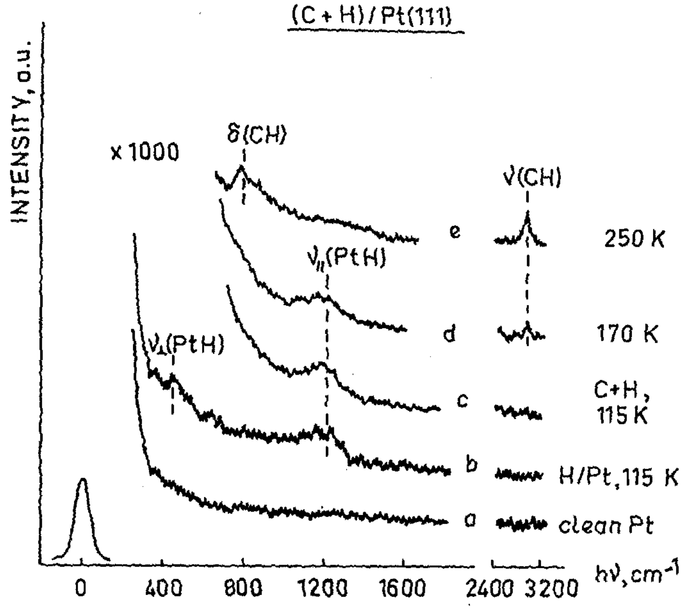

Fig. 2. HREEL spectra obtained in the reaction between adsorbed carbon and hydrogen atoms on Pt(111) proceeding:
a–clean surface;
b–H_2 adsorption at 115 K and exposure of 300 L;
c–carbon deposition on the layer of (b) at $T = 115$ K, $\theta_C \approx 0.15$;
d–e–heating of (c) for 3 min at 170 and 250 K, respectively.

ν(CH) band intensity. The bending mode δ(CH) becomes substantial at 800 cm^{-1}. These losses may be attributed to CH_{ads} particle detected earlier under the ketene [11] and methylhalides [12] decomposition on the Pt(111) surface, which reveals ν(CH) ~ 2950 and δ(CH) ≈ 770 cm^{-1}. The authors of [4,11] inferred the sp^3-character of carbon atom from the ν(CH) band position. The latter permits us to assume that the CH_{ads} particle is bonded with three platinum atoms.

$(C_nH)_{ads}$ (where $n \geqslant 2$) species produced under the decomposition of ethylene, ethyne, benzene on Cu(100) [13], Ir(111) [14], Rh(111) [9] surfaces, have ν(CH) stretching frequencies in the region of 3000–3050 cm^{-1}. The predominant formation of CH_{ads} species is stated in the present paper. However, it is noteworthy that rather large FWHM of ca. 150 cm^{-1} makes it impossible to exclude the presence of more complex surface species such as C_nH.

The results obtained give evidence for a high reactivity of carbon atoms at low temperatures. The reaction with hydrogen starts at temperatures as low as 170 K. The first stage of hydrocarbon formation has been identified: the addition of the hydrogen atom to the carbon one to form the CH particle.

The thermal stability of CH species was also investigated in the range of 250–800 K (fig. 3). The absence of any changes in the energy loss spectra indicates the stability of C–H bond at 250–500 K. According to the TDS data,

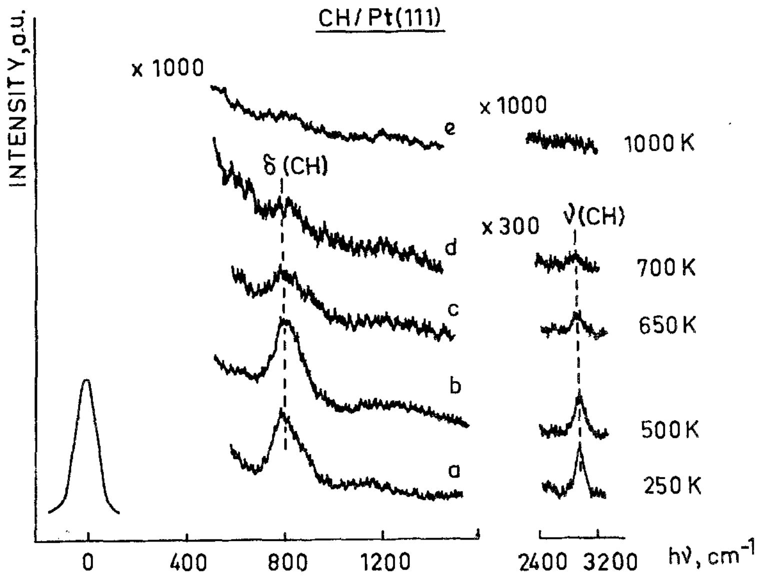

Fig. 3. HREEL spectra of CH_{ads} layer on Pt(111) obtained after heating at different temperatures, $\tau = 2$ min; initial spectrum (a) is registered after the subsequent treatment with hydrogen ($P_{H_2} = 2 \cdot 10^{-7}$ Torr) of the layer of fig. 2e, $T = 250$ K, $\tau = 3$ min. The treatment was carried out to enrich the CH_{ads} coverage.

hydrogen is observed to desorb in the temperature region of 500–700 K, that is connected with dissociation of CH_{ads}. The energy loss intensities at 2960 and 800 cm^{-1} decrease simultaneously to attain the spectrum typical of that for carbon islands. Carbon of the latter kind, as one would expect, does not produce hydrocarbon species upon reaction with hydrogen.

3. Conclusion

The high reactivity of isolated carbon atoms adsorbed on Pt(111), C_{ads}, with respect to H_2, has been established: the reaction starts already at 170 K to form methine CH_{ads} species which remain unchanged on heating up to ca. 500 K. Dissociation of these species in the temperature range 500–750 K is accompanied by hydrogen desorption and by the formation of an unreactive, graphite-like carbon layer.

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