ELSEVIER

Study of H_2, O_2, CO adsorption and $CO + O_2$ reaction on Pt(100), Pd(110) monocrystal surfaces

V.V. Gorodetskii [a,*], A.V. Matveev [b], P.D. Cobden [c], B.E. Nieuwenhuys [c]

[a] *Boreskov Institute of Catalysis, Russian Academy of Sciences, Prospect Lavrentieva 5, Novosibirsk, 630090 Russia*
[b] *Novosibirsk State University, Novosibirsk 630090, Russia*
[c] *Leiden Institute of Chemistry, P.O.Box 9502, 2300 RA Leiden, The Netherlands*

Abstract

Nanoscale changes in the surface morphology of Pd particles that accompany the uptake of hydrogen have been studied in situ by Field Electron Microscopy (FEM). Exposure of a Pd tip to H_2 at low temperatures led to the formation of extruding PdH_x particles on top of the Pd tip. Growth of these particles proceeds in a "staccato" manner. When most of the hydrogen have been removed from the sample by heating in vacuum, Pd crystallites remain on the surface. They are quite stable up to about 700 K, where they melt back into the bulk of the tip. A sharp low temperature H_2-peak (220 K) appears in the TD spectra as a result of decomposition of PdH_x hydrides on Pd(110) single crystal surface. During the $O_2 + H_{ads}$ reaction, a hydrogen-modified Pt(100)-(hex) surface shows an increase in the population of atomic oxygen states: three O_{ads} states are observed by high resolution electron energy loss spectroscopy (HREELS) as a result of the presence of defect sites. The reactivity of these new oxygen states to CO has been investigated with thermal desorption spectroscopy (TDS). © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Subsurface hydrides; Platinum metals; CO oxidation

1. Introduction

CO and H_2 oxidation on the platinum group metals (Pt, Pd) have been considered for a long time as a catalytic model reaction. Various phenomena of non-linear dynamics (oscillations, chemical waves) have been observed with single crystals [1] as well as with sharp field emitter tips (< 1000 Å) [2,3]. Mechanisms of these oscillations are connected with the surface reconstruction (Pt(100): (hex) $\Leftrightarrow$ (1 × 1)) or associated with subsurface oxygen formation (Pd(110)): $O_{ads} \Leftrightarrow O_{sub}$).

Since the first discovery of a relationship between reconstruction and kinetic oscillations in CO oxidation on Pt(100) by Ertl [1], this surface has become one of the most extensively investigated oscillatory systems in heterogeneous catalysis. The packing density of the upper layer of the reconstructed Pt(100)-(hex) surface is known to be higher by 20% than that of the non-reconstructed Pt(100)-(1 × 1) surface. According to STM data [4], the phase transition of the Pt(100)-(hex) → (1 × 1) surface initiated by CO molecular adsorption or dissociative hydrogen adsorption causes the excess of Pt atoms

* Corresponding author. Fax: +7-3832-343056.
E-mail address: gorodetsk@catalysis.nsk.su (V.V. Gorodetskii).

to be ejected out over the layer of the metal. This is accompanied by an increase in the oxygen sticking coefficient from $\approx 10^{-3}$ (hex) to $\approx 10^{-1}$ (1×1), thus inducing a transition from a catalytically inactive state into an active state with a high sticking coefficient for oxygen.

The adsorption of H_2 on Pt and Pd is of fundamental importance to the understanding of catalytic hydrogenation reactions. The H/Pd system is a unique one in the membrane catalysis due to its ability to form metallic hydrides. Two non-stoichiometric (α and β) hydride phases can co-exist below the critical temperature ($\sim 300°C$). There are large changes in volume going from the α- to the β-phase; the lattice constant increases by $\sim 3.3\%$, volume increase of the order of $\sim 11\%$. These changes occur continuously over the phase transition. It is surprising that only a few studies have focused on the structural changes occurring at the surface under the strain of the expanding lattice. Triangular shapes have been seen to develop during the early stages of hydrogen loading of a Pd(111) single crystal. These structures have sizes of the order of 10–20 μm [5].

The existence of these two different groups of morphological changes of the catalyst metal surface due to the strong adsorption of reactants can be connected with the different kinds of surface defects, which appear as a result of (i) the lattice parameter changes at Pd $\rightarrow$ PdH$_x$ hydride synthesis or (ii) the variation of the atomic density in the topmost layer of the metal surface during Pt(100)-(hex) $\Leftrightarrow$ (1×1) phase transition. The fact that surface defects have a pronounced influence on the rate of O_2 adsorption may also alter the conditions for the occurrence of rate oscillations. Since Taylor [6] proposed the concept of active centers in heterogeneous catalysis, a variety of methods have been developed to characterize their properties.

In this work the role of surface defects in the adsorption behaviour of H_2, O_2 and CO on Pd(110), Pt(100) single crystal surfaces have been studied by high resolution electron energy loss spectroscopy (HREELS), and thermal desorption spectroscopy (TDS). The growth of subsurface hydride particles has been investigated *in situ* on Pd tips by Field Electron Microscopy (FEM).

2. Experimental

HREELS, TDS, FEM experiments were performed in different UHV chambers (base pressure $< 5 \times 10^{-11}$ mbar). The energy loss spectra (VG ADES 400 electron spectrometer) were obtained under the specular direction at an electron energy of ~ 2.5 eV and an incident angle of $\sim 35°$ with respect to the surface normal. The resolution of the elastically reflected beam was about 9–11 meV (~ 70–90 cm^{-1}). The TD spectra were measured by a quadrupole mass spectrometer using a heating rate of 6–10 K/s. The cleaning procedure of the Pt(100) and Pd(110) surfaces included Ar$^+$ etching and annealing cycles in oxygen and in vacuum. The structure of the clean Pt(100)-(hex) and Pd(110) surfaces were confirmed by LEED. The experimental setup is described in detail in Ref. [7]. The FEM experimental device on the sharp field emitter tips is described in detail in Ref. [2].

3. Results and discussion

3.1. Formation and decomposition of Pd surface hydride particles: FEM and TDS

3.1.1. FEM

The uptake of H_2 during exposure at 147 K at a pressure of 2×10^{-4} Torr by a Pd tip as viewed by FEM, is shown in Fig. 1. Fig. 1a is characteristic of a clean Pd tip. Fig. 1b shows the growth of high emission intensity patches first around (551) surfaces and then on the very open (320) surfaces (hydride particles synthesis). The final image, Fig. 1c, represents the situation at saturation; above this dosing no further changes in the images were observed. Since the work function and HREEL spectra measure-
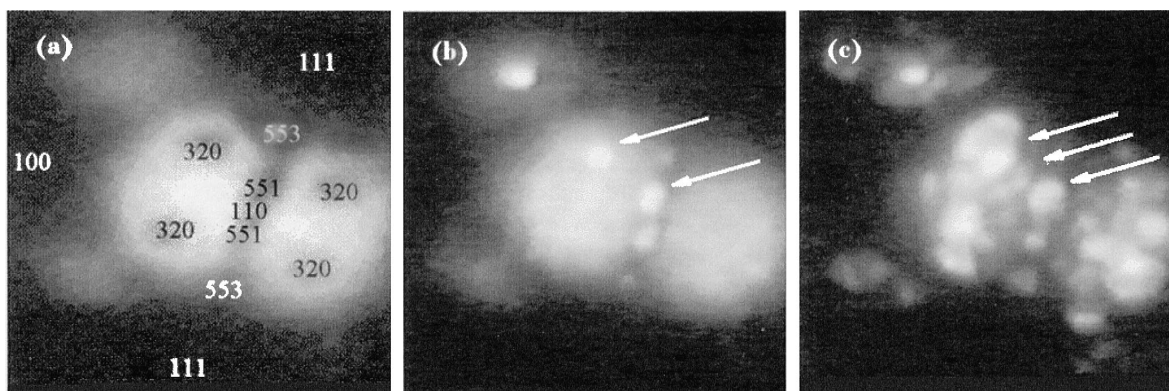
Fig. 1. (a) A clean palladium tip, showing the disposition of the principal planes. (b–c) After hydrogen adsorption at 147 K: (b) exposure 780 L; (c) exposure 2×10^4 L.

ments are insensitive to the H_{sub} [8], the PdH_x microcrystal growth as observed by FEM is due to the field enhancement factor. The shape of most of the particles is either rectangular or triangular. The latter has been seen on a larger scale on the Pd(111) surface [5]. On heating the tip in vacuum up to 500 K, the majority of the hydrogen desorbs from palladium ∼ 200 K with appearance of a fast surface wave due to decomposition of the *hydride particles*, but many of the structures formed on the surface at 147 K remain intact. At 700 K, these crystallites disappeared, the obvious interpretation being that the Pd atoms are now becoming mobile and the Pd microcrystals are melting back into the tip. Therefore, it is possible to conclude that the patches left on the surface at this point are microcrystals of Pd on top of the Pd tip.

3.1.2. TDS

TDS of hydrogen from macroscopic Pd(110) single crystal surface obtained after various exposures to hydrogen at 135 K are shown in Fig. 2a. There are two desorption states. The α state (220 K) originates from hydride decomposition, and the β state (265 K) results from recombination of chemisorbed atomic hydrogen. The results are in agreement with recently published data [8]. At 5×10^{-4} Torr, only the β state is formed with a H_{ads} coverage up to $\theta = 1$ ML (monolayer). For a pressure of 2×10^{-3} Torr,

the α low temperature state appears with a H_{ads} coverage up to 1.5 ML. As the pressure increases up to 1.2×10^{-2} Torr, further hydrogen absorption ($\theta = 12$ ML) is possible, where the excess of hydrogen atoms are incorporated into subsurface hydride. Our results, illustrated in Fig. 2b, demonstrate that at 135 K the hydride is readily synthesised under a critical hydrogen pressure. The driving force for phase transition $Pd \rightarrow PdH_x$ at critical point is thermodynamics [9].

A comparison between FEM and TDS shows that the sharp α peak occurs simultaneously with the surface wave of the subsurface hydride
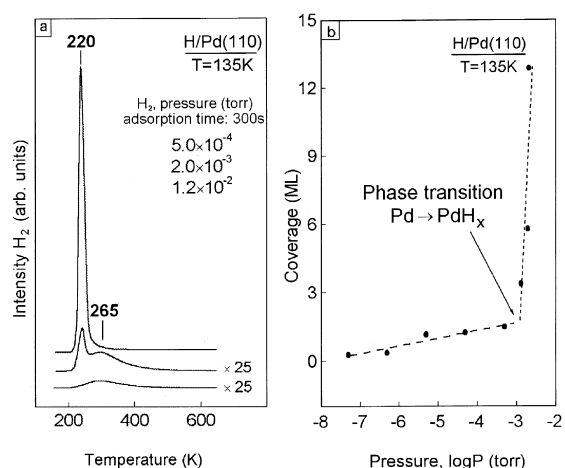

Fig. 2. (a) Series of TD spectra of hydrogen from a Pd(110) surface obtained after adsorption at 135 K. (b) Variation of the H coverages with hydrogen pressure.

decomposition. One of the questions that remains is whether the structures formed on the surface under H_2 dosing at lower temperature also contain hydrogen, or are they pure Pd crystals on the top of surface hydride. The staccato growth of particles shows that the structures are actually PdH_x crystallites at low temperature.

3.2. Modifier effect of defects on the adsorption properties and reactivity of Pt(100) with respect to H_2 and O_2

At 300 K, no hydrogen could be adsorbed on the reconstructed Pt(100)-(hex) surface [10]. At $T < 300$ K, H_2 adsorption leads to characteristic changes in the surface structure: the (hex) $\rightarrow$ (1 × 1) back reconstruction is observed. However, it has been established that the obtained $H/(1 × 1)$-like structure does not constitute a perfect (1 × 1) phase, since it contains a certain concentration of structural defects and residual (hex) patches remaining as well on the surface [11]. Fig. 3a shows the TD spectrum of hydrogen adsorbed on the (hex) surface at 90 K. The H_2 spectrum after 20-L exposure is similar to those published in literature [12]: four peaks are easily recognized at 190, 240, 350 and 380 K. After

heating up to 220 K, the two low-temperature peaks disappeared. The loss spectrum of hydrogen at 90 K exhibits three bands at 555, 820 and 1260 cm^{-1}. Annealing at 220 K leads to a decrease in intensity of the two low-frequency bands. According to our study reported in Ref. [10], the low-temperature desorption peaks (190 K, 240 K), which are related to the two low-frequency bands at 555 and 820 cm^{-1}, result due to the population of the residual (hex) patches and defects created in the course of the (hex) $\rightarrow$ (1 × 1) phase transition. The concentration of the defect sites and (hex) patches for saturated H_{ads} layer at 90 K (~ 1.2 ML) corresponds to ca. 20% of the total hydrogen layer. It has been proposed that the bands at 555 and 1260 cm^{-1} are associated with the bridge H_{ads} state [10].

Fig. 4b presents a family of HREEL spectra of an atomic oxygen layer formed after 3 L NO exposure on the non-reconstructed Pt(100)-(1 × 1) surface at 300 K with the temperature increasing up to 500 K for NO_{ads} desorption and after titration reaction $O_2 + H_{ads}/Pt(100)$-(hex) at 220 K. The band at 540 cm^{-1} represents $\nu(PtO)$ stretching of adsorbed atomic oxygen as a result of NO dissociation on defect sites. For comparison, on the flat Pt(111) surface, a single
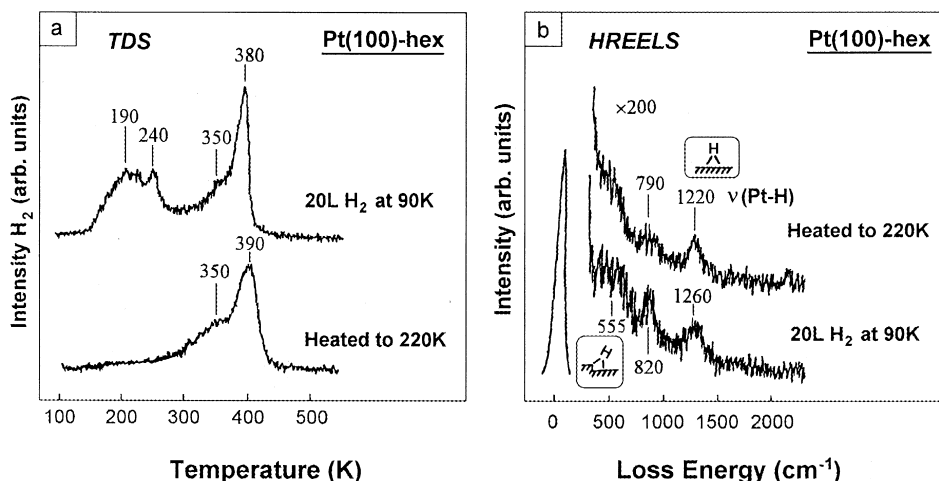

Fig. 3. (a) Hydrogen TD spectra obtained after an exposure of a 20 L H_2 on the Pt(100)-(hex) surface at 90 K and subsequent heating in vacuum up to 220 K. (b) HREEL spectra obtained after a 20 L H_2 exposure on the Pt(100)-(hex) surface at 90 K and subsequent heating in vacuum up to 220 K.
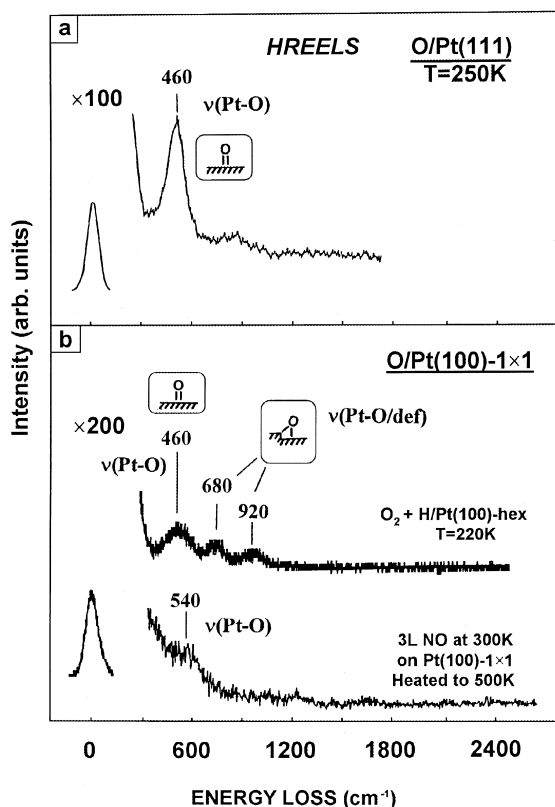
Fig. 4. (a) HREEL spectrum obtained after a 9 L O_2 exposure on the Pt(111) surface at 105 K and subsequent (O_{2ads}) heating in vacuum up to 250 K. (b) HREEL spectra (i) for the atomic oxygen appearing in the course of 220 K H_{ads} titration by oxygen (30 L) on the Pt(100)-(hex) surface; (ii) for the atomic oxygen produced by NO dissociation on the Pt(100)-(1×1) surface at 300 K.

ν(PtO) band is observed at 460 cm^{-1} after O_2 adsorption at 250 K (see Fig. 4a). Fig. 4b shows that interaction of an atomic hydrogen layer H/Pt(100)-(hex) with oxygen molecules (220 K, 30 L) is accompanied by the formation of an oxygen adatom layer (O_{ads}) with Pt−O bond vibration frequencies of 460, 720 and 920 cm^{-1}. According to TDS data, oxygen desorption occurs with a maximum around 710 K. Comparable TDS results were found after exposure to O_2 at high temperature (575 K, 3×10^5 L) on the Pt(100)-(hex): two desorption peaks at 660 and 710 K are observed. Hence, in agreement with O_2/Pt(321) [13], the bands at 720 and 920 cm^{-1} are intrinsic to atomic states of oxygen on the structural defects (presumably like steps or kinks) induced by the O + H reaction and can

serve as a good spectral indicator of the strong structural transformation of the Pt (100)-(hex) surface.

3.3. Effect of defects on CO_{ads} interaction with preadsorbed atomic O_{ads} states

The mechanism of CO oxidation on Pt is ascribed to the Langmuir–Hinshelwood-type between chemisorbed CO and O_{ads} atoms. It is known that this reaction on the flat Pt (111) surface is observed as a single CO_2 formation peak at ~ 320 K [14]. Fig. 5 depicts our result of the temperature-programmed reaction spectra of coadsorbed carbon monoxide and oxygen on Pt(100) surface. For comparison, an atomic oxygen layer was formed by NO dissociation at 300 K on Pt(100)-(1 × 1) surface, prepared by the Bonzel method [15], followed by CO exposure (0.3 L) at 100 K (Fig. 5). CO_2 is mainly evolved at a peak centred at 340 K.

During O_2 adsorption at 220 K on the non-reconstructed H/Pt(100)-(1 × 1) surface, prepared by hydrogen adsorption, three atomic oxygen states are formed (Fig. 4b). Exposure of 10 L CO at 100 K to the O/Pt(100)-(1 × 1) surface results in formation of CO_{ads} molecules in the bridge (1920 cm^{-1}) and on-top (2125 cm^{-1}) states. Fig. 5 shows that interaction of an atomic O_{ads} layer with CO_{ads} during heating up

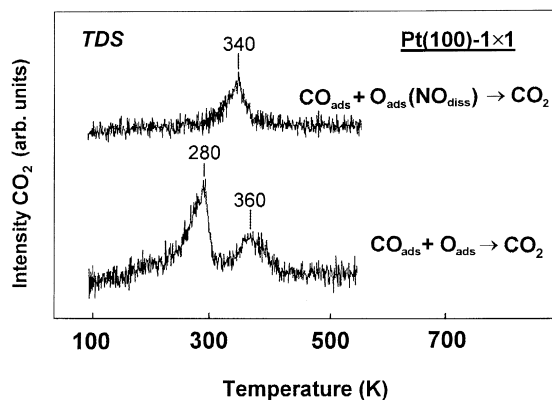Fig. 5. Temperature-programmed reaction spectra of coadsorbed CO and O on the Pt(100)-(1×1) surface: the atomic oxygen produced by NO dissociation and H_{ads} titration by oxygen (similar conditions as used in the HREELS experiments shown in Fig. 4b).

in the temperature interval 100–600 K may result in formation of two CO_2 desorption peaks: at 280 and 360 K. The production of distinct CO_2 desorption peaks may be the result of different reaction rates between the two types of CO_{ads} with three types of atomic oxygen O_{ads} available at terrace/step/kink sites on the defect-enriched Pt(100)-(1 × 1) surface. The low temperature carbon dioxide formation at 280 K indicates a lower activation energy pathway, because at large coverages of the CO and atomic oxygen these must be adsorbed very close to each other prior to TP reaction.

The oscillation cycle of CO oxidation on macroscopic Pt(100) single crystal surface has been described by Imbihl [16]. The initiating role of the reversible phase transition Pt(100)-(hex) ⇔ (1 × 1) has been established. The Pt(100) surface in the form of the (1 × 1) phase (defects side of oscillation cycle) is catalytically active due to its ability to dissociate O_2 molecule; S_0 sticking probabilities are 0.3 and 10^{-3} for the (1 × 1) and (hex) (no defects) phases, respectively.

In contrast to the Pt(100) crystal, the clean Pd(110) surface does not change its surface structure upon CO adsorption or the catalytic CO oxidation. Oscillation of the reaction rate on Pd(110) surfaces is associated with changes in oxygen adsorption (S_0) induced by depletion of subsurface oxygen: $O_{ads} \leftrightarrow O_{sub}$ [1,16].

4. Conclusion

The morphology of a clean Pd-tip and of Pd(110) surfaces is reversibly modified upon the creation of surface defects by the low-temperature palladium hydride synthesis. Defects on the more open surfaces of a Pd tip are very important for the low temperature uptake of hydrogen [17]. TDS of H_2 and a «staccato»-like growth of PdH particles can be used to monitor the high concentration of the defect density. The Pd microcrystals formed are stable until the temperature at which the Pd atoms become

thermally activated. The structure of these surfaces can be returned to its original shape only by annealing the sample at 700 K.

The hydrogen-modified Pt(100)-(hex) single crystal surface shows an increase in both the atomic oxygen states population at the $O_2 + H_{ads}$ titration reaction and the reactivity of oxygen atoms towards CO for formation of CO_2. The nature of the defects has not been directly investigated, but chemically the defect sites behave like the kink and steps on a Pt(100) surface. These results may lead to better understanding of the mechanism of rate oscillations in the $CO + O_2$ reaction on the Pt(100) surface.

References

[1] G. Ertl, Adv. Catal. 37 (1990) 213.
[2] V. Gorodetskii, J. Lauterbach, H.H. Rotermund, J.H. Block, G. Ertl, Nature 370 (1994) 276.
[3] V.V. Gorodetskii, P.D.Cobden, B.E. Nieuwenhuys, III Intern. Conf. on Unsteady-State Processes in Catalysis, 30 June–3 July, 1998, St. Petersburg, Russia, Abstracts, pp. 128–129
[4] A. Borg, A.M. Hilmen, E. Bergene, Surf. Sci. 306 (1994) 10.
[5] T.J. Tiedema, B.C. de Jong, W.J. Burgers, Proc. Kon. Ned. Akad. Wet. 63B (1960) 422.
[6] H.S. Taylor, Proc. R. Soc. Lond. A 108 (1925) 105.
[7] M.Yu. Smirnov, D. Zemlyanov, V.V. Gorodetskii, E.I. Vovk, Surf. Sci. 414 (1998) 409.
[8] U. Muschiol, P.K. Schmidt, K. Christmann, Surf. Sci. 395 (1998) 182.
[9] A.W. Aldag, L.D. Schmidt, J. Catal. 22 (1971) 260.
[10] D.Yu. Zemlyanov, M.Yu. Smirnov, V.V. Gorodetskii, Catal. Lett. 43 (1997) 181.
[11] Ch. Romainczyk, J.R. Manson, K. Kern, K. Kuhnke, R. David, P. Zeppenfeld, G. Gomsa, Surf. Sci. 336 (1995) 362.
[12] B. Pennemann, K. Oster, K. Wandelt, Surf. Sci. 249 (1991) 38.
[13] J.L. Gland, M.R. McClellan, F.R. McFeely, J. Chem. Phys. 79 (1983) 6349.
[14] W. Ho, J. Phys. Chem. 100 (1996) 13050.
[15] H.P. Bonzel, G. Broden, G. Pirug, J. Catal. 53 (1978) 96.
[16] R. Imbihl, Progr. Surf. Sci. 44 (1993) 185.
[17] P.D. Cobden, B.E. Nieuwenhuys, V.V. Gorodetskii, V.N. Parmon, Platinum Met. Rev. 42 (1998) 141.