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Absorption and oxidation of hydrogen at Pd and Pd-Au (111) surfaces

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Abstract

The kinetics of the H₂-O₂ reaction over Pd, Pd₇₀Au₃₀ and Au (111)-oriented surfaces has been studied in a static reactor near room temperature, using pressures in the torr range. The Pd-Au surface is highly enriched in gold (75 at.%) and unreconstructed, as shown by previous AES, LEIS and LEED analysis. While Au(111) is inert, Pd(111) and Pd-Au(111) are very active to catalyze the oxidation of hydrogen. The clean Pd surface is firstly more efficient to form water than the Pd-Au surface, but deactivates upon exposure to the reactive mixture. A careful analysis of the reactant partial pressures allows deriving the amount of hydrogen absorbed in the crystal during each reaction cycle. This shows that Pd-Au absorbs much more hydrogen than Pd, and that bulk dissolution directly competes with surface oxidation of hydrogen. Gold-induced lowering of the oxygen sticking probability and absorption-induced structural modification of Pd(111), through formation of a surface hydride, are invoked to rationalize the results.

Keywords

Heterogeneous catalysis; Palladium; Gold; Bimetallic alloys; Hydrogen oxidation; Hydrides; Low index single crystal surfaces

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1. Introduction

The observation that platinum-group metals facilitate water production from gaseous oxygen and hydrogen gave rise to the concept of catalysis in the nineteenth century [1]. In more recent years, numerous surface science studies were devoted to the $H_2+\frac{1}{2}O_2\rightarrow H_2O$ reaction on platinum-group materials, such as Pt(111) [1], Pd(111) [2-5], Pd-MOS structures [6] and Pd polycrystals [7] in ultra-high vacuum (UHV) conditions. These fundamental studies allowed a general comprehension of the low-pressure Pd-catalysed H_2-O_2 reaction. It proceeds mainly *via* a rate-limiting $O+H\rightarrow OH$ step in the adsorbed phase (Langmuir-Hinshelwood mechanism), possibly at defect sites, although direct reaction of H_2 with adsorbed oxygen (Eley-Rideal mechanism) may also occur under oxygen excess. In addition to studies of supported platinum-group metal catalysts [8-10], the investigations of this reaction at higher pressures were mainly performed on Pd polycrystalline foils, films and membranes [11-13].

Besides, Haruta and co-workers recently initiated [14] a worldwide interest in gold catalysis [15]. While most of the published studies of highly dispersed gold catalysts were devoted to low-temperature CO oxidation, some of them concerned the oxidation of hydrogen to form water and/or hydrogen peroxide (H_2O_2) [8,14-21]. These Au catalysts are highly efficient near room temperature; however their support plays a key role in most cases.

Lam et al. [8] studied water formation over supported Pd-Au catalysts with a large excess of oxygen, and found a great rate enhancement for 40-80 at.% Au, explained by a decrease of the binding energy of oxygen through a ligand effect. More recently, supported Au-Pd alloyed nanoparticles were also found superior to pure metals for the direct synthesis of hydrogen peroxide [16,17]. Besides, Weissman-Wenocur and Spicer [3] investigated the catalytic properties of a Pd-Au surface alloy on Pd(111). In ultra-high vacuum, the reaction probability of hydrogen with an adsorbed oxygen layer was measured lower on Pd-Au than on Pd. The apparent discrepancy with the results of Lam et al. was tentatively ascribed to the gold-induced lowering of the O-Pd bond, which would favour hydrogen adsorption. As the latter step was claimed to be rate-limiting only in the conditions of Lam et al. (atmospheric pressure, large oxygen excess), it would explain the superiority of Pd-Au over Pd in that sole case. Finally, the oxidation of hydrogen was investigated on polycrystalline Pd-Au surfaces at low pressure by Obuchi et al. [7]. A few percents of atomic Au suppressed the activity of Pd, in agreement with the findings of Weissman-Wenocur and Spicer.

In this paper, we present the first work, to the best of our knowledge, performed at elevated pressures on the hydrogen-oxygen reaction catalysed by Pd-based single-crystal surfaces. We

analyse the effect of Au by comparing the catalytic behaviours of Pd(111) and Pd₇₀Au₃₀(111) surfaces. Moreover, we emphasize the crucial role of hydrogen absorption in the reaction kinetics.

2. Experimental

The preparation and characterisation of the surfaces were achieved in a standard ultra-high vacuum (UHV) system described elsewhere [22]. The Pd(111), Au(111) and Pd₇₀Au₃₀(111) samples (10 mm diameter, 1 mm thickness, 5N purity, 0.1° miscut, 0.1 μm polishing) were cleaned by repeated cycles of Ar ion sputtering and annealing at 660, 440 and 460°C, respectively. This procedure allows obtaining contaminant-free and well-crystallized surfaces, as attested by Auger electron spectroscopy (AES) and low energy electron spectroscopy (LEED), respectively. As reported in another article [22], the well-annealed Pd₇₀Au₃₀(111) surface exhibits a (1×1) unreconstructed structure and strong surface segregation of gold. By additional low energy ion scattering (LEIS) investigations, a gold concentration of 75±5 at.% in the topmost layer was measured. As usual, the Pd(111) and Au(111) surfaces presented (1×1) and herringbone-type (22×√3) structures, respectively.

Catalytic reactions were performed in a UHV-compatible stainless-steel static reactor (120 cm³) coupled to the preparation chamber [22]. Prior to reaction, reactive gas mixtures were prepared in a separate chamber, with the help of capacitance diaphragm gauges. The purities of the gases were N5.5 for oxygen, N6.0 for hydrogen and N4.5 for argon (used for internal calibration). During reactions, the reactor content was sampled through a leak valve. Sampled gases were analyzed by a UHV-pumped quadrupole mass spectrometer (QMS). The reaction kinetics was followed by analyzing mass spectrometry peaks 2, 18, 32 and 40, which correspond to the masses of H₂, H₂O, O₂ and Ar molecules, respectively. After normalisation by the Ar signal, data were corrected for spectrometer sensitivity to obtain partial pressures.

Numerous H₂-O₂ reaction (“one-step”) experiments have been carried out both on Pd₇₀Au₃₀(111) and Pd(111), from room temperature (RT) to 120°C, and from 0.2 to 6 Torr partial pressures for each reactant. This H₂ pressure range was supposed to avoid the formation of the β-hydride phase in the bulk of the Pd(111) sample (H:Pd ≤ 0.8±0.2 at.% at 20°C) [23]. In the case of Au(111), oxygen pressures up to 160 Torr were employed to tentatively optimize the catalytic conditions. Repeated cycles (from 2 to 7), including injection of the reactants, reaction, and evacuation of the reacted gases, were performed in each experiment in order to

investigate the stability of the model catalysts. Sequential (“two-step”) experiments, described in Section 3, have also been performed.

3. Results

The Au(111) surface exhibited no measurable activity, even if it was Ar^+ -sputtered prior to reactions performed at temperatures up to $110^\circ C$. Conversely, Pd-based surfaces were found very active, even at RT, as can be observed in Fig. 1a and Fig. 1b for Pd(111) and Pd-Au(111), respectively. Here the reaction was performed in stoichiometric conditions at intermediate pressures ($P_{H_2} : P_{O_2} = 1 \text{ Torr} : 0.5 \text{ Torr}$ at $t=0$).

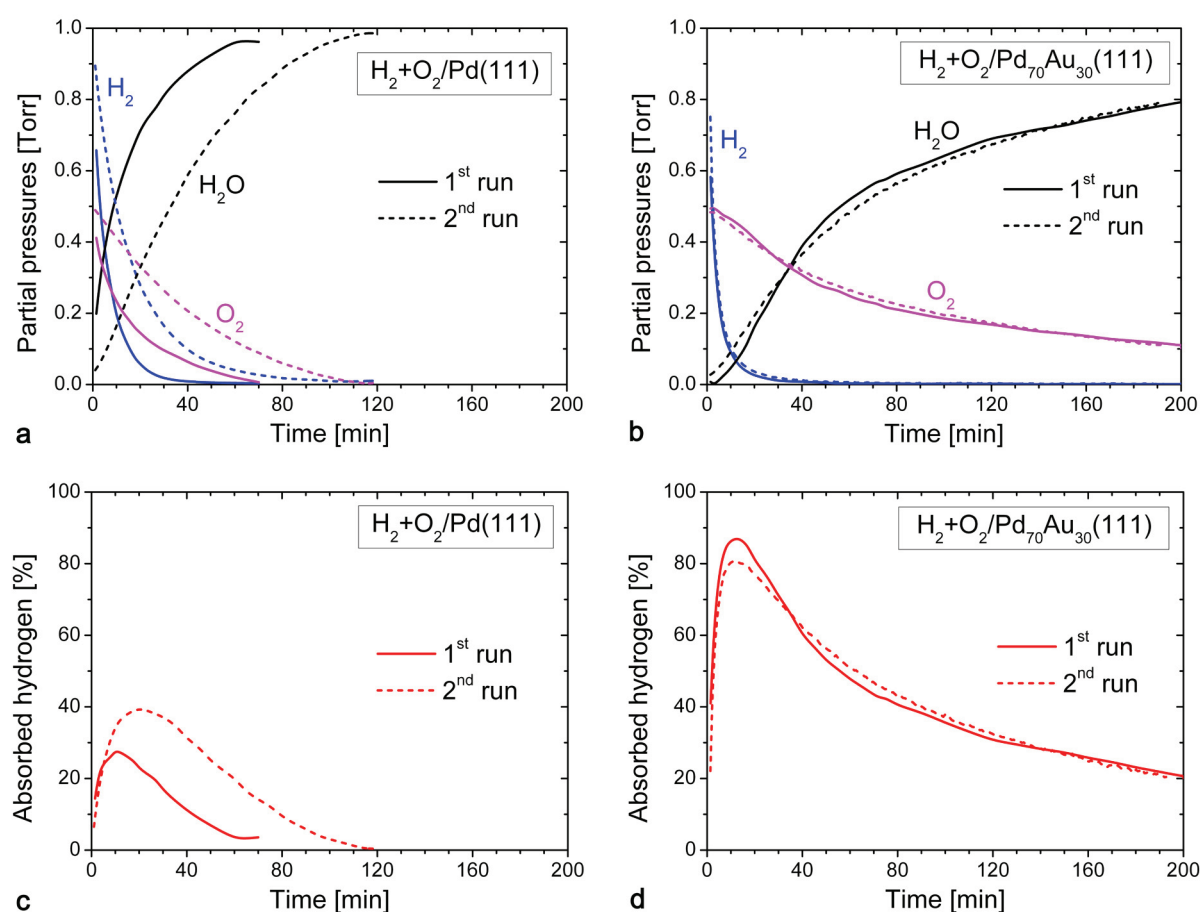


Fig. 1. (a,b) Partial pressures of H_2 , O_2 and H_2O as a function of time during the H_2-O_2 reaction at $24^\circ C$ over Pd(111) (a) and Pd-Au(111) (b) during two consecutive runs (2 minutes of pumping between the runs). (c,d) Amount of atomic hydrogen absorbed in Pd(111) (c) and in Pd-Au(111) (d) during the reaction runs of (a) and (b), respectively (see text for details).

The oxygen conversion rate per surface metal atom (oxygen turnover frequency) is defined as follows:

$$TOF_{O_2} = -\frac{1}{N_{at}^{surf}} \frac{dN_{O_2}}{dt} = -\frac{V}{n_{at}^{surf} S k T} \frac{dP_{O_2}}{dt} \quad (1)$$

where N_{O_2} is the number of oxygen molecules, P_{O_2} the oxygen pressure, N_{at}^{surf} the number of surface atoms, n_{at}^{surf} the density of surface atoms, S the sample surface, V the reactor volume, k the Boltzmann constant and T the reactor temperature. From the data of Fig. 1a and Fig. 1b, assuming a surface density of 1.5×10^{15} metal atoms per cm^2 , the initial turnover frequencies ($TOF_{O_2}^0 = TOF_{O_2}(t=0)$) are found equal to 2.1 s^{-1} and 0.24 s^{-1} for fresh Pd and Pd-Au surfaces, respectively. If we assume that the surface composition is not affected by the presence of the reactants with respect to UHV conditions, the initial turnover rate per surface Pd atom for Pd-Au(111) is 0.96 s^{-1} , since the surface concentration of Pd is 25 at.% on the fresh Pd-Au surface [22]. Oxygen is not fully converted by Pd-Au during the timescale investigated here (200 min), whereas it is fully converted by Pd within ~ 70 min. On the other hand, the pressure of hydrogen drops to zero within similar timescales (~ 40 min) on Pd and Pd-Au.

The astonishing fact that hydrogen disappears faster than oxygen is converted to water, implies that some of the hydrogen amount initially present in the gas phase has been absorbed (i.e. dissolved) into the crystals. The following formula was used to define n_H^{abs} , the normalized amount of absorbed hydrogen (relative to the initial amount of H atoms present in the gas phase):

$$n_H^{abs}(t) = 100 \frac{N_H^{gas}(t=0) - N_H^{gas}(t)}{N_H^{gas}(t=0)} \quad (2)$$

where N_H^{gas} , the number of hydrogen atoms in the gas phase, is calculated as follows:

$$N_H^{gas} = 2(P_{H_2} + P_{H_2O}) \frac{V}{kT} \quad (3)$$

In equation (3), P_{H_2} and P_{H_2O} stand for the hydrogen and water partial pressures, respectively. Fig. 1c and Fig. 1d show the evolution of $n_H(t)$ during the reaction runs depicted in Fig. 1a (Pd(111)) and Fig. 1b (Pd-Au(111)), respectively. The amount of absorbed hydrogen is much larger in Pd-Au than in Pd. At $t=13$ min, during the course of the reaction on the fresh Pd-Au(111) surface, almost 90% of the initial hydrogen amount is in a dissolved state (Fig. 1d).

In addition, one can note that diffusion of hydrogen into both samples (i.e. bulk dissolution) is fully reversible, that is no detectable amount of hydrogen remains absorbed at the end of the reaction processes.

Another striking difference between Pd and Pd-Au concerns the evolution of the reaction/absorption kinetics from the first to the second run. While the activity of Pd-Au is constant along the reaction cycles, on Pd the initial rate of oxygen conversion decreases by a factor ~ 5 ($TOF^0_{O_2}=0.39\text{ s}^{-1}$) and the total oxygen conversion time grows from ~ 70 to ~ 110 min, going from the first to the second run. In other words, the initial oxygen conversion activity of Pd(111) becomes similar to that of Pd-Au(111) ($TOF^0_{O_2}=0.24\text{ s}^{-1}$), whereas the mean oxidation activity of Pd remains the highest one. The lower efficiency of the Pd catalyst during the second run is correlated to a larger amount of absorbed hydrogen. More generally, the kinetics of oxygen-to-water conversion appears to be closely linked to the kinetics of hydrogen dissolution.

The same set of experiments has been performed using different conditions: $P_{H_2}=P_{O_2}=6.2$ Torr at $t=0$ and $T=52^\circ\text{C}$. The results (not shown here) are mostly unchanged. Indeed Pd is first found more active than Pd-Au (for which $TOF^0_{O_2}=6.8\text{ s}^{-1}$) but deactivates from the first to the second run and, to a much lower extent, from the second to the third run ($TOF^0_{O_2}$ decreases from 21 s^{-1} to 6.5 s^{-1} , going from the 1st to the 3rd run). The fourth run is identical to the third one, in spite of an evacuation time of 17 hours between these last two runs (15 min in other cases). On Pd-Au, the kinetics of hydrogen oxidation is roughly independent of the reaction cycle, as in Fig. 1b. Here again, the extent of hydrogen absorption appears to be anti-correlated with the hydrogen oxidation rate.

Besides, by varying the oxygen pressure for both (T, P_{H_2}) couples investigated, we have measured a reaction order of 1 with respect to oxygen in each case for both Pd and Pd-Au surfaces, i.e. the water formation rate is proportional to the oxygen pressure in the reaction regime investigated.

The different behaviours of Pd and Pd-Au along the reaction cycles can be ascribed to an irreversible structural modification of the Pd surface induced by hydrogen sorption, as discussed below. Conversely, the Pd-Au surface seems to be unaffected by the hydrogen dissolution process, in spite of the greater quantity absorbed in Pd-Au, as compared to Pd. In order to directly confirm the probable hypothesis of that large and reversible hydrogen dissolution in the Pd-Au(111) crystal, the following sequential experiment was carried out (Fig. 2).

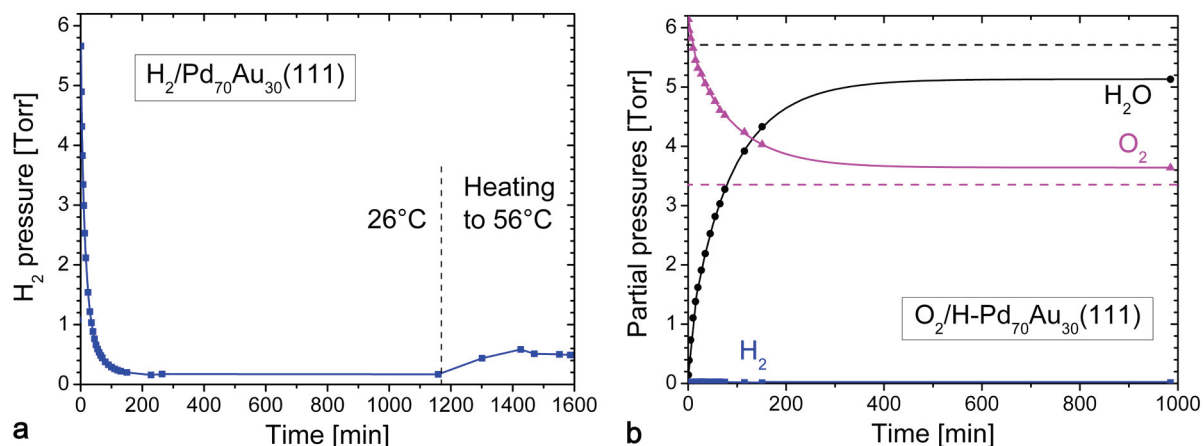


Fig.2. Results of a two-step experiment on Pd₇₀Au₃₀ (111) including sorption of pure hydrogen (initially 6.2 Torr) at room temperature, heating of the sample at 56°C, pumping of the reactor and reaction of oxygen (initially 6.2 Torr) with the hydrogenated Pd-Au surface. (a) Evolution of the hydrogen pressure as a function of time. (b) Evolution of the partial pressures of H₂, O₂ and H₂O at 56°C. The horizontal dashed lines depict the maximum H₂O (black) and the minimum O₂ (magenta) pressures that could have been reached from the final state of the experiment described in (a). Continuous lines are guides to eye.

The freshly prepared sample was exposed to a hydrogen pressure of 6.2 Torr at RT, and the hydrogen signal was recorded as a function of time (Fig. 2a). The H₂ pressure decreased to 0.2 Torr within ~200 min and then stabilised. After that, the reactor temperature was elevated by 30°C, which induced an increase of the H₂ pressure due to a modification of the gaseous/dissolved phase equilibrium. Then the reactor was evacuated, and an oxygen pressure of 6.2 Torr was subsequently introduced. As expected, a decrease of the O₂ pressure and a related increase of the H₂O pressure were detected (Fig. 2b). The amount of water produced was nearly equal to the amount of hydrogen absorbed during the first stage of the experiment. These results confirm the high hydrogen absorption capacity of the Pd-Au(111) crystal. Moreover, since no gaseous hydrogen is necessary ($P_{H_2}=0$, Fig. 2b) to produce water, it shows that hydrogen oxidation proceeds *via* a Langmuir-Hinshelwood's type mechanism. In addition, the oxygen-to-water conversion rate was about two times lower than the one measured during a classical one-step reaction experiment at the same temperature. This implies that hydrogen diffusion toward the surface is rate-limiting when the hydrogen pressure is very low.

The same experiment was performed on the Pd(111) sample (results not displayed). The reaction of hydrogenated Pd with oxygen produced a much lower amount of water than hydrogenated Pd-Au did (factor 8). Thus, unlike under the one-step H_2+O_2 reaction conditions, a *stable* bulk hydride could have formed in the near-surface region of Pd(111)

upon exposure to pure H_2 . This would support the above hypothesis of an irreversible structural modification of the Pd surface induced by hydrogen absorption during the first reaction cycles. However this restructuring should be moderate since LEED investigations performed after hydrogen sorption experiments revealed no significant change.

4. Conclusive discussion

We have studied the H_2-O_2 reaction over Pd(111), Pd₇₀Au₃₀(111) and Au(111) in a “batch”-type reactor, in the [20-120°C] temperature range and in the [0.1-10 Torr] pressure range.

On the clean surfaces, the activity for hydrogen oxidation follows the order: Pd(111) > Pd₇₀Au₃₀(111) >> Au(111) ~ 0. However, unlike Pd-Au(111), Pd(111) deactivates throughout the reaction cycles. When stabilised, the initial activities of Pd(111) and Pd-Au(111) become similar. For the near-stoichiometric experimental conditions used in this study, the reaction order with respect to oxygen is unity on both Pd(111) and Pd-Au(111), in agreement with the work of Petersson et al. on a Pd surface at low pressures [6]. Dissociative chemisorption of oxygen is rate-limiting on both Pd and Pd-Au surfaces. The reaction follows a Langmuir-Hinshelwood mechanism on these surfaces under elevated pressures, similarly to what was found by Engel and Kuipers on Pd(111) under low pressures [2].

While hydrogen absorption under elevated pressure has been widely studied in Pd [23-26] and, to a lower extent, in Pd-Au [27-29] bulk materials, published work concerning high-pressure hydrogen absorption at clean Pd single-crystal surfaces [30,31] is very scarce to our knowledge. Conversely, numerous low-pressure studies have mentioned hydrogen absorption at the subsurface of low-index single-crystal surfaces, such as Pd(111) [32- 39], Pd(100) [40-42], Pd(110) [43,44], Pd(331) [45,46] and Pd(210) [47]. Under our high-pressure conditions, bulk dissolution of hydrogen strongly competes with its surface oxidation on both Pd(111) and Pd₇₀Au₃₀(111). The latter crystal absorbs much more hydrogen than the former in the presence of oxygen. The decrease of the oxidation rate on Pd(111) through the reaction cycles is correlated with an increase of the amount of dissolved hydrogen, until stabilisation of the kinetics. Diffusion of dissolved hydrogen atoms toward the surface determines the oxidation rate under low hydrogen pressure.

On gold single-crystals, the sticking probability of O_2 is very low [48,49], whereas this molecule easily dissociates on palladium surfaces (see e.g. Ref. [2]). Thus, as oxygen chemisorption is hindered by surface gold atoms on Pd-Au(111) (in agreement with Ref. [3]), most of hydrogen adatoms are not readily oxidized and, consequently, are free to diffuse into the bulk material. This could explain the higher oxidation activity of fresh Pd(111) over Pd-

Au(111) and the larger amount of hydrogen dissolved in Pd-Au during the reaction, as compared to Pd.

Whereas dissolution of hydrogen is fully reversible in Pd-Au(111), an irreversible process occurs upon exposure of the fresh Pd(111) surface to hydrogen and evacuation of the reactor. Unlike bulk Pd-Au which does not form the β -hydride phase for a gold concentration higher than 17 at.% at RT [27], pure Pd can form a two-phase hydride [23]. The subsequent structural modification of the Pd(111) near-surface region, e.g. through the formation of structural defects, should increase the probability of hydrogen absorption (see e.g. Ref. [41]), leading to the observed lowering of the hydrogen oxidation activity.

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