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HREELS characterization of hydrogen adsorption states on the Pt(100)-(hex) and (1×1) surfaces

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The adsorption states of hydrogen on Pt(100)-(hex) and (1×1) surfaces have been studied using TDS and HREELS in the temperature range of 170–330 K. Hydrogen atoms are shown to adsorb on the (1×1) surface in bridge and 4-fold hollow sites. On the (hex) surface hydrogen adsorption induces a partial lifting of the (hex) reconstruction with the consequent appearance of the bridge and 4-fold hollow states on (1×1) patches. Additional adsorption states appear due to the population of structural defects and patches of the (hex) phase.

Keywords: hydrogen adsorption, Pt(100), surface vibrations, thermal desorption, surface reconstruction

1. Introduction

The hydrogen adsorption on the reconstructed Pt(100)-(hex) and unreconstructed Pt(100)-(1×1) surfaces is the subject of numerous investigations. It has been shown that the rate of adsorption and limiting H_{ads} uptake depend strongly on the temperature and initial structure of the surface. At 300 K, once the adsorption occurs on the unreconstructed surface, a saturation H_{ads} concentration is 7.9×10^{14} cm^{-2} ($\theta_H \approx 0.6$ ML, 1 ML is defined as 1.28×10^{15} cm^{-2} – the density of Pt atoms in the (1×1) phase), whereas the reconstructed surface is populated to only a small extent of ca. 10^{14} cm^{-2} and seems to be restricted to defect sites [1,2]. The limiting uptake both on the (1×1) and (hex) surfaces builds up by lowering the temperature down to 150 K. As determined by nuclear microanalysis, the resulting concentration on both surfaces at 150 K is 1.54×10^{15} cm^{-2} ($\theta_H \approx 1.20$ ML) [3].

A LEED investigation evidences that the low-temperature adsorption on the (hex) surface is accompanied by the (hex) $\rightarrow$ (1×1) back reconstruction [1,3–6]. However, it has been established that the resulting surface does not constitute a perfect (1×1) phase, since it contains a great quantity of structural defects and the residual (hex) reconstruction remains as well [3–7].

Thermal desorption spectra obtained after the low-temperature hydrogen adsorption up to saturation on the reconstructed and unreconstructed surfaces have a complex structure and contain several low-temperature ($T_{des} < 300$ K) and high-temperature ($T_{des} > 300$ K) features [4,6,8–10]. All TD-features observed are originated from dissociative H_{ads} states [8]. After the (hex) surface has been saturated with H_{ads} at 150 K, six different desorption states have been detected at $T_{des} \approx 194$, 216, 237, 246, 336 and 377 K, labelled as γ_1, γ_2, γ_3, α_1, α_2 and α_3, respectively [9]. Basing on the work function measurements, it has been proposed that hydrogen atoms in the adsorption state revealing the highest desorption temperature occupy 4-fold hollow sites on the (1×1) patches, and H_{ads} penetrates deeply into the surface layer [6]. A nature of adsorption states corresponding to other TD-features has not been determined yet.

The aim of this work is to study the different H_{ads} states produced under the low-temperature hydrogen adsorption on the Pt(100)-(hex) and (1×1) surfaces using high resolution electron energy loss spectroscopy technique with a high sensitivity to the configuration of the adsorption state. A correspondence between the vibrational bands obtained for H_{ads}/Pt(100) and TD-features has been set up. To our knowledge, ref. [11] contains the only mentioning of the vibrations of hydrogen adsorbed on Pt(100) surface. It reports without assignment an in-specular band at 580 cm^{-1} possessed by H_{ads}.

2. Experimental

The experiments were performed in a VG ADES 400 spectrometer with a base pressure of 5×10^{-11} mbar or less. The HREELS studies were carried out with a monochromatic EMU 50 electron gun and a deflector type 150° hemispherical analyzer. The loss spectra were recorded under the specular conditions at an electron energy of ~ 2.5 eV and an incident angle of $\sim 35°$ with respect to the surface normal. FWHM (resolution) of the elastically reflected beam was about 9–11 meV ($\sim$ 70–90 cm^{-1}). The TD spectra were obtained by a VG QXK 400 quadrupole mass-spectrometer with a heating rate of 10 K/s.

The Pt single crystal was oriented within $< 0.5°$ of the (100) face. The crystal was spot-welded between two tantalum wires, thus allowing to heat it up to 1200 K by passing current through the wires. Circulation of the liquid nitrogen through a reservoir in thermal contact with the sample holder allowed the crystal to be cooled down to 170 K. The temperature was measured by a chromel–alumel thermocouple, spot-welded to the edge of the crystal. Cleaning procedure included Ar^+ etching and annealing in oxygen and in vacuum. The clean Pt(100) surface showed a sharp (5 × 20) pattern which is characteristic of the (hex) surface. The unreconstructed (1 × 1) surface was prepared using the following technique: (i) NO adsorption on the (hex) surface at 300 K up to saturation, (ii) annealing of the saturation adsorption layer in vacuum at 415 K in order to dissociate a portion of NO_{ads}, (iii) removal of surface oxygen and residual NO_{ads} via the reaction with hydrogen at 300 K, (iv) thermal desorption of hydrogen via flashing up to 365 K. The resulting surface shows a (1 × 1) diffraction pattern. The corresponding loss spectrum reveals a weak band at ~ 1450 cm^{-1} also observed when the (1 × 1) surface is prepared by a traditional technique of Bonzel et al. [12]. It has been shown elsewhere [13] that the band at ~ 1450 cm^{-1} is due to a minor NH_{2ads} contamination in an amount of 0.01 ML.

3. Results

Fig. 1 presents TD-spectra obtained after 20 L H_2 exposure (1 L = 10^{-6} mbar s) on the (hex) and (1 × 1) surfaces at 170 K. The shapes of the TD curves in fig. 1 are in good agreement with those reported in refs. [4,6,8–10]. After adsorption on the (hex) surface, six different desorption states can be identified at 210 (γ_1), 230 (γ_2), 255 (γ_3), 290–300 (α_1), ~ 350 (α_2) and 395 K (α_3). As distinguished from the (hex) surface, the TD-spectrum obtained after H_2 adsorption on the (1 × 1) surface does not contain the γ_1 and γ_3 peaks, but shows a much more intensive α_2 feature. The saturation hydrogen coverages on the (hex) and (1 × 1) surfaces evaluated from the areas under the corresponding TD-curves coincide with an accuracy of 5%. Once the adsorption layer prepared on the (hex) surface is heated up to 250 K, three low-temperature γ-features are eliminated from the TD-spectrum (fig. 1). After heating up to 330 K only the high-temperature α_3 peak remains. Under pre-heating of the adlayer prepared on the (1 × 1) surface at 325 K, only the α_2 and α_3 desorption states remain unchanged and appear in the TD-spectrum as the peaks at 365 and 402 K (fig. 1).

Fig. 2 presents a family of HREEL spectra after 20 L H_2 exposure on the reconstructed Pt(100)-(hex) surface at 170 K and after the subsequent heating in vacuum up to 250 and 330 K. The loss spectrum of H_{ads} at 170 K exhibits three bands at 555, 810 and 1260 cm^{-1}. The frequency of the first band is close to that reported for H_{ads} on Pt(100) in ref. [11]. The heating up to 250 K removes two low-frequency bands from the spectrum. The high-frequency band retains and shifts slightly down to 1230 cm^{-1}. Once the adlayer is heated up to 330 K, the band at 1230 cm^{-1} disappears. A weak band at

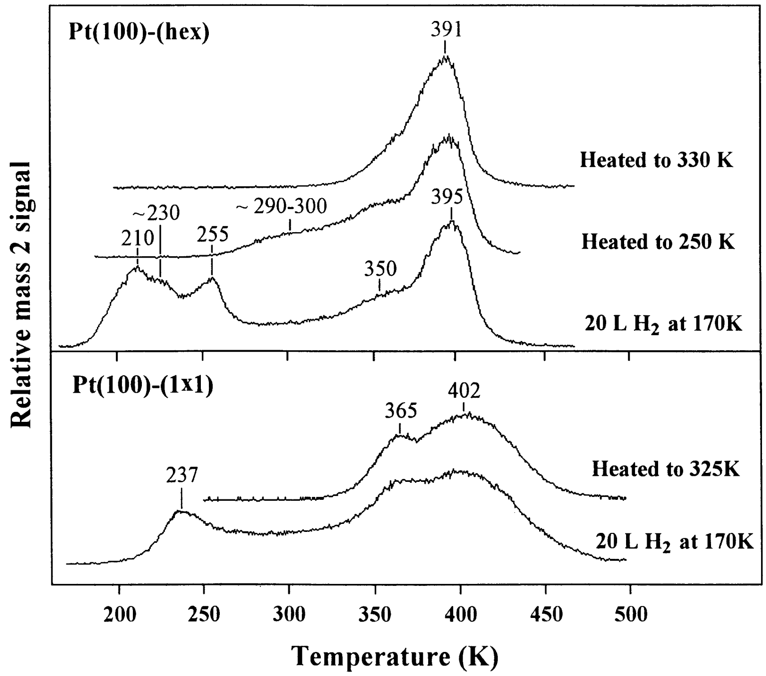

Fig. 1. Hydrogen TD-spectra obtained after 20 L H_2 exposure on the (hex) and (1 × 1) surfaces at 170 K and subsequent H_{ads} heating in vacuum up to the temperatures indicated. The heating rate is 10 K/s.

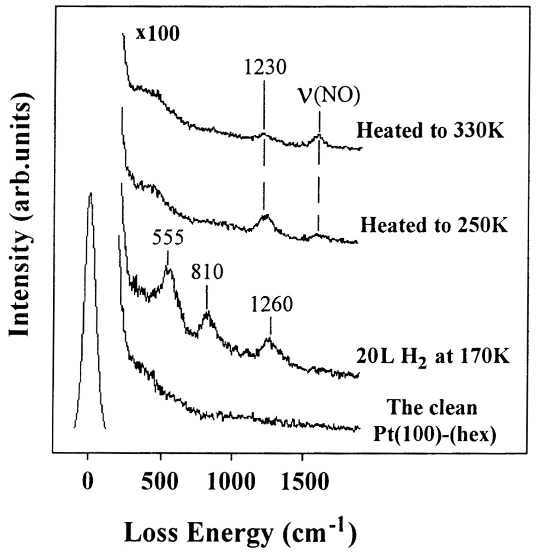

Fig. 2. HREEL spectra obtained after 20 L hydrogen exposure on the Pt(100)-(hex) surface at 170 K and subsequent H_{ads} heating in vacuum up to 250 and 330 K.

~ 1600 cm^{-1} and a weak feature in the range of ~ 350–500 cm^{-1} belong to the vibrational modes of nitric oxide contamination adsorbed from the background in the course of spectrum acquisition [14]. An intensity of the ν(NO) band at 1600 cm^{-1} corresponds to the nitric oxide coverage of ~ 10^{-3} ML or less [15].

In order to confirm the assignment of the above bands to the H_{ads} states, the loss spectrum was obtained after 20 L deuterium exposure on the (hex) surface at 170 K. Fig. 3 presents the loss spectra of the H_{ads} and D_{ads} layers prepared under the same conditions. It is obvious that the replacement of hydrogen for deuterium results in the red shift of the bands at 555, 810 and 1260 cm^{-1} down to 390, 605 and 935 cm^{-1}, respectively, as is expected in the case of vibrational modes involving the movement of hydrogen atoms.

Fig. 4 presents a family of HREEL spectra obtained after 20 L H_2 exposure on the unreconstructed Pt(100)-(1 × 1) surface at 170 K and after the subsequent heating in vacuum up to 300 and 340 K. The bottom spectrum corresponds to the clean Pt(100)-(1 × 1) surface as prepared by the procedure described under section 2. As has been established in ref. [13], the band at ~ 1450 cm^{-1} is due to NH_{2ads} species produced in amounts of ~ 0.01 ML by the NO + H_2 reaction during the (1 × 1) surface preparation. The frequency and intensity of this band remain unchanged in the experiment considered (fig. 4), and we believe that the NH_{2ads} particles exert no action on the H_{ads} layer. The hydrogen adsorption at 170 K results in the only additional band at 1230 cm^{-1}. The band undergoes the downward shift by ~ 40 cm^{-1}, once the adsorption layer is heated up to 300 K, and disappears completely after the heating up to 340 K. As before, the low-temperature feature in the range of ~ 350–500 cm^{-1} is due to the adsorption of NO and CO from background.

4. Discussion

4.1. *The basics for the interpretation of H_{ads} loss spectra*

The hydrogen atoms occupying adsorption sites of

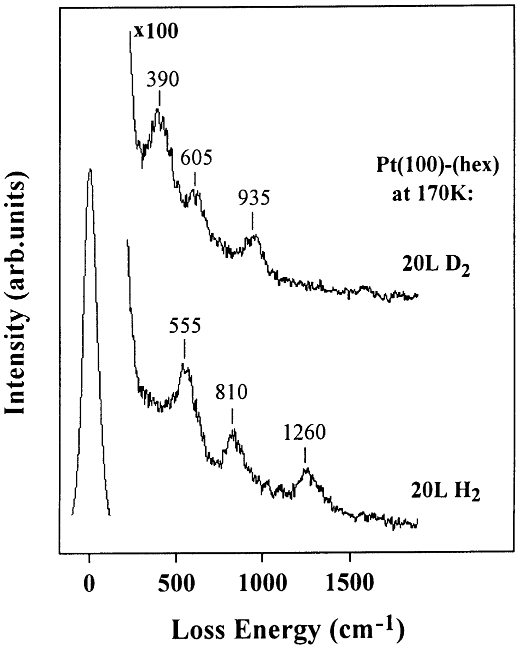

Fig. 3. HREEL spectra obtained after 20 L hydrogen and 20 L deuterium exposures on the Pt(100)-(hex) surface at 170 K.

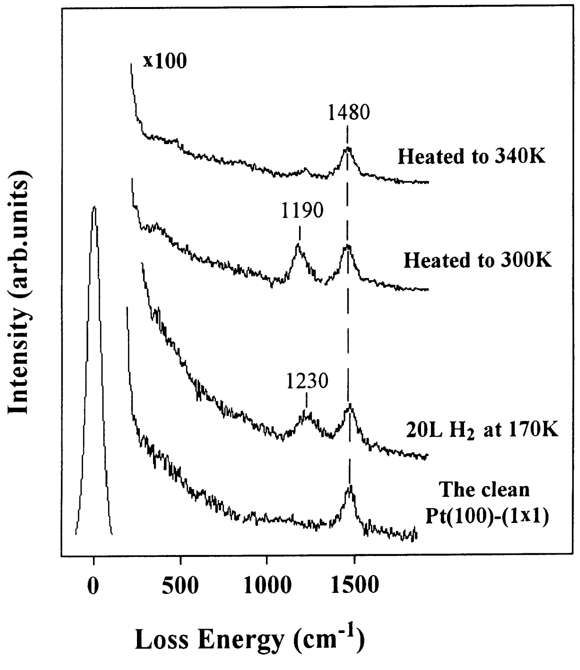

Fig. 4. HREEL spectra obtained after 20 L hydrogen exposure on the Pt(100)-(1 × 1) surface at 170 K and subsequent H_{ads} heating in vacuum up to 300 and 340 K.

the same type possess three fundamental vibrational modes. One of them, labelled as ν_{sym} or $\nu_{\perp}$, consists in the motion of hydrogen atoms normally to the surface and two other modes, labelled as ν_{as} or $\nu_{\|}$, present the motions parallel to the surface [16,17]. In accordance with the selection rules for a dipole mechanism of the inelastic electron scattering, solely the modes belonging to the total symmetric representation and possessing a non-zero dynamic dipole moment normal to the surface can be measured by HREELS [18], the inelastic intensity peaking strongly about the specular direction. The ν_{sym} band is the most intensive in the loss spectrum of the hydrogen adsorption layer acquired under specular conditions, since it belongs to the total symmetric representation and among all other modes it has the maximum normal component of the dynamic dipole moment. The ν_{as} modes are forbidden in the framework of "dipole selection rules" and interact with electrons via an impact scattering mechanism exhibiting very weak bands which, as a rule, can be observed solely under off-specular conditions [16,17,19].

Table 1 summarizes the frequencies of the ν_{sym} vibrational modes measured for hydrogen adsorbed on a variety of single crystal metal surfaces in three different adsorption sites: the 4-fold hollow, 3-fold hollow and 2-fold bridge ones. It is seen that the ν_{sym} frequency depends strongly on the structure of the adsorption site populated by H_{ads}, namely, it increases drastically as a number of surface platinum atoms bonded to the hydrogen atom (a coordination number) decreases. For hydrogen adsorbed in the 4-fold hollow site on fcc(100) surfaces, the band is observed in the range of 470–630 cm^{-1}. In spite of the wide scatter of the data obtained for H_{ads} populating the 3-fold hollow sites on fcc(111) and hcp(0001) surfaces, it might be concluded that the frequency of the ν_{sym} mode in this situation is higher and falls in the broad range of 550–1250 cm^{-1}. On the average, the bridge states exhibit higher ν_{sym} frequencies than the 3-fold hollow state (1030–1330 cm^{-1}). The ν_{sym} frequencies evaluated theoretically for the different H_{ads} coordination lie within the ranges determined above on the basis of the experimental approach [38,39].

As regards the hydrogen adsorption on platinum, the vibrational spectra were extensively studied for H_{ads} on Pt(111) surface: three bands were observed by HREELS at ~ 550, ~ 860–900 and ~ 1230 cm^{-1} [29,30] and the only band by IRAS at ~ 1250 cm^{-1} [31]. As it is indicated in table 1, the authors propose for H_{ads} the 3-fold hollow coordination, however, assign dissimilar bands to the ν_{sym} mode. The ν_{sym} frequency calculated theoretically for the 3-fold hollow H_{ads} state is equal to 1339 cm^{-1} [39,40]. In ref. [41] the vibrational bands observed in the experiment were reassigned, so that the band at ~ 860 cm^{-1} is suggested to be due to the ν_{sym} of the 3-fold hollow state. The bands at ~ 550 and ~ 1230 cm^{-1} are proposed to be associated with the bridge H_{ads} state, the high-frequency band being assigned to the ν_{sym} mode. Admittedly, at the moment there are no reliable unambiguous assignments of the vibrational bands for H_{ads} adsorbed on the Pt(111) face.

TD and HREEL spectra obtained in this work allow to set up a relation between the hydrogen desorption states and vibrational bands in the loss spectra (table 2). The low-temperature γ_1 and γ_3 desorption peaks, observed after adsorption exclusively on the (hex) surface, are related to the vibrational bands at 555 and 810 cm^{-1}. The γ_2, α_1 and α_2 desorption states escaping from the surface in the temperature range of 225–350 K appear under adsorption on both (hex) and (1 × 1) surfaces. They are responsible for the single vibrational band at 1190–1260 cm^{-1}. The frequency of the band depends on the initial surface structure and ratio between the γ_2, α_1 and α_2 states in the adlayer composition. The high-temperature α_3 desorption state provides no characteristic band in the loss spectrum acquired under specular conditions.

Using the data presented in table 1, we shall make an effort to assign the vibrational bands observed in this

Table 1
The ν_{sym} mode frequencies measured for hydrogen adsorbed on a variety of single-crystal metal surfaces in the 4- and 3-fold hollow and bridge states

4-fold hollow			3-fold hollow			Bridge		
surface	ν_{sym} (cm^{-1})	ref.	surface	ν_{sym} (cm^{-1})	ref.	surface	ν_{sym} (cm^{-1})	ref.
Ni(100)	530–630	[20]	Ni(111)	1120	[17]	Rh(100)	1330	[33]
Ni(510)	470	[21]	Ru(001)	1140	[24]	Ni(510)	1110–1145	[21]
Rh(100)	660	[22]		685, 1140	[25]	Fe(110)	1060	[19]
Pd(100)	510	[23]	Rh(111)	1100	[26]	Cu(111)	1040	[34]
			Ir(111)	560	[27]	W(100)	1050	[17,35]
			Pd(111)	1000	[28]		1260–1300	[36]
			Pt(111)	905	[29]	Mo(100)	1200–1220	[36]
				550	[30]		1030, 1125	[37]
				1255	[31]			
			Ag(111)	820–855	[32]			

Table 2
The correlation between the desorption temperatures and frequencies of the vibrational bands measured after the hydrogen adsorption on the Pt(100)-(hex) and (1 × 1) surfaces

Desorption states labelled in terms of ref. [9]	Appearance on the (1 × 1) surface	Appearance on the (hex) surface	T_{des} (K)	Frequencies of the vibrational bands (cm^{-1})	Proposed adsorption site
γ_1	−	+	210		adsorption on defects
γ_3	−	+	255	555, 810	and/or (hex) patches
γ_2	+	+	225–240		bridge site on the
α_1	+	+	290–300	1190–1260	(1 × 1) phase
α_2	+	+	~ 350		
α_3	+	+	390–400	no bands	4-fold hollow site on the (1 × 1) phase

work and elucidate the location of hydrogen atoms adsorbed on the Pt(100) surfaces.

4.2. The hydrogen adsorption on Pt(100)-(1 × 1) surface

First we consider the more simple case of the adsorption on the unreconstructed Pt(100)-(1 × 1) surface. The adsorption state escaping from the surface in the temperature range of 225–350 K as the γ_2, α_1 and α_2 TD features shows in the loss spectrum the only band that shifts downward from 1230 to 1190 cm^{-1} with decrease in the H_{ads} coverage. The structure of the (1 × 1) surface provides the following adsorption sites of a high symmetry: the 4-fold hollow site (C_{4v} point group symmetry), bridge site (C_{2v}) and on-top site (C_{4v}). The last-named configuration is unusual for the hydrogen atoms adsorbed on the metal surfaces. The comparison of the frequency obtained in this work with those summarized in table 1 indicates that the bridge H_{ads} state is responsible for the ν_{sym} band at ~ 1200 cm^{-1}.

We have failed to observe under specular conditions the vibrational bands peculiar to the most high-temperature α_3 peak that is conventionally identified with the 4-fold hollow state [6]. It is believed that the H_{ads} atom positioned between four platinum atoms penetrates deeply into the surface layer [6]. Therefore the dynamic dipole moments attendant to the vibrational motion of the hydrogen atoms are effectively screened from the interaction with the electron beam by the surrounding platinum atoms, and because of this the corresponding bands do not appear in the in-specular loss spectrum. The examination of the hydrogen adsorbed on the surfaces of platinum catalysts (Pt/SiO_2, Pt in Y-zeolite, Raney Pt) with neutron inelastic scattering that has no selection rules reveals some vibrational bands, among which the band observed in the range of 580–645 cm^{-1} has been attributed to the ν_{sym} mode of hydrogen adsorbed in the 4-fold hollow site on (100)-oriented facets [42].

Thus, on the strength of these data we suggest that hydrogen on the unreconstructed Pt(100)-(1 × 1) surface can populate sites of two types, the 4-fold hollow and bridge ones. The results obtained do not allow to conclude unambiguously whether these two states coexist in the saturation H_{ads} layer after the 170 K adsorption or the adlayer includes solely the bridge state and the hollow state appears only after the removal of a quantity of bridge hydrogen under heating. A portion of the bridge state escapes from the surface as the low-temperature γ_2 peak at 237 K, probably, due to the repulsion between adatoms in the dense H_{ads} layer. As θ_H coverage decreases, the interaction between adatoms reduces which seems to be responsible for the downward shift of the bridge ν_{sym} band.

4.3. The hydrogen adsorption on Pt(100)-(hex) surface

Let us turn to the adsorption on the reconstructed Pt(100)-(hex) surface. First, it should be noted that the adsorption states peculiar to the (1 × 1) surface – the 4-fold hollow and bridge states – reveal themselves after the adsorption on the (hex) surface. Based on the LEED measurements, it is well-known that the hydrogen adsorption at $T < 250$ K lifts partially the (hex) reconstruction and, therefore, a great portion of H_{ads} populates the resulting (1 × 1) patches. Numerous evidences show that after the low-temperature hydrogen adsorption the surface contains a great deal of structural defects and, perhaps, the patches retaining the initial (hex) structure [3,6,7]. As has been shown by scanning tunneling microscopy in the case of the (hex) → (1 × 1) phase transition induced by the NO or CO adsorption [43–45], the structural defects like monoatomic steps and kinks are created due to the 20% difference in the atomic densities between two surface phases. The low-temperature γ_1 and γ_3 peaks and the vibrational bands at 555 and 810 cm^{-1} appear after the hydrogen adsorption solely on the (hex) surface and are evidently attributed to the population of the adsites on the defects or/and (hex) patches. The bands at 555 and 810 cm^{-1} can be assigned to two different H_{ads} states. However, the low symmetry of the adsorption state configuration anticipated at the occupation of the defect site by hydrogen atom can cause more than one vibrational mode allowed for each individual adsorption state; that is, both bands considered can belong to the only adsorption state positioned on the structural defect.

In order to evaluate the combined hydrogen coverage on the defects and (hex) patches, $\theta_H^{def} + \theta_H^{hex}$, the amount of the hydrogen desorbed as the low-temperature γ_i peaks following the 170 K adsorption on the (hex) and (1×1) surfaces were determined from the areas under the corresponding TD curves, S_γ^{hex} and $S_\gamma^{1\times1}$ (the bottom spectra in fig. 1). If it is admitted that the γ_2 desorption state originated from the bridge H_{ads} on the (1×1) phase makes an equal contribution to both surfaces then the low limit of $\theta_H^{def} + \theta_H^{hex}$ can be estimated from the $S_\gamma^{hex} - S_\gamma^{1\times1}$ difference. For the saturation hydrogen layer prepared under adsorption on the (hex) surface, the population of the defects and (hex) patches constitutes ca. 20% of the total H_{ads} coverage, or ~ 0.25 ML.

5. Conclusion

The 170 K adsorption of hydrogen on the unreconstructed Pt(100)-(1×1) surface populates two types of adsites – the 4-fold hollow and bridge sites. Hydrogen desorbs from the bridge state as γ_2, α_1 and α_2 TD features in the temperature range of 240–350 K. The bridge H_{ads} state exhibits in HREEL spectrum the characteristic band of the ν_{sym} vibrational mode at ~ 1200 cm^{-1}. The 4-fold hollow H_{ads} state escapes from the surface as the sharp peak with a maximum near 400 K. No characteristic bands which could be attributed to the hollow state have been observed by HREELS under specular conditions. The hydrogen atom in the hollow state is believed to penetrate deeply into the surface layer and therefore its dipole moment is effectively screened from the interaction with the electron beam by the dipole scattering mechanism.

The 170 K adsorption of hydrogen on the reconstructed Pt(100)-(hex) surface yields the 4-fold hollow and bridge states owing to the population of the (1×1) patches arising as a result of the (hex)→(1×1) back reconstruction. The adsorption on the (hex) surface produces additionally one or two further H_{ads} states which are responsible for the γ_1 and γ_3 peaks in TDS and two vibrational bands at 555 and 810 cm^{-1} in HREELS. These states are not observed after adsorption on the (1×1) surface and therefore are proposed to be due to the population of the residual (hex) patches and defects created in the course of the (hex) → (1×1) transition. For the saturation hydrogen layer, ca. 20% of the total H_{ads} amount occupies the defects and (hex) patches.

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