

Mechanism of surface intermediate formation during the reactions between adsorbed molecules and atoms: $\text{NO} + \text{H}$, $\text{NO} + \text{C}$, $\text{O}_2 + \text{H}$, $\text{C}_2 + \text{H}$, on platinum

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Abstract

The $\text{NO}_{\text{ad}} + \text{H}_{\text{ad}}$, $\text{NO}_{\text{ad}} + \text{C}_{\text{ad}}$, $\text{O}_{2\text{ad}} + \text{H}_{\text{ad}}$, $\text{C}_{2\text{ad}} + \text{H}_{\text{ad}}$ reactions were studied on Pt(111) surface by HREELS. It was shown that at low temperatures these catalytic reactions are promoted via addition of the active atomic adsorbates to the diatomic molecules resulting in 3-atom intermediates. On the $\text{NO} + \text{H}_2$ reaction, it was discovered that an adsorbed hydrogen atom adds to a bridge NO_{ad} molecule resulting in a $\eta^2\text{-HNO}_{\text{ad}}$ intermediate. In turn, the intermediate reacts with other H_{ad} to produce first a dissociative nitrogen and then N_2 and NH_3 . An isolated C_{ad} obtained by evaporation from a special source of carbon atoms was found to react with NO_{ad} even at 100 K producing an intermediate fulminate particle CNO_{ad} . On being heated, it converts via an intramolecular rearrangement reaction into the more stable isocyanate NCO_{ad} , and further into on-top CO_{ad} and N_{ad} . The peroxide-type molecular oxygen $\text{O}_{2\text{ad}}^-$ was observed to react with hydrogen even at 105 K yielding first a hydroxyl intermediate and an atomic oxygen adsorbate and, subsequently, water molecules. Hydrogen atom was observed to add to a $\text{C}_{2\text{ad}}$ molecule yielding first an ethynyl moiety. The subsequent addition of two other hydrogen atoms produces ethynidyne. Details of the experimental evidence for these reaction mechanisms are discussed.

Keywords: Platinum; Nitric oxide; Oxygen; Hydrogen; Surface carbon; Mechanisms; Monocrystal surface; Surface intermediates

1. Introduction

The kinetics and mechanism of such catalytic reactions as $\text{NO} + \text{H}_2$, CO and H_2 oxidation on group VIII metals were the object of extended research. The fascinating kinetic phenomena were discovered [1–3]: oscillations of the reaction rate, moving of the concentration chemical

waves over the surface of catalyst. The knowledge of the steps of the mechanism and of the nature of interaction between the reactant particles (adsorbed atoms and molecules) is necessary to gain a better insight into these phenomena. It should be noted that very little is yet known about the nature of surface transient species.

Atoms and molecules adsorbed on metal surfaces are distinct by their bonding energies and type of coordination. So, the atomic adsorbates

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– H_{ad} , C_{ad} , N_{ad} , O_{ad} – occupy preferentially hollow sites yielding tightly bonded multi-coordinated (3- or 4-fold) adsorption sites. At the same time, they reveal a very high reactivity. Molecules (for instance, CO, NO, etc), usually, populate on-top and bridge sites in a linear, bent or tilt configuration showing a rather loose bonding to the surface. In heterogeneous catalysis by platinum metals, an initial activation of reactant molecules is frequently confined to an appropriate bond breaking as the result of the dissociative adsorption.

The adsorption usually does weaken the intrinsic chemical bond of the molecule and still serves as an active matrix which enables the adsorbed atom and molecule to be brought close enough together to produce an intermediate. This work presents some examples of a so called molecular catalysis where the reaction initiates via an addition of active atomic adsorbates, H_{ad} and C_{ad} , to the molecules NO_{ad} , O_{2ad} , C_{2ad} resulting in 3-atom intermediates. The experiments have been performed on a 3-fold symmetric Pt(111) surface at low temperatures (100–350 K) using HREELS.

2. Experimental

Experiments were performed in a VG ADES 400 spectrometer (with a base pressure of 10^{-10} mbar or less) equipped with an EMU 50 monochromatic electron gun and rotatable 150° -hemispherical deflector type analyzer for HREELS. Loss spectra were recorded in the specular direction at an electron energy of ≈ 2.5 eV and an incident angle of $\approx 45^\circ$ with respect to the surface normal. The resolution of an elastically reflected electron beam was 9–11 meV ($75\text{--}90\text{ cm}^{-1}$). The C_{ad} atoms and C_{2ad} clusters (molecules) were obtained by evaporation of carbon atoms from a special source [4]. Other experimental details, including the surface cleaning procedure, were described earlier [5].

3. Results and interpretation

3.1. NO + H

Fig. 1 shows loss spectra obtained after the 300 K adsorption of NO on the Pt(111) surface

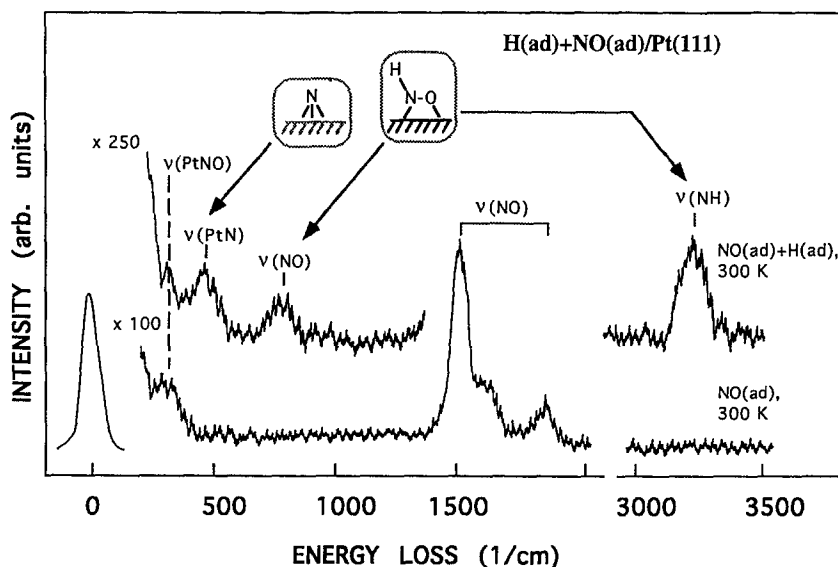


Fig. 1. The formation of the HNO_{ad} and N_{ad} intermediates on Pt(111). The lower spectrum: the NO_{ad} layer on the clean surface prepared by 6 L exposure of NO at 300 K. The upper spectrum: after NO + H_2 reaction performed at $P_{H_2} = P_{NO} = 10^{-8}$ mbar and 300 K.

(the lower spectrum) and after the $\text{NO} + \text{H}_2$ reaction performed in a steady state conditions at 300 K (the upper spectrum). The NO_{ad} layer contains three molecular states: a bridge (or a 3-fold hollow) state reveals bands of $\nu(\text{NO})$ at 1490 and $\nu(\text{PtNO})$ [or $\delta(\text{PtNO})$] at 320 cm^{-1} ; two other $\nu(\text{NO})$ losses at 1600 and 1820 cm^{-1} are intrinsic of two states on defect sites [6–8]. Once the reaction has been performed at $P_{\text{H}_2} = P_{\text{NO}} = 10^{-8} \text{ mbar}$ and $T \approx 300\text{--}350 \text{ K}$, three new bands of intermediates – at 480, 800 and 3280 cm^{-1} – are observed. The replacement of hydrogen by deuterium leads to the shift of the band at 3280 cm^{-1} down to 2430 cm^{-1} and leaves the frequencies of two other bands essentially unchanged: 455 and 770 cm^{-1} . The iden-

tification of the particles was based on the frequencies of the bands, the behaviour of the loss spectrum during the adlayer heating and under the isotopic replacement. The bands at 3280 and 800 cm^{-1} , which are not found in any known adsorption states of nitrogen oxides or $\text{NH}_{x\text{ad}}$ ($x = 1\text{--}3$), were assigned to the $\nu(\text{NH})$ and $\nu(\text{NO})$ stretchings, respectively, of an HNO_{ad} species bonded to the surface via both nitrogen and oxygen atoms. According to Ref. [9], the band at 480 cm^{-1} was assigned to a $\nu(\text{PtN})$ stretching of a dissociative nitrogen N_{ad} since it is known from Ref. [7] that this band disappears under adlayer heating synchronously with the nitrogen desorption in the temperature interval of 450–500 K. The HNO_{ad} intermediate

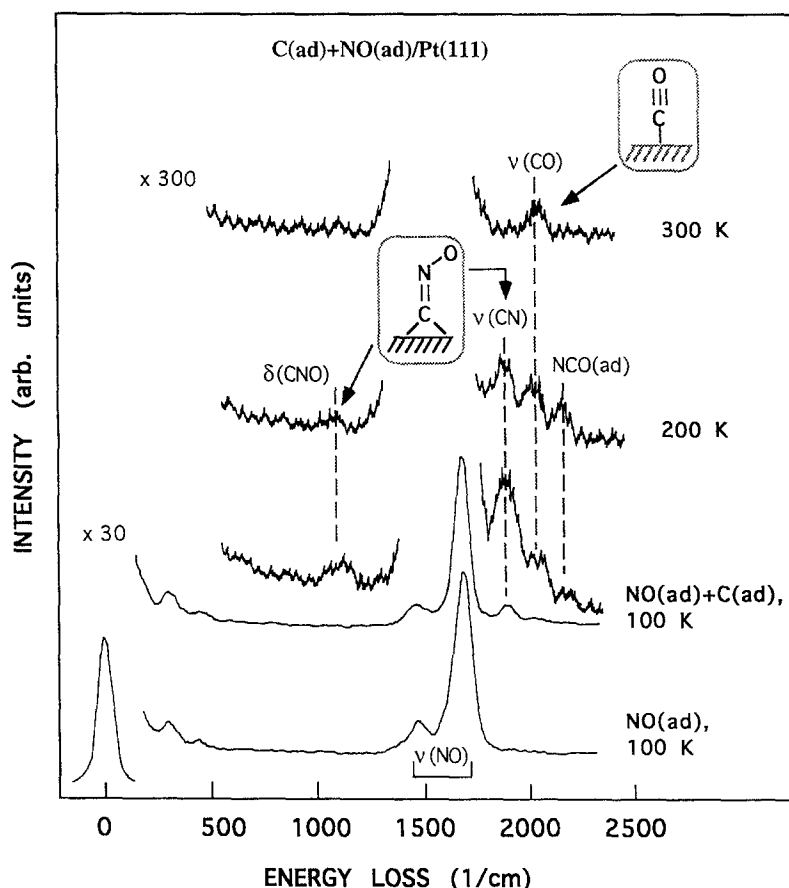
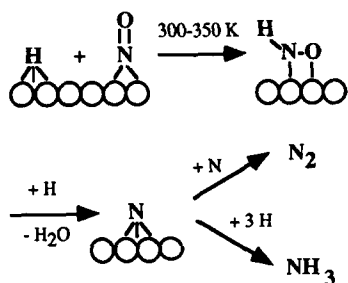


Fig. 2. The isocyanate and fulminate intermediates on Pt(111). The lowest spectrum: the NO_{ad} layer on the clean surface prepared by 4 L exposure of NO at 100 K. The next spectra from bottom to top demonstrate the NCO_{ad} and CNO_{ad} production resulted from 6 L exposure of NO on the C_{ad} -covered surface at 100 K and further reactions of these intermediates under heating at 200 and 300 K.

is assumed to appear as a result of the addition of a hydrogen adatom to a bridge NO_{ad} . It has been shown [6] that the subsequent step involves the reaction of HNO_{ad} with hydrogen yielding N_{ad} that can add hydrogen atoms in the further steps yielding ammonia. The recombinative desorption of nitrogen molecules becomes possible at $T > 450$ K.



3.2. $\text{NO} + \text{C}$

Fig. 2 illustrates the low-temperature reaction ($T = 100$ K) between carbon atoms and NO molecules on the $\text{Pt}(111)$ surface. At first, carbon was evaporated on the surface at 100 K up to concentration of $2 \cdot 10^{14} \text{ cm}^{-2}$. Under such conditions carbon should be predominantly in the state of isolated carbon atoms which is known to exhibit no particular vibrational bands [5,10]. Upon the subsequent 100 K adsorption of NO , characteristic bands of the bridge and on-top states of NO_{ad} (see the second spectrum from the bottom) are observed. However, when this spectrum is compared with that for NO_{ad} on the clean surface (the lowest spectrum), it is evident that new species form in the mixed $\text{NO}_{\text{ad}} + \text{C}_{\text{ad}}$ layer; they reveal the bands at 1180, 1910, 2100 and 2220 cm^{-1} . The last two bands

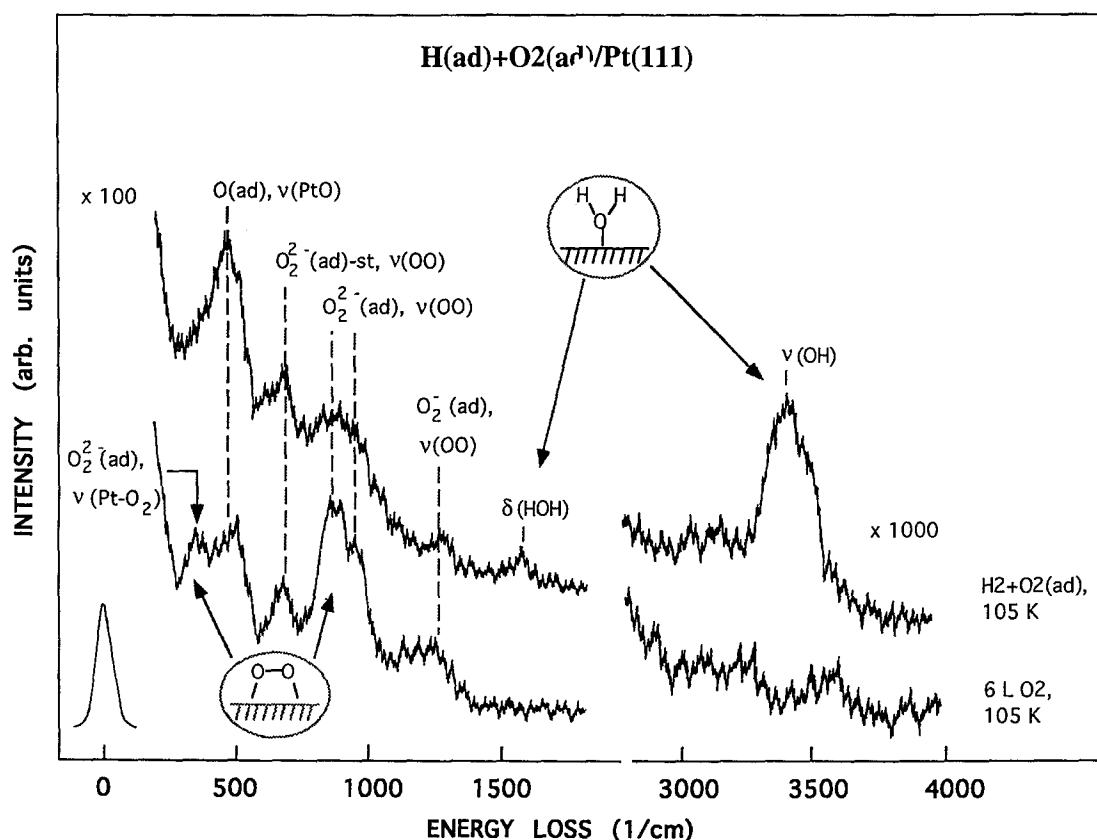


Fig. 3. The reaction of molecularly adsorbed oxygen with hydrogen on $\text{Pt}(111)$. The lower spectrum is obtained after 6 L exposure of O_2 at 105 K. The upper spectrum is obtained after subsequent 24 L exposure of hydrogen at 105 K.

are assigned to stretching $\nu(\text{CO})$ of an on-top CO_{ad} and $\nu_{\text{as}}(\text{NCO})$ of an isocyanate particle NCO_{ad} [11], respectively. The other two bands are likely to belong to a fulminate particle CNO_{ad} which is the most expected product in the addition of an NO_{ad} molecule to a carbon atom. The bands at 1180 and 1910 cm^{-1} are assigned to the $\nu(\text{NO})$ and $\nu(\text{CN})$ stretchings, respectively. By analogy with methyl isocyanate adsorbed on Pt(111) [12], the fulminate particle is assumed to be bound in the end-side configuration via the carbon atom. According to the dipole selection rules for HREELS, this configuration correlates well with the high intensity of the $\nu(\text{CN})$ band. Under heating from 100 to 300 K, NCO_{ad} and CNO_{ad} dissociate into the on-top CO_{ad} and N_{ad} . Since the fulminate bands disappear in the

lower temperature interval (200–250 K) and the isocyanate band at 2220 cm^{-1} becomes stronger in the process, it is believed that an intramolecular rearrangement into the more stable NCO_{ad} precedes the yield of CO_{ad} and N_{ad} [11,13]:

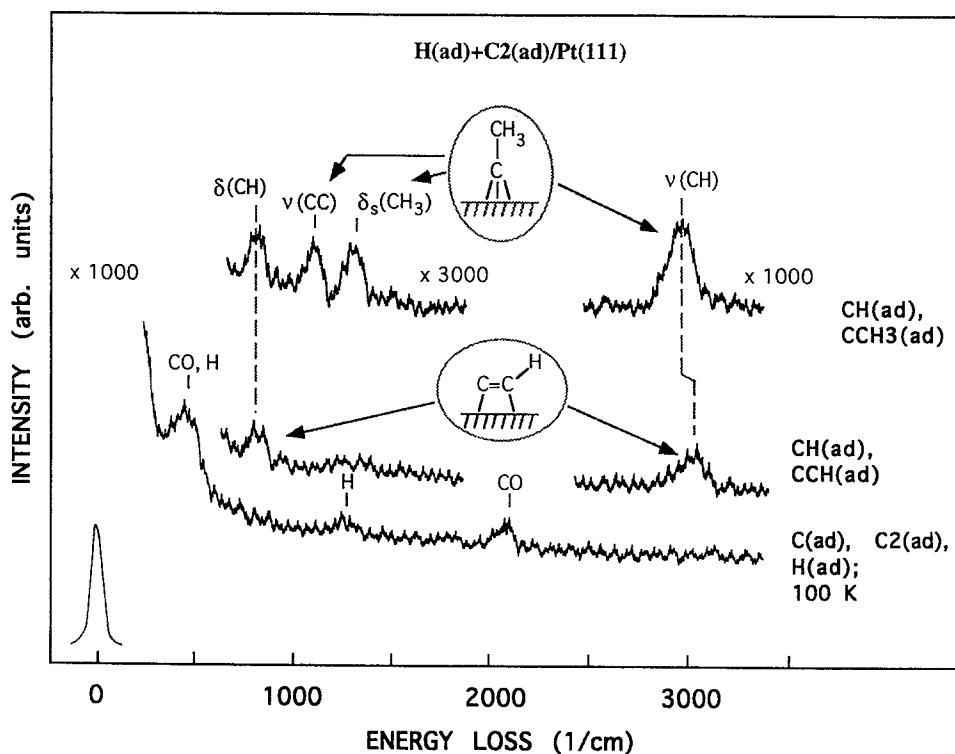
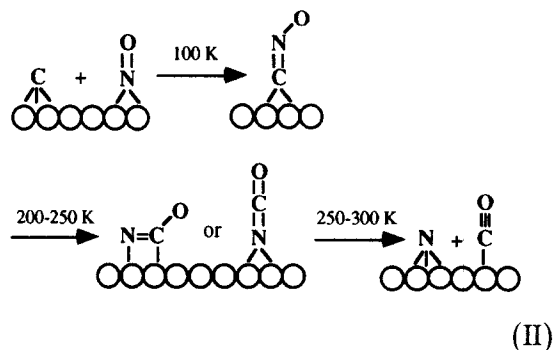
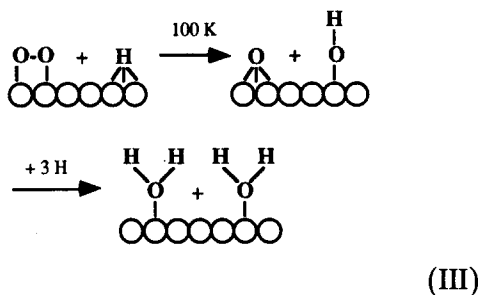


Fig. 4. The hydrogenation of $\text{C}_{2\text{ad}}$ molecules into ethylidyne $\text{CCH}_{3\text{ad}}$. The lowest spectrum is obtained after preparation of a mixed C_{ad} , $\text{C}_{2\text{ad}}$, H_{ad} layer by subsequent carbon evaporation up to $n_{\text{C}} \approx 8 \cdot 10^{14} \text{ cm}^{-2}$ and 1000 L exposure of hydrogen at 100 K. The middle spectrum is characteristic of ethynyl CCH_{ad} particles produced by partial dehydrogenation of ethylidyne at 550 K. The upper spectrum characterizes ethylidyne produced by heating of the mixed layer at 250 K or in hydrogenation of CCH_{ad} by 1000 L exposure of H_2 at 250 K.

3.3. $O_2 + H$

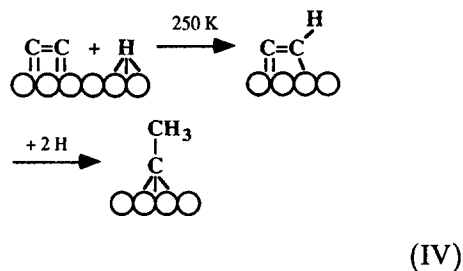
Molecular oxygen adsorbed on the Pt(111) was obtained under O_2 exposure of 6 L at 105 K, Fig. 3. The corresponding spectrum exhibits a variety of molecular states which can be defined by frequencies of the characteristic $\nu(OO)$ mode: a superoxide state O_{2ad}^{2-} $\nu(OO)$ at 1240 cm^{-1} [14]; some peroxide states O_{2ad}^{2-} which are distinct in their coordination to the surface, $\nu(OO)$ at 690 and 850–950 cm^{-1} [15]. A dissociative oxygen is also present: $\nu(PtO)$ at 490 cm^{-1} . A subsequent reaction with hydrogen at 105 K depletes essentially molecular oxygen (it concerns especially the O_{2ad}^{2-} state characterized by the $\nu(OO)$ losses at 850–950 cm^{-1}) and results in a reaction product H_2O_{ad} that is evidenced from the appearance of characteristic bands: the $\nu(OH)$ stretching at ≈ 3400 cm^{-1} and the $\delta(HOH)$ deformation at 1620 cm^{-1} . The $\nu(PtO)$ band becomes simultaneously stronger indicating that at the early stages of the reaction, the hydrogen atom adds to an O_{2ad}^{2-} molecule followed by the cleavage of the O–O bond yielding OH_{ad} and O_{ad} . The hydroxyl is not observed, since its characteristic bands [16,17] – $\delta(OH)$ at 725 and $\nu(OH)$ at 3500 cm^{-1} – are likely to be obscured by the intensive bands of water and oxygen. The reaction between molecularly adsorbed oxygen and atomic hydrogen can be imaged as follows:



3.4. $C_2 + H$

After evaporation onto the cooled Pt(111) ($T = 100$ K), carbon atoms have random distribution over the surface [5,18]. As indicated

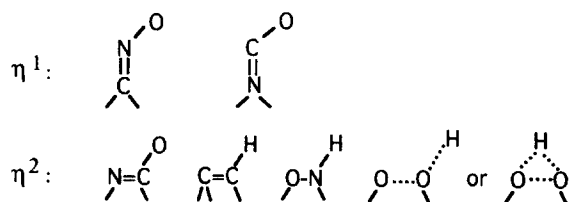
earlier, at low concentration ($n_C < 2 \cdot 10^{14}$ cm^{-2}) surface carbon is predominantly in the form of isolated adsorbed atoms C_{ad} . At higher concentration, $n_C > 5 \cdot 10^{14}$ cm^{-2} , clusters C_{nad} , for the most part C_{2ad} , appear in addition to C_{ad} . Fig. 4 shows the reaction between H_{ad} and C_{2ad} molecule. The lowest spectrum corresponds to a mixed adsorption layer of C_{ad} , C_{2ad} and H_{ad} prepared through the carbon evaporation up to $n_C \approx 8 \cdot 10^{14}$ cm^{-2} followed by the hydrogen exposure of 1000 L at 100 K. A weak loss at 2070 cm^{-1} appears because of minor CO contamination of $\approx 3 \cdot 10^{13}$ cm^{-2} . H_{ad} features two weak bands of $\nu(PtH)$ at 500 and 1240 cm^{-1} [19]. C_{2ad} reveals no detectable losses in the spectrum. A variety of hydrocarbon species is formed under heating of the mixed layer in the interval of 250–350 K; methine and ethylidyne particles are identified among them, CH_{ad} : $\delta(CH)$ at 800 and $\nu(CH)$ at 2975 cm^{-1} (for CD_{ad} : 590 and 2220 cm^{-1} , respectively), [5] CCH_{3ad} : $\nu(CC)$ at 1130, $\delta_s(CH_3)$ at 1370 and $\nu(CH)$ at 2975 cm^{-1} (for CCD_{3ad} : 1170, 1030 and 2220 cm^{-1} , respectively) [20]. The methine and ethylidyne molecules are known to be bonded to three platinum atoms via one carbon atom, and axes of the molecules are aligned along the surface normal [21]. The methine is formed in the reaction between atoms C_{ad} and H_{ad} . The ethylidyne is a product of the subsequent addition of three hydrogen atoms to one of two carbon atoms in C_2 molecule. An ethynyl CCH_{ad} is likely to be formed first. It is characterized by bands $\delta(CH)$ at 780, $\nu(CH)$ at 3040 cm^{-1} and by weak losses in the region of 1200–1400 cm^{-1} assigned to the $\nu(CC)$ stretchings [22] (the middle spectrum in Fig. 4).



4. Discussion

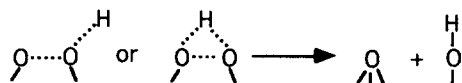
The results of this work show that at low temperatures a catalytic reaction can follow the molecular mechanism via a formation of a 3-atom surface intermediate. The following steps can be determined in this mechanism:

1. *The activation.* Molecules of certain reactants dissociate ($\text{H}_2_{\text{gas}} \rightarrow 2 \text{H}_{\text{ad}}$) and chemical bonds in other reactant molecules become weaker ($\text{NO}_{\text{gas}} \rightarrow \text{NO}_{\text{ad}}$) by the adsorption on the Pt(111) surface.
2. *The synthesis.* As a result of the direct interaction between an atom and a molecule located close together on the surface, a 3-atom intermediate appear in end-side (η^1 -) or side-on (η^2 -) configurations:



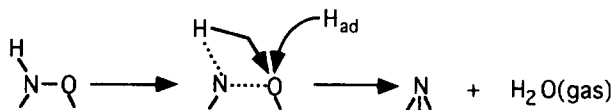
3. The further conversions of the intermediate can be realized in a variety of ways:

- 3.1. By *addition* of atoms to the intermediate (Eq. IV).
- 3.2. By *dissociation*



followed by the formation of the products (Eq. III). The dissociation can be preceded by *the intramolecular rearrangement* (Eq. II).

- 3.3. By *addition* of an atom followed by *dissociation*:



4.1. The reaction mechanism

The different properties of Pt(111) and Pt(100) [23] in the NO dissociation offer the different types of mechanism in the $\text{NO} + \text{H}_2$ reaction: the reaction follows the molecular mechanism via the HNO_{ad} intermediate on the (111) but the dissociative mechanism on the (100) (as outlined in Table 1).

The major distinction between these mechanisms is that the molecular mechanism, which is possible only on Pt(111), proceeds at low temperatures and seems to exhibit a low activation energy, whereas the dissociative mechanism requires a significant energy consumption for the breaking of chemical bonds and occurs at elevated temperatures.

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Table 1

The molecular and dissociative mechanisms compared

Pt(111), $T \approx 300 \text{ K}$ The molecular mechanism	Pt(100), $T > 385 \text{ K}$ [24] The dissociative mechanism
1. $\text{NO}_{\text{gas}} \rightleftharpoons \text{NO}_{\text{ad}}$	1. $\text{NO}_{\text{gas}} \rightarrow \text{NO}_{\text{ad}}$
2. $\text{H}_2_{\text{gas}} \rightleftharpoons 2\text{H}_{\text{ad}}$	2. $\text{H}_2_{\text{gas}} \rightleftharpoons 2\text{H}_{\text{ad}}$
3. $\text{H}_{\text{ad}} + \text{NO}_{\text{ad}} \rightarrow \text{HNO}_{\text{ad}}$	3. $\text{NO}_{\text{ad}} \rightarrow \text{N}_{\text{ad}} + \text{O}_{\text{ad}}$
4. $\text{HNO}_{\text{ad}} + \text{H}_{\text{ad}} \rightarrow \text{N}_{\text{ad}} + \text{H}_2\text{O}_{\text{gas}}$	4. $\text{N}_{\text{ad}} + 3\text{H}_{\text{ad}} \rightarrow \text{NH}_{3\text{ad}}$
5. $\text{N}_{\text{ad}} + 3\text{H}_{\text{ad}} \rightarrow \text{NH}_{3\text{ad}}$	5. $\text{N}_{\text{ad}} + \text{N}_{\text{ad}} \rightarrow \text{N}_{2\text{gas}}$
6. $\text{N}_{\text{ad}} + \text{N}_{\text{ad}} \rightarrow \text{N}_{2\text{gas}}$	6. $\text{O}_{\text{ad}} + 2\text{H}_{\text{ad}} \rightarrow \text{H}_2\text{O}_{\text{gas}}$

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