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HREELS study: low-temperature reaction of NO with isolated carbon atoms adsorbed on Pt(111) surface

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The reaction between isolated carbon atoms and nitrogen oxide molecules in the adlayer on Pt(111) surface has been studied. Carbon atoms have been deposited on the surface from the special source. The reaction was found to proceed at $T \approx 100$ K and to provide, at least, two intermediate surface species, which have been assigned to adsorbed isocyanate NCO_{ads} and fulminate CNO_{ads} particles. Both intermediates dissociated into on-top state of CO_{ads} and N_{ads} under heating to $T \leqslant 300$ K.

Keywords: High resolution electron energy loss spectroscopy; platinum; nitric oxide; isolated carbon atoms

1. Introduction

The activity of isolated carbon atoms on metal surfaces is the important factor for elucidating the detailed mechanism of catalytic reactions of carbon-containing molecules (Fischer–Tropsch synthesis, conversions of hydrocarbons) [1]. Nevertheless, there are few reliable data about the properties of isolated carbon atoms C_{ads}, the possible intermediates of the reactions mentioned, since the routine way of surface carbon production via hydrocarbon decomposition leads to the formation of a surface graphite layer, which exhibits an extremely low activity. In our previous works, the adlayer containing the isolated C_{ads} atoms and small $C_{n\,ads}$ clusters was obtained on Pt(111) surface using a special carbon source. The low-temperature reactions of carbon particles with hydrogen were studied, and the stepwise synthesis of ethylidyne, $\geqslant C{-}CH_3$, was performed in the adlayer [2,3].

The present work is a part of a study on the surface chemistry of the isolated carbon atoms reactions. Interaction between C_{ads} and NO_{ads} has been investigated by high resolution electron energy loss spectroscopy (HREELS).

2. Experimental

Experiments were performed in a VG ADES-400 spectrometer (residual pressure $\leqslant 2 \times 10^{-11}$ Torr). Monochromatic electron beams with kinetic energy of ca. 2.5 eV and 10 meV (ca. 80 cm^{-1}) energy resolution were used. In-specular spectra were recorded. The details of the HREELS technique, the procedure of surface cleaning, the carbon adlayer formation and its analysis were described earlier [2–4].

3. Results

3.1. C + NO_{ads} REACTION

The interaction of C_{ads} atoms with the preadsorbed NO layer is shown in fig. 1. Spectrum (a) corresponds to the saturated NO_{ads} layer at $T \approx 100$ K, $n_{NO} \approx 1 \times 10^{15}$ cm^{-2} [5].The spectrum reveals the vibration bands ν(NO) of the bridge and on-top states at 1475 and 1685 cm^{-1}, respectively, and also the bands at

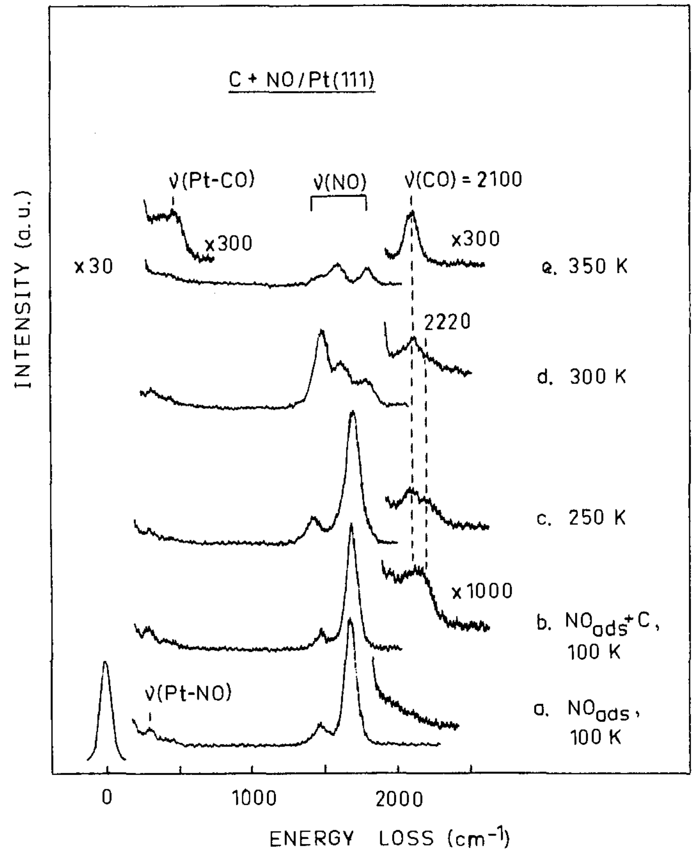


Fig. 1. HREEL spectra obtained (a) after NO adsorption on the clean Pt(111) surface at exposure of 3 L (1 L = 10^{-6} Torr s) and $T \approx 100$ K; (b) after the sequent carbon deposition to $n_C \approx 10^{14}$ cm^{-2}; (c)–(e) after the stepwise heating of the adlayer.

300 and 435 cm^{-1} tentatively assigned to ν(PtNO) and δ(PtNO) vibrations [4]. The sequent carbon deposition is carried out over $\mathrm{NO_{ads}}$ layer at 100 K up to $n_\mathrm{C} \approx 10^{14}$ cm^{-2}. Under such conditions carbon should be predominantly in the state of isolated adsorbed atoms [3]. Appearance of a new wide band at ca. 2150 cm^{-1} proves the reaction to proceed in the adlayer (fig. 1b). Heating up to 200–250 K results in the splitting of the band to two other bands at 2100 and 2220 cm^{-1} (fig. 1c). The band at 2100 cm^{-1} is assigned to ν(CO) stretchings of the on-top $\mathrm{CO_{ads}}$ state [6]. Apparently, the band at 2220 cm^{-1} corresponds to an intermediate like isocyanate $\mathrm{NCO_{ads}}$. Further temperature increase up to 300–350 K is accompanied by the decrease of the 2220 cm^{-1} band intensity. At the same time, the intensity of ν(CO) stretchings increases and the ν(Pt–CO) band at 460 cm^{-1} appears (figs. 1d, 1e). According to the measured calibration, the concentration of $\mathrm{CO_{ads}}$ produced in the $\mathrm{C_{ads} + NO_{ads} \rightarrow CO_{ads} + N_{ads}}$ reaction is equal to $n_\mathrm{CO} \approx 5 \times 10^{13}$ cm^{-2}. Changes in N–O stretchings observed upon heating from 100 to 350 K correspond to the sequent desorption of the on-top and bridge states of $\mathrm{NO_{ads}}$. Only two states remain on the Pt(111) surface at 350 K occupying the defect sites, such as atomic steps, with ν(NO) at 1600 and 1810 cm^{-1} [4].

A control experiment has been provided to estimate the possibility of CO appearance due to its adsorption from the residual gas. The same operations as described above (NO adsorption, carbon evaporation, stepwise heating of the adsorbed layer) as well as spectra registering have been accomplished, only Pt(111) crystal was removed from the zone of carbon beam spreading. CO accumulation was about $n_\mathrm{CO} \approx 5 \times 10^{12}$ cm^{-2} ($\theta_\mathrm{CO} \approx 3 \times 10^{-3}$), i.e., lower by an order of magnitude than that after $\mathrm{NO_{ads}}$ + C reaction. Thus, CO appears actually due to the decomposition of the C + $\mathrm{NO_{ads}}$ reaction intermediate.

3.2. NO + $\mathrm{C_{ads}}$ REACTION

Fig. 2 displays the interaction between NO and preadsorbed carbon: at first, the layer of isolated carbon atoms is formed on the clean platinum surface at 100 K, then NO adsorbs until the saturation occurs. This could provide the "hot" carbon atoms effect on $\mathrm{C_{ads} + NO_{ads}}$ reaction.

Carbon deposition is accompanied by the increase of the background pressure up to $\sim 10^{-9}$ Torr resulting in CO adsorption up to $n_\mathrm{CO} \approx 3 \times 10^{13}$ cm^{-2} (fig. 2a). The $\mathrm{C_{ads}}$ layer appeared to have no particular vibration bands [2,3]. The subsequent NO adsorption at 100 K provides the characteristics of the saturated $\mathrm{NO_{ads}}$ layer (fig. 2b). At the same time, three new bands appear at 1180, 1910 and 2220 cm^{-1}. The $\mathrm{NO_{ads} + CO_{ads}}$ reaction is known not to proceed under such conditions [7]. So these bands can be assigned to the intermediates of the $\mathrm{C_{ads} + NO_{ads}}$ reaction. Heating causes the simultaneous weakening of the bands at 1180 and 1910 cm^{-1}; the band at 2220 cm^{-1} is more stable and disappears upon the heating to 300 K (fig. 2e). The ν(CO) band of the on-top $\mathrm{CO_{ads}}$ remains in the spectrum;

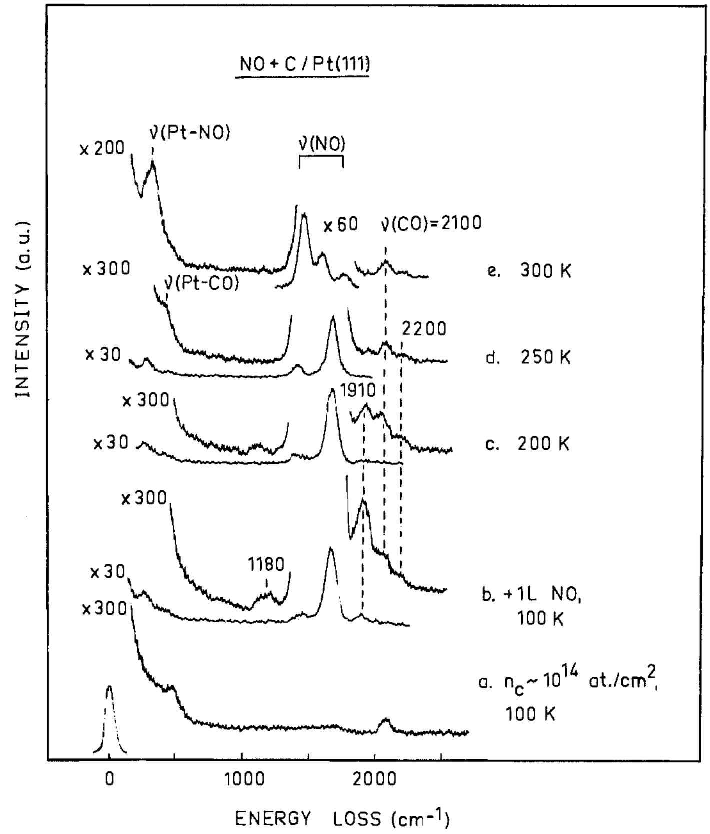


Fig. 2. HREEL spectra obtained (a) after carbon deposition on the clean Pt(111) surface at 100 K up to $n_C \approx 10^{14}$ cm^{-2}; (b) after the sequent NO adsorption at 100 K and exposure of 1 L; (c)–(e) after the stepwise heating of the adlayer.

its intensity is slightly higher than that before the reaction proceeded: $n_{CO} \approx 4.5 \times 10^{13}$ cm^{-2}.

4. Discussion

The main result of this study is the detection of the low-temperature reaction of carbon atoms with nitrogen oxide molecules proceeding in the adlayer on Pt(111) surface at $T \approx 100$ K. Hence, the isolated carbon atoms seem to be very active not only in the reaction with hydrogen [2,3], but also in binding molecular NO_{ads} providing intermediates, which convert consecutively into products: carbon monoxide CO_{ads} and nitrogen atoms N_{ads}.

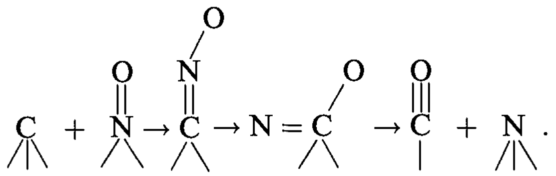
The intermediates formed in the course of NO + C_{ads} and NO_{ads} + C reactions were found to be characterized by the following set of vibration frequencies: 1180, 1910, 2100 and 2220 cm^{-1}. No problems raised in identifying CO_{ads} molecules with ν(CO) at 2100 cm^{-1}, while the assignment of other vibration bands meets serious difficulties. Apparently, two types of species are formed: one with a band in the 2150–2220 cm^{-1} region, another with two bands at 1180 and 1910 cm^{-1}. The first band can be assigned to NCO_{ads} isocyanate complexes, which can be produced on metal surfaces in the course of CO + NO reaction [8,9]. Table 1 shows the characteristic vibration frequencies of NCO in adsorbed states and in coordination compounds. The disappearance of the band at 2220 cm^{-1} in the 300–350 K temperature region (fig. 1) is the result of isocyanate dissociation into CO_{ads} and N_{ads} and agrees well with the thermal stability of NCO_{ads} on platinum surface [15]. Unfortunately, we failed to observe ν(Pt–N) stretching at 480 cm^{-1}, since this region is obscured by other intensive ν(Pt–CO) and ν(Pt–NO) bands.

Another intermediate of the reaction could be the surface fulminate complex CNO_{ads}, and two bands at 1180 and 1910 cm^{-1} (fig. 2) may correspond to its ν(NO) and ν(CN) stretching. For unidentate C-bonded fulminate ion in $[Pt(CNO)_4]^{2-}$ complex these vibration modes are known to appear at 1174 and 2195 cm^{-1} [10]. ν(CN) frequencies can differ essentially due to various coordinations of the adsorbed particle. Indeed, when methyl isocyanate molecule CH_3CN adsorbs on Pt(111) surface two bands at 2250 and 1770 cm^{-1} are observed for the on-top and bridge states, respectively [16].

Because of the location and the strong intensity of the band at 1910 cm^{-1} the fulminate complex is assumed to coordinate in the bridge state and the C=N bond is near the line of the surface normal [16]. The bands at 1180 and 1910 cm^{-1} disappear simultaneously under heating in the 200–250 K temperature range, since fulminate complex decomposes producing CO_{ads} and N_{ads}. This appears to be followed by the intramolecular rearrangement into a more stable isocyanate complex according to the scheme:

Table 1
The frequencies of vibration modes of NCO adsorbed on catalysts surfaces and coordinated in metal complexes (in cm^{-1})

Catalyst	ν_{as}(NCO) or ν(CN)	Other modes	Ref.
Pt(foil)	2180		[8]
Rh/SiO Si-NCO	2300	ν_s(NCO) 1460	[9]
Rh-NCO	2170–2190		
coordination in metal complex			
M–NCO	2160–2280	ν_s(NCO) 1300–1480	[10,11]
$\genfrac{}{}{0pt}{}{M\diagdown}{M\diagup}NCO$	2170–2230	ν_s(NCO) 1300–1360 δ(NCO) 600–670	[12,13]
M–OCN	2205–2225	ν_s(NCO) 1300, 1140 δ(NCO) 600–670	[14]



The composition of products in the adlayer depends on the sequence of the surface filling with reactants: C_{ads} + NO reaction produces both isocyanate and fulminate in appreciable amounts (fig. 2); $NO_{ads} + C$ reaction results in the predominant formation of NCO_{ads} (fig. 1). Spectral transformation at 1900–2200 cm^{-1} (figs. 1b–1d) as well as the presence of the very weak shoulder at 1180 cm^{-1} (not presented) at $T < 250$ K indicate, that a small amount of fulminate is indeed produced in $NO_{ads} + C$ reaction. A comparatively low fulminate content in this case is likely to be provided by the "hot" carbon atoms participating in the reaction, which get on the surface from the source directly. Apparently, these atoms have enough time to react with NO_{ads} before their kinetic energy relaxation is completed. Thus, it helps to overcome the activation barrier in an intramolecular rearrangement from fulminate into isocyanate surface complex.

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