

Effect of NO on D₂ adsorption on the Pt(100)–(hex) surface

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Abstract

The influence of NO on the adsorption of D₂ on the Pt(100)–(hex) surface was studied by means of temperature-programmed reaction (TPR). Deuterium adsorbs negligibly on Pt(100)–(hex) at $T = 270$ K, whereas an addition of a small amount of NO to D₂ increases drastically the adsorption capacity of Pt(100)–(hex) towards deuterium. The same phenomenon was observed on the surface pre-covered with NO_{ads} as well. As the NO_{ads} pre-coverage increases, the uptake of D_{ads} first increases, then reaches a maximum at $\theta_{\text{NO}} \approx 0.25$ ML, and finally falls down to zero for the NO_{ads} saturated layer.

The following explanation is supposed. Upon adsorption on the Pt(100)–(hex) surface, NO lifts the (hex) reconstruction and forms the dense NO_{ads}/(1 × 1) islands surrounded by the clean (hex) surface. A limited area of the (hex) phase, which is immediately adjacent to the boundaries of the NO_{ads}/(1 × 1) islands, is supposed to be distorted and could be able to adsorb deuterium. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Pt(100); Deuterium adsorption; TPR; NO; D₂

1. Introduction

The reaction between NO and H₂ on the Pt(100) surface is a subject of numerous studies [1]. In pursuit of a better understanding of the kinetics and mechanism of this reaction, it is necessary to have a solid background knowledge of the adsorption and desorption phenomena of each of the individual reactants and products. The adsorption of H₂ and NO has been subject of considerable research interest in the past [2–7].

As shown in Refs. [2,3], the adsorption of H₂ on the Pt(100)–(hex) surface depends strongly

on the temperature and pressure, and is accompanied by the (hex) → (1 × 1) back reconstruction. The H_{ads} coverage at 300 K and pressure of 6×10^{-8} mbar reaches 0.1 ML¹ [2,4], and likely, is restricted by the amount of defect sites. On the other hand, the adsorption-induced (hex) → (1 × 1) back reconstruction, which takes place at low temperatures or high H₂ pressures, leads to the increase of the saturated H_{ads} coverage up to 0.6 ML at 300 K [2] and up to 1.2 ML at 150 K [5]. NO adsorbs readily on the Pt(100)–(hex) surface and locally lifts the (hex) reconstruction at < 380 K [6]. The

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¹ A 1 monolayer (ML) is equal to the number of platinum atoms of the topmost layer of the unreconstructed (1 × 1) surface, $1.28 \times 10^{15} \text{ cm}^{-2}$.

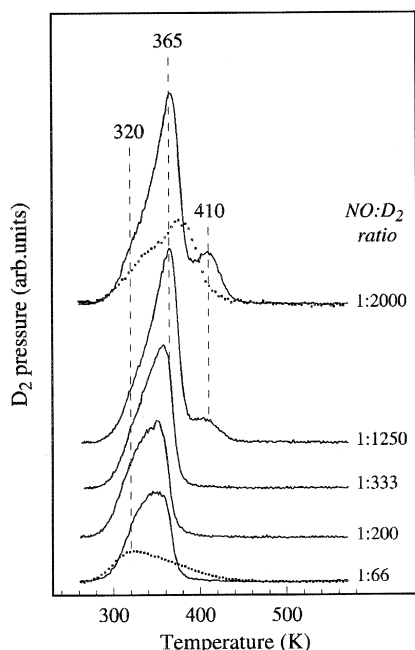


Fig. 1. TPR spectra of deuterium taken after an exposure of the Pt(100)–(hex) surface to mixtures with different NO/D₂ ratio at 270 K, $P_{\text{NO}} = 8 \times 10^{-10}$ mbar for 500 s. TPR spectra shown by dotted lines were taken after corresponding exposures of pure D₂.

NO-induced (hex) \rightarrow (1 \times 1) back reconstruction results in the formation of NO_{ads}/(1 \times 1) islands on the unreconstructed patches surrounded by the clean hexagonal phase [7].

Little information is known on the mutual influence of NO and H₂ upon adsorption on the Pt(100)–(hex) surface. It is remarkable that the H₂ + NO reaction proceeds at temperatures where hydrogen practically does not adsorb on Pt(100)–(hex). The present work is aimed to considerate an effect of NO on the adsorption of D₂ on the Pt(100)–(hex) surface.

2. Experimental

The experimental system was described in details elsewhere [8]. Shortly, the experiments were carried out in an UHV chamber of an ADES-400 electron spectrometer. Temperature-programmed reaction (TPR) spectra were obtained by means of a VG QXK 400 quadru-

pole mass spectrometer at a heating rate of 10 K/s. The clean Pt(100) surface exhibits a (5 \times 20) LEED pattern, which characterizes the reconstructed (hex) surface. D₂ and ¹⁵NO were used for the TPR experiments in order to increase the reliability of the identification of the products by mass spectrometry.

3. Result

Fig. 1 shows TPR spectra of D₂ taken after an exposure of the Pt(100)–(hex) surface to mixtures with different NO/D₂ ratio (solid lines) and to pure D₂ (dotted lines) at 270 K. The addition to D₂ of small amount of NO results in the significant increase in area of the D₂ TD-curve and in the change of its shape. One should bear in mind that some amount of D_{ads} is consumed upon TPR with NO, yielding D₂O and N₂ (TPR spectra not shown here), and therefore, does not contribute to the TD-peak of D₂. The peak at 410 K in two upper curves corresponds to deuterium atoms adsorbed in fourfold hollow sites on the unreconstructed (1 \times 1) phase [9,10].

In order to understand such strong effect of NO on the adsorption of D₂, TPR spectra of D₂

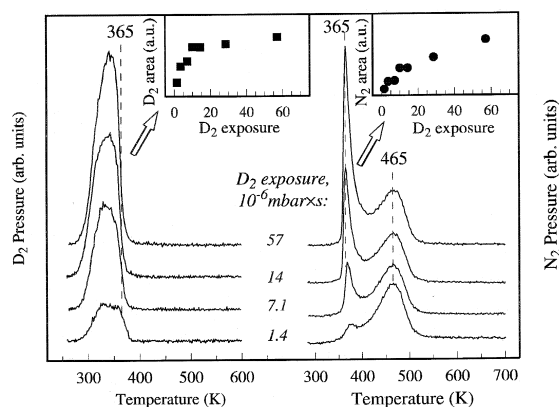


Fig. 2. TPR spectra of deuterium (left panel) and nitrogen (right panel) taken after an exposure of the Pt(100)–(hex) surface pre-covered with 0.2 ML of NO_{ads} to D₂ at pressure of 5.7×10^{-8} mbar. The left and right insets show the areas of deuterium peak and the first “explosive” peak of N₂ as function of D₂ exposure.

and N_2 were taken after D_2 adsorption at 270 K on the Pt(100)–(hex) surface pre-covered with 0.2 ML of NO_{ads} as shown in Fig. 2. D_2 desorbs as a single peak with sharp back front. The desorption of D_2 precedes the reaction between D_{ads} and NO_{ads} and stops abruptly at the onset temperature of the «explosive» evolution of N_2 (right panel) and D_2O (spectra not shown here) at ~ 365 K. This phenomenon is usually referred to in the literature as «surface explosion» and results from an autocatalytic behavior of the surface reaction [11]. The second broad TD-peak of N_2 at 465 K is characteristic of NO_{ads} dissociation [12]. The areas under the «explosive» peaks of N_2 and the peaks of D_2 as a function of D_2 exposure show the similar behavior; the areas increase with D_2 exposure and flatten out at D_2 exposure of 1.4×10^{-5} mbar \cdot s (insets of Fig. 2).

Fig. 3 shows the TPR spectra of N_2 taken after an exposure of the NO_{ads} layers with dif-

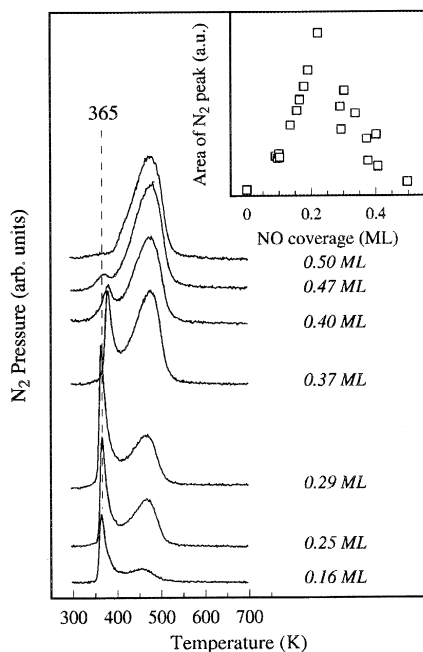


Fig. 3. TPR spectra of N_2 taken after an exposure of NO adsorption layers on the Pt(100)–(hex) surface to D_2 (1.4×10^{-5} mbar \cdot s) at pressure of 5.7×10^{-8} mbar. NO pre-coverages are shown to the right of spectra. The inset represents the area of the first «explosive» peak of N_2 as function of NO pre-coverage.

ferent pre-coverages to 1.4×10^{-5} mbar \cdot s of D_2 . The area under the «explosive» peak of N_2 as a function of the NO_{ads} pre-coverage shown in the inset of Fig. 3 passes through the maximum at ≈ 0.25 ML and falls down to zero at the saturated NO_{ads} coverage. The amount of desorbed D_2 as a function of NO_{ads} coverage demonstrates the same behavior.

4. Discussion

The following model could be offered for the explanation of the observed phenomena. The adsorption of NO on the Pt(100)–(hex) at 270 K locally induces the (hex) \rightarrow (1×1) back reconstruction and results in the formation of the dense $NO_{ads}/(1 \times 1)$ islands [7]. Since D_2 does not adsorb over a saturated NO_{ads} layer on Pt(100)–(hex), deuterium cannot incorporate inside the dense $NO_{ads}/(1 \times 1)$ islands. It is expected that D_2 cannot adsorb on the surrounding (hex) phase too. It is believed that the structure of limited areas of the (hex) phase, which are immediately adjacent to the boundaries of the islands, is distorted in such a way that it could offer a possibility for D_2 adsorption. This supposition is in agreement with the experimental fact. In the beginning, while an average size of the island increases with θ_{NO} [13], the distorted area increases too, creating more space for D_2 adsorption. However, as the $NO_{ads}/(1 \times 1)$ islands continue to grow, at some moment, the distorted areas start to overlap, resulting in the deuterium uptake decreasing.

Acknowledgements

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