

^{47 0042-207}X/\$ - see front matter © 2005 Published by Elsevier Ltd. doi:10.1016/j.vacuum.2005.07.035

E-mail address: a.winkler@tugraz.at (A. Winkler).

+43 316 873 8466.

45

The experiments were carried out in an ultrahigh vacuum chamber, equipped with an Auger 63

65

49

51

53

55

57

59

ARTICLE IN PRESS

G. Pauer et al. / Vacuum **I** (**IIII**) **III**-**III**

1 electron spectrometer (AES), low-energy electron diffraction (LEED) optics, a differentially pumped

in-line quadrupole mass spectrometer (QMS) and
 a time-of-flight (TOF) spectrometer. An extractor
 ion gauge, a spinning rotor gauge and a further
 QMS allowed the quantitative partial pressure

7 determination in the vacuum system. A calibrated standard sample (tungsten filament) for thermal
9 desorption allowed the quantitative measurement

of hydrogen desorption rates, as well as the 11 determination of the effective pumping speed of the vacuum chamber [5]. Thus, quantitative 13 adsorption, desorption and reaction measurements were possible. For the modification of the palla-

dium surface with potassium an SAES getter source was used.

17 The TOF spectrometer was applied to determine the translational energy distribution of desorbing19 particles like hydrogen and water as reaction

 products. It comprises two differentially pumped
 UHV chambers, housing the chopper motor and the QMS detector, respectively. A detailed descrip-

23 tion of the TOF spectrometer has been given elsewhere [6].

25 The polycrystalline palladium sample was part of a permeation source, which allowed studying 27 the water reaction not only for hydrogen and oxygen coming from the gas phase, but also for 29 reaction studies with segregating hydrogen. In addition to that, continuous and isothermal reaction studies are possible. The permeation 31 source is depicted in Fig. 1. A high-purity palladium disc (10 mm in diameter, 1 mm thick-33 ness) was vacuum soldered with gold onto a high purity nickel cylinder. This cylinder was soldered 35 onto a stainless steel disc, which in turn was 37 welded to a stainless steel tube (1/16'' diameter) for gas inlet. The whole assembly was tightly covered 39 by two concentric ceramic tubes containing a coil of molybdenum wire for resistive heating, up to 41 1000 K. Several layers of tantalum foil were wrapped around the outer ceramics for radiation 43 shielding and fixed into a stainless-steel tube by thin pointed screws. A NiCr-Ni thermocouple for 45 temperature measurements was spot-welded to the rim of the sample. The permeation source was 47 attached to a LN₂ cooled sample holder, which allowed the positioning of the sample in front of

49 51 53 55 1 2 3 4 5 6 59

Fig. 1. Cross-section of the permeation source: (1) polycrystal-
line Pd sample disc; (2) high-purity Ni cylinder; (3) molybde-
num heating coil embedded in ceramics; (4) several layers of
tantalum foil for radiation shielding; (5) stainless-steel cap; (6)
stainless-steel tube (1/16 inch), welded to the stainless-steel cap.61

65

all necessary analytical devices. A continuous flux of hydrogen could be achieved with this device by applying a proper back-pressure and a convenient choice of the palladium sample temperature. A piezoelectric membrane gauge served as pressure measurement in the gas inlet system of the permeation source. A Knudsen cell, used for calibration of the TOF spectrometer, was also mounted on the manipulator. 75

3. Results

3.1. Hydrogen desorption from clean and potassium covered palladium

For the measurement of the translational energy 83 distribution of hydrogen from the palladium surface a continuous hydrogen permeation flux 85 in the order of 1×10^{16} H₂-molecules/s was established, using sample temperatures between 87 360 and 520 K and back-pressures between 1 and 1700 mbar. The total flux F (molecules/s) was 89 determined from the total pressure increase Δp (mbar) and the effective pumping speed S (1/s) in 91 main chamber $(F = KS\Delta p,$ the with $K = 2.47 \times 10^{19}$ molecules/(mbar l)). The determi-93 nation of the effective pumping speed with a calibrated desorption standard is described else-95 where [5]. Details to the data acquisition with the

77

79

81

ARTICLE IN PRESS

87

89

1 TOF spectrometer and data analysis were also given in a previous paper [6]. The data acquisition 3 time for the TOF spectra was typically 20–100 min. A TOF spectrum for hydrogen desorbing from the 5 clean polycrystalline palladium source at T =450 K is depicted in Fig. 2 (curve a). This spectrum 7 can be best fitted by the TOF spectrum of a Maxwellian beam with a temperature of 427 K. 9 This corresponds to a mean translational energy $\langle E \rangle = 0.074 \,\mathrm{eV}$, according to $\langle E \rangle = 2kT$. Thus, 11 recombinative desorption of hydrogen from clean palladium is largely inactivated. In contrast to 13 that, recombining hydrogen from a potassiumcovered surface exhibits a clear hyper-thermal 15 desorption flux (Fig. 2, curve b). The sample temperature was again 450 K. However, the TOF spectrum could not be fitted by simple Maxwel-17 lians in this case. Therefore, the mean kinetic 19 energy was evaluated by the moment method [7]. We obtained $\langle E \rangle = 0.150 \,\text{eV}$ or $\langle E \rangle \approx 4kT$. The 21 expression of the mean energy in terms of a Maxwellian temperature according to $\langle E \rangle = 2kT$ 23 yields an effective temperature of 880 K. This 25 Pd - poly

 H_2 27 T_{Bd} = 450 K b: K covered a u 29 Norm. mass 2 counts 31 a: clean 33 35 37 0.0 0.2 0.4 0.5 0.6 07 0.8 0.9 0.1 0.3 10 39 Time [ms]

41 Fig. 2. Time-of-flight (TOF) spectra of H₂ molecules desorbing from the Pd-poly permeation source at a temperature of 450 K. (a) H₂-TOF-spectrum from the clean Pd surface together with a least-squares-fit of a Maxwellian TOF-distribution with T_{fit} = 427 K (black line). (b) H₂-TOF-spectrum after covering the Pd surface with potassium up to saturation at 450 K. The dotted line represents a Maxwellian TOF-spectrum (880 K) with the same mean kinetic energy as obtained from the experimental data by the moment method (curve b). All data are normalized to the same area. means that recombinative desorption of hydrogen 49 from the potassium covered surface is an activated process. The potassium coverage in this case was $4 \times 10^{14} \text{ K}$ atoms/cm², which is about 80% of a saturated chemisorption layer ($5 \times 10^{14} \text{ K}$ atoms/ 53 cm²), as inferred from Refs. [8,9].

In addition to the translational energy distribu-55 tion measurements we can use the TOF spectrometer to obtain information on the angular 57 distribution of the desorption flux. Because of the large distance between sample and detector 59 (870 mm) and the small aperture diameter of the OMS detector (5 mm), this device is an excellent 61 directional detector. Although we could not tilt the sample in front of the entrance aperture, which 63 would allow the angular distribution measurement directly, we could measure the ratio between the 65 desorption flux in normal direction $D(0^{\circ})$ and the total flux D_{tot} desorbing into the hemisphere. If we 67 assume an angular desorption flux distribution in the form of $D(\Theta) = D_0 \cos^n \Theta$, which is actually 69 frequently done in the Ref. [10], then the measured ratio $D(0^{\circ})/D_{tot}$ should directly yield the exponent 71 n of the above mentioned equation. Simple mathematics shows that $D(0^{\circ})/D_{tot} = (n+1)/2\pi$. 73 The hydrogen desorption from the clean palladium surface has been shown to be non-activated. 75 In this case the angular distribution for desorption can be described by $D(\Theta) = D_0 \cos \Theta(n = 1)$. 77 Taking the experimentally obtained ratio $D(0^{\circ})/$ D_{tot} for this case as reference, we can easily 79 calculate the value n of the angular desorption distribution for the potassium covered palladium 81 case. We obtain a value n = 3.8. This is qualitatively in accordance with the obtained hyperther-83 mal flux, because n > 1 characterizes activated desorption [11]. A more quantitative interpretation 85 will be given in the discussion section.

3.2. Water formation on clean and potassium covered palladium

For the quantitative examination of the reaction 91 between impinging oxygen and permeating hydrogen the reproducibility of the hydrogen flux as a 93 function of sample temperature, hydrogen backpressure and permeation time had to be checked 95 first. This is necessary because the hydrogen

ARTICLE IN PRESS

1 permeation flux cannot be monitored under reaction conditions. It could be shown that the time dependent evolution of the hydrogen flux 3 after a sudden increase of the backpressure can be 5 predicted with an accuracy of about 15% for the experimental timeframe. The hydrogen flux in-7 creases roughly exponentially after a time delay of about 50 s. A steady state situation for the 9 hydrogen flux is only reached after extended time. Based on this information the time dependent 11 evolution of the hydrogen (m = 2) and water signals (m = 18) in a constant oxygen atmosphere 13 could be determined, as shown in Fig. 3. Throughout this experiment, performed at a sample temperature of 440 K, the oxygen partial pressure 15 in the main chamber was 5.3×10^{-7} mbar. At the start of the experiment (t_0) the hydrogen back-17 pressure in the permeation source was instantly 19 raised to about 100–150 mbar and henceforth kept constant. Under these conditions we observe a 21 clear increase of the mass 18 signal at the time when the onset of the hydrogen flux is expected, 23 but no increase of the mass 2 signal. This clearly shows that in this case all of the effusing hydrogen 25 reacts with impinging (adsorbed) oxygen to water. After some time the water formation rate levels off 27 and at the same time the hydrogen signal starts to increase. At this point of the experiment the

31 Pd - poly. T_{Pd}= 440 K 33 $p_{02} = 5.3 \times 10^{-7} \text{ mbar}$ QMS - signal [a.u.] 35 37 mass 2 39 mass 18 mmm 41 43 0 20 40 60 80 100 120 140 160 180 200 220 Time $(t - t_0)$ [s]

Fig. 3. Temporal evolution of the H₂O signal and the hydrogen flux after applying a particular hydrogen backpressure at t_0 in the permeation source, in the presence of a constant isotropic O₂ background pressure of 5.3×10^{-7} mbar.

hydrogen flux becomes too large to be totally 49 converted into water.

In order to obtain a more quantitative picture of 51 the water formation between emanating hydrogen and impinging oxygen molecules on palladium we 53 have plotted the water formation rate as a function of the emanating hydrogen flux (Fig. 4), for 55 different oxygen partial pressures (impingement rates $N_{i,0}$). From this representation a linear 57 correlation between the water formation rate and the hydrogen permeation rate becomes apparent. 59 Furthermore, proportionality between the oxygen partial pressure and the hydrogen permeation 61 fluxes, at which the sharp bend appears, is observed. These features suggest that all effusing 63 hydrogen reacts towards water until the permeation rate passes a limiting value, defined by the 65 availability of hydrogen and adsorbed oxygen on the active surface in a ratio of 2:1. Above this 67 value the water formation rate should remain constant, limited by the amount of continuously 69 adsorbing oxygen. The slight further increase of the water signal above the sharp bend is due to the 71 formation of water on the chamber walls with increasing hydrogen partial pressure, which was 73 proved experimentally.



75

Fig. 4. H_2O partial pressure signals as a function of the hydrogen permeation flux for different oxygen impingement ratios. The vertical dotted lines at the bends in the water signals mark the points in time where the ratio between permeating hydrogen and adsorbing oxygen atoms reach the stoichiometric value. 95

29

45

VAC: 3585

ARTICLE IN PRESS

Pd - poly.

2.0

T_{Pd} = 450 K



Fig. 5. Time-of-flight (TOF) spectra of H₂O formed by permeating hydrogen and isotropically impinging oxygen at 17 450 K on the clean (a) and potassium covered (b) polycrystalline palladium surface. The black lines represent least-squares 19 fits of Maxwellians to the experimental data, corresponding to $T_{fit} = 460 \text{ K}$ for (a) and $T_{fit} = 480 \text{ K}$ for (b).

21

Additionally, we have measured time-of-flight 23 distributions for water and hydrogen during the reaction process under steady state conditions (with the hydrogen permeation rate much larger 25 than the oxygen impingement rate). Interestingly, 27 we found a thermalized flux distribution for both molecules. The TOF spectrum for desorbing water 29 from the clean palladium surface is depicted in Fig. 5 (curve a). The water formation on the potassium covered palladium surface is somewhat 31 more complex. First of all, the water formation 33 rate under this condition is significantly smaller than on the clean Pd surface, but again the H₂O-TOF spectrum can be best approximated 35 by a thermalized flux distribution (Fig. 5, curve b). 37 Finally, even the TOF distribution for hydrogen obeys a thermalized distribution during the water 39 formation reaction, although potassium remains on the surface. A possible explanation for this

somewhat puzzling result will be given in the next 41 paragraph.

43

45 4. Discussion

47 The observed inactivated desorption of hydrogen from clean palladium and activated adsorp-

tion from the potassium covered palladium surface 49 is in good agreement with previous experiments on the sticking coefficient on similar systems [12,13]. 51 Molecular beam experiments for H₂ on Pd(110) + K showed a high sticking coefficient 53 for the clean surface and an angular distribution of $S(\Theta) = S_0(\Theta) \cos^{n-1}\Theta$, with *n* close to 1, but a 55 strongly decreased sticking for a potassium covered Pd(110) surface (at about 0.5 ml of potas-57 sium), with an exponent n = 3 for the angular distribution of adsorption [12]. This demonstrates 59 that detailed balancing is largely fulfilled for this system. A second interesting aspect refers to the 61 correlation between the angular distribution and the mean translational energy. If the adsorption/ 63 desorption process obeys normal energy scaling, a clear correlation between the angular distribution 65 and the translational energy distribution (and hence the mean translational energy) should exist. 67 It could be shown [14] that for an energy distribution in the form of $\cos^n \Theta$, the mean kinetic 69 energy can be expressed by $\langle E \rangle = (n+3)kT/2$. It is obvious that this is true for the unactivated case: 71 n = 1, $D(\Theta) \sim \cos \Theta$, $\langle E \rangle = 2kT$. For the Pd+K surface we obtained n = 3.8 for the angular 73 distribution and a mean kinetic energy of $\langle E \rangle =$ 4kT from independent experiments. One can easily 75 check that the above postulated expressions are largely fulfilled. 77

The water reaction between permeating hydro-79 gen and impinging molecular oxygen on palladium vields a thermalized distribution for the water flux. Recently, we have studied the water reaction on 81 palladium for other types of hydrogen supply [4]. But neither the supply with hydrogen from the gas 83 phase in molecular form nor in atomic form led to hyper-thermalized flux distributions of the water 85 reaction products. This shows that independent of the hydrogen supply the water reaction is of the 87 Langmuir-Hinshelwood type, i.e. both reactants (oxygen and hydrogen) are accommodated to the 89 surface (adsorbed) prior to reaction. The reason why we emphasize this point is that with atomic 91 hydrogen supply also non-thermal reactions could be expected (Eley-Rideal-type reactions and hot-93 atom reactions). For example the associative reaction between adsorbed hydrogen and imping-95 ing atomic hydrogen on several metal surfaces is of

ARTICLE IN PRESS

 the above-mentioned type [15]. The products of such reactions are characterized by strongly
 forward focused angular distributions and by hyperthermal distributions for the translational,
 rotational and vibrational energies. Apparently, this is not the case for the water formation
 reaction.

- Finally, some notes on the water formation on 9 the potassium covered palladium surface. The translational energy distributions for water and
- for hydrogen have been observed to obey a thermalized Maxwellian. But the question remains
 why the hydrogen flux does not show a hyperther-
- mal distribution in this case, although the surface is potassium-covered? This might be explained by
- is potassium-covered? This might be explained by some recent findings on a similar system: Günther
 et al. [16] have examined the similar system of
- $H_2 + O_2$ reaction on potassium covered Rh(110)/ Pt surfaces. They found that adsorbing oxygen on
- 19 Pt surfaces. They found that adsorbing oxygen on the potassium covered surface leads to the forma-
- tion of islands consisting of a dense K–O layer. These islands are surrounded by large potassium
 free areas. Therefore we believe that the water
- reaction as well as the hydrogen permeation/
 desorption takes place predominantly on the potassium free areas of the palladium surface.
- 27

29 5. Summary

We have investigated the hydrogen permeation and desorption from a polycrystalline palladium
sample as well as the water formation with impinging molecular oxygen and permeating
hydrogen. Time-of-flight measurements revealed

- that the associative hydrogen desorption is inactivated on the clean palladium surface, but activated on the potassium covered surface. The
- 39 water formation is inactivated both on the clean and on the potassium-covered surface. This shows

that the reacting particles are accommodated to the surface prior to their reaction. On the	41
potassium covered surface impinging oxygen leads to the formation of dense K–O islands, sur-	43
rounded by potassium free areas, where water reaction and hydrogen desorption proceed. There-	45
fore, hydrogen desorption can take place as an inactivated process in this case.	47
	49
Acknowledgements	51
This work has been supported by the Austrian Science Fund, Project No. S9006-N02. We gladly	53
acknowledge the technical assistance of Martin Kornschober and the Labor für Messtechnik Dr.	55
Hans Stabinger GmbH.	57
References	59
[1] Engel T, Kuipers H. Surf Sci 1979;90:181.	61
[2] Weissman-Wenocur DL, Spicer WE. Surf Sci 1983;133;499.	63
 [3] Mitsui I, Rose MK, Fomin E, Ogletree DF, Salmeron M. Surf Sci 2002;511:259. [4] Pauer G Winkler A J Chem Phys 2004:120:3864 	65
 [5] Winkler A. J Vac Sci Technol 1987;A5:2430. [6] Eibl C, Winkler A. J Chem Phys 2002;117:834. 	67
[7] Eadie WD, Drijad D, James FE, Roos M, Sadoulet B. Statistical methods in experimental physics. Amsterdam: North-Holland: 1971	69
[8] Pratt SJ, Escott DK, King DA. Phys Rev B 2003;68:235406.	71
 [9] Matsushima T. J Phys Chem 1987;91:6192. [10] Rendulic KD, Winkler A. Surf Sci 1994;299/300:261. 	73
 [11] Kendulic KD. Surf Sci 1992;272:34. [12] Resch C, Berger HF, Rendulic KD, Bertel E. Surf Sci 1994:316:L1105. 	75
 [13] Solymosi F, Kovacs I. Surf Sci 1992;260:139. [14] Anger G, Winkler A, Rendulic KD, Surf Sci 1989:220:1. 	77

- [15] Winkler A. Appl Phys 1998;A67:637.
- [16] Günther S, Marbach H, Hoyer R, Imbihil R, Gregoratti L, Barinov A, et al. J Chem Phys 2002;117:2923.