Manipulating the Activation Barrier for H_2 (D_2) Desorption from Potassium Modified Palladium Surfaces

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In this work the permeation and desorption of hydrogen (deuterium) from potassium-modified Pd(111) and polycrystalline palladium surfaces have been studied in the temperature range from 350 K to 523 K. Time-of-Flight (TOF) spectroscopy has been used to determine the translational energy distributions of associatively desorbing H_2 (D_2) molecules as a function of the potassium coverage and additional isotropic O_2 and CO background pressures. It turned out that the energy distribution of the hydrogen desorption flux is thermalized for the clean Pd-surfaces but hyperthermal for the potassium covered surfaces. The activation barrier for adsorption was found to increase with the potassium coverage but to decrease again in the presence of coadsorbates like O_2 or CO. Especially by choosing different isotropic CO pressures, the effective desorption barrier for hydrogen could be reversibly decreased and increased, which resulted in equivalent changes of the mean kinetic energies of the desorbing H_2 molecules.

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I. INTRODUCTION

The influence of adlayers like potassium on Ni, Rh or Pd surfaces has been of great interest in catalysis since they often act as inhibitors as well as promotors in many surface reactions. Typical examples are the hindering of dissociative H_2 adsorption [1–4], the adsorption and bond-weakening/dissociation of CO on Pt and Rh [5–7] or the HCOOH stabilisation on Pd by potassium [8]. Especially, the frequently observed attenuating effect of potassium on the reaction efficiency for hydrogen could be attributed to the developement of a high barrier for dissociative adsorption [4, 9]. In a recent work we have studied the water formation reaction on a potassium-modified polycrystalline palladium permeation source under steady state conditions [10]. This setup allowed to continually supply hydrogen onto the potassium covered Pd surface (which is inert to adsorption of gas-phase H_2 molecules) by diffusion from bulk and subsurface states. In the framework of this study, some peculiar results concerning the kinetic energy of the simultaneously desorbing hydrogen have been observed. Therefore, in the present work we put emphasis on the behavior of the mean kinetic energy of permeating/desorbing hydrogen from single- and polycrystalline palladium surfaces with changing potassium coverage. In addition to that we demonstrate that we can deliberately change the effective barrier for H_2 desorption by coadsorption and reaction of potassium with oxygen and carbon monoxide.

II. EXPERIMENTAL

The experiments were carried out in an ultra-high vacuum chamber, equipped with an Auger 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 determination in the vacuum system. A calibrated standard sample (tungsten filament) for thermal desorption allowed the quantitative measurement of hydrogen desorption rates, as well as the determination of the effective pumping speed of the vacuum chamber [11]. Thus, quantitative adsorption, desorption and reaction measurements were possible. For the modification of the palladium surface with potassium an SAES-getter source was used. The TOF spectrometer was applied to determine the translational energy distribution of desorbing 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 description of the TOF spectrometer has been given elsewhere [12]. TOF data have been evaluated either by least-squares-fits of Maxwellian distributions or by the *moment method* [13], if the spectra exhibited non-Maxwellian behaviour. All TOF experiments have been performed with the sample surface oriented normal to the detection direction. The Pd(111) and polycrystalline palladium samples (with a diameter of 10.0 mm and a thickness of 1.0 mm) were each part of a permeation source, which allowed studying the associative desorption of H_2 continuously as well as the water reaction. The latter could be done not only for hydrogen and oxygen coming from the gas phase, but also for reaction with segregating hydrogen. A detailed description of the permeation source is given in [10]. The permeation source was attached to a LN_2-cooled sam-

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ple holder which allowed the positioning of the sample in front of all analytical devices. A continuous flux of hydrogen could be achieved with this device by applying a proper back-pressure (1 mbar to 1700 mbar) and a palladium sample temperature between 350 K and 550 K. A piezoelectric membrane gauge served as a 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. The sample cleanliness has been checked by Auger electron spectroscopy after regular Ar$^+$-Ion sputtering at elevated temperatures ($T_{Pd} \approx 700$ K), annealing and subsequent carbon removal by baking in oxygen atmosphere ($p_{O_2} = 4 \times 10^{-8}$ mbar and $T_{Pd} \approx 550$ K). The remaining oxygen could be easily removed by reaction with hydrogen. The potassium coverage has been quantified by determination of the AES peak-to-peak ratios between the K(252 eV)-peak and the Pd(330 eV)-peak of the clean palladium surface. Due to the partial overlap of the K(252 eV)-peak with the Pd(243 eV)-peak and due to an additional quenching of the palladium peak intensities, the true heights of the potassium peaks had to be determined from difference spectra according to Refs. [14, 15]. The saturation coverage of potassium on Pd(111) of $\Theta_K = 1/3$ monolayers (ML) [$\Theta_K \approx 5 \times 10^{14}$ atoms/cm^2; 1 ML $= 1.53 \times 10^{15}$ atoms/cm^2] at the onset of the K-multilayer at $T_{Pd} = 395$ K, as obtained from thermal desorption measurements, served as point-of-reference for the determination of the absolute coverage values [16].

III. RESULTS & DISCUSSION

A. H_2 (D_2) permeation/desorption from K covered Pd surfaces

The measurement of the kinetic energy distribution of desorbing H_2 (D_2) molecules has been performed with the time-of-flight (TOF) spectrometer. Measuring the effective pumping speed S_{H_2} (S_{D_2}) of the UHV system, after the method described in Ref. [11], allowed the quantitative determination of the total permeation flux Φ_{H_2} (molecules/s) from the total pressure increase in the main UHV chamber. To obtain TOF-spectra with high signal-to-noise ratio, a hydrogen (deuterium) permeation flux in the order of 1×10^{16} molecules/s (∼6 ML/s) has been established, at sample temperatures ranging from 450 K to 523 K. By additional measurements it was found that the contribution of scattered H_2 molecules to the TOF-spectra could be neglected. The aquisition time was generally around 20 minutes. The back-pressure in the permeation source was (depending on the temperature) in the order of 1 mbar to 1700 mbar. Potassium was always dosed up to the saturation coverage at the respective sample temperature. Using the method described in the previous section, the saturation coverage has been determined to linearly decrease from $\Theta_K(450K) = 4.0 \times 10^{14}$ atoms/cm^2 down to $\Theta_K(523K) = 3.5 \times 10^{14}$ atoms/cm^2 for both the Pd(111) and polycrystalline palladium sample. On Pd(111) these coverages would correspond to $\Theta_K(450K) = 0.26$ ML and $\Theta_K(523K) = 0.23$ ML, respectively. The TOF-spectra obtained for hydrogen permeation/desorption from clean and potassium covered palladium surfaces at $T_{Pd} = 523$ K are presented in Fig. 1. The corresponding D_2 TOF-spectra for Pd(111) are shown in Fig. 2.

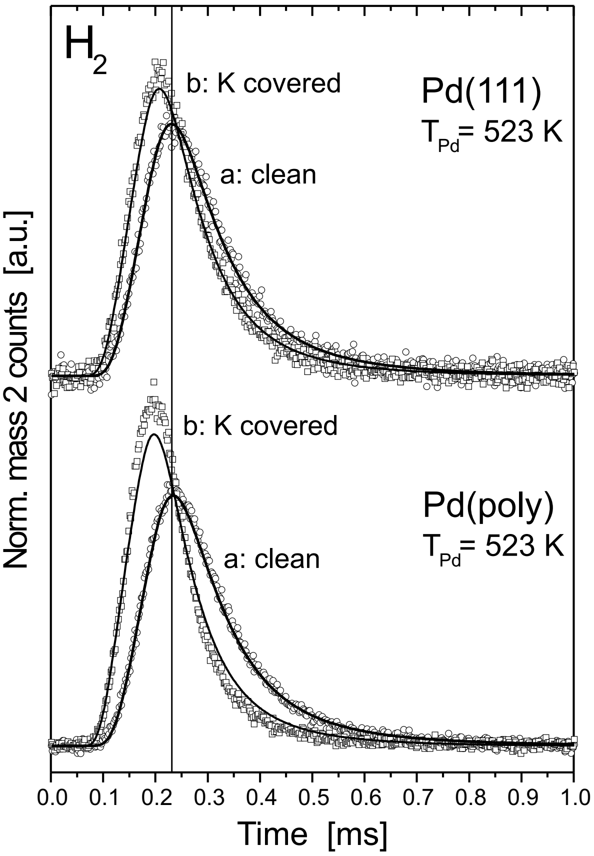

FIG. 1: TOF spectra of desorbing H_2 after permeation from clean (circles) and K-covered (squares) palladium surfaces ($\Theta_K = 3.5 \times 10^{14}$ atoms/cm^2). The thick lines represent least-squares-fits of Maxwellian TOF-distributions corresponding to the actual sample temperature. The thin lines represent artificial Maxwellian distributions with the same mean kinetic energy $\langle E_{kin} \rangle$ as obtained from the measured TOF distributions (squares) by the *moment method*. All data are normalised to the same area.

It can be seen that for the clean Pd surfaces the measured time-of-flight distributions (open circles in Figs. 1 and 2) can be well approximated by Maxwellian distributions with mean translational energies according to $\langle E_{kin} \rangle = 2kT_{Pd}$ (black lines). This means that no activation barrier for adsorption exists for H_2 (D_2) on the clean single- and polycrystalline palladium surfaces. This is in accord with the seminal measurements by Comsa and David [17, 18]. On the contrary, the recombining and desorbing H_2 (D_2) from the potassium covered surfaces

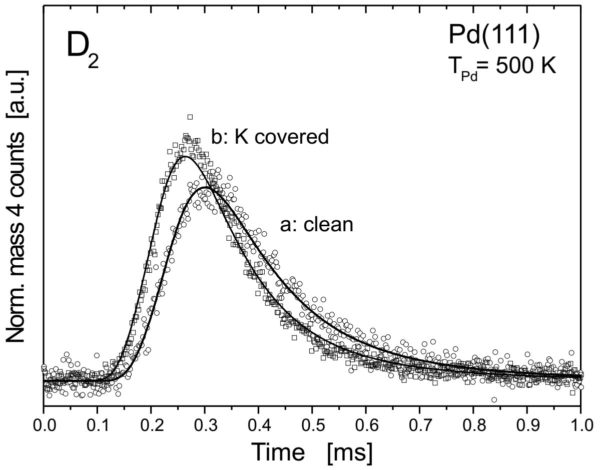

FIG. 2: TOF spectra of desorbing D_2 after permeation from clean (circles) and K-covered (squares) Pd(111). The potassium coverage was $\Theta_K(500\mathrm{K}) = 3.8 \times 10^{14}$ atoms/cm^2. The D_2-TOF spectrum from the potassium covered surface (squares) corresponds to $T_{out} = \langle E_{kin}\rangle/2k \approx 715$ K. All data are normalised to the same area.

exhibits a clear hyperthermal desorption flux, equivalent to the existence of an activation barrier for adsorption (open squares in Figs. 1 and 2). Whereas the shapes of the TOF-spectra from the K-modified Pd(111) surface still resemble Maxwellian flux distributions to a high degree, the distributions from the activated polycrystalline surface deviates from the Maxwellian behaviour (dashed line). This is just an effect of the specific potential-energy-surface generated by the potassium for this adsorption system. The mean kinetic energy of the desorbing flux expressed by T_{out} obtained by the moment method, according to $\langle E_{kin}\rangle = 2kT_{out}$, has been found to be $T_{out} = 735$ K for Pd(111) [equivalent to $\langle E_{kin}\rangle = 2.8kT_{surf}$] and $T_{out} = 900$ K for Pd(poly) [equivalent to $\langle E_{kin}\rangle = 3.4kT_{surf}$]. These findings are in good agreement with the K-dependent decrease of the H_2-sticking coefficient as described in literature [1, 2, 4]. For the system D_2/Pd(111)+K we obtained $T_{out} = \langle E_{kin}\rangle/2k = 715$ K [equivalent to $\langle E_{kin}\rangle = 2.9kT_{surf}$].

Actually, the shape of the TOF-spectrum is a direct result of the potential energy surface for the respective adsorption/desorption system. If detailed balancing holds, and this has been shown to be true for a number of hydrogen-metal surface systems [19], we should be able to figure out the energy dependence of the sticking coefficient from the TOF distribution, and vice versa. The energy dependent adsorption probability $A(E)$ is obtained by multiplying the energy dependent impingement rate $N(E)$ (Maxwell distribution) with the energy dependent sticking coefficient $S(E)$. On the other hand, dividing the energy dependent desorption probability $D(E)$ by a Maxwell distribution according to the surface temperature should also yield the energy dependence of the sticking coefficient. For the clean Pd(111) surface the energy dependent sticking coefficient for H_2 has been recently measured by nozzle beam experiments [1]. Taking the experimental data curve $S(E)$ and multiplying it by a Maxwellian distribution $N(E)$ of hydrogen at 523 K (in the energy domain), yields the curve $A(E)$ as depicted in Fig. 3a. This curve fits nicely to the experimentally observed desorption distribution $D(E)$, when converting the TOF-spectrum from the clean Pd(111) surface into a desorption distribution in the energy domain. This curve is very close to a Maxwellian according to the surface temperature, because the sticking coefficient is only slightly energy dependent in this case. This evaluation tells us that detailed balancing holds for the system H_2/Pd(111). With a similar procedure we can deduce the energy dependent sticking coefficient for hydrogen on the potassium covered Pd(111) by converting the TOF spectrum (upper curve b in Fig. 1) into a desorption distribution $D(E)$ in the energy domain and dividing it by a Maxwellian of 523 K (in the energy domain). The resulting curve in Fig. 3b then represents $S(E)$, except for a constant factor. The shape of this curve is very similar to $S(E)$-curves obtained by nozzle beam experiments for hydrogen on Pd(110) + K [1] or Ni(111)+K [9].

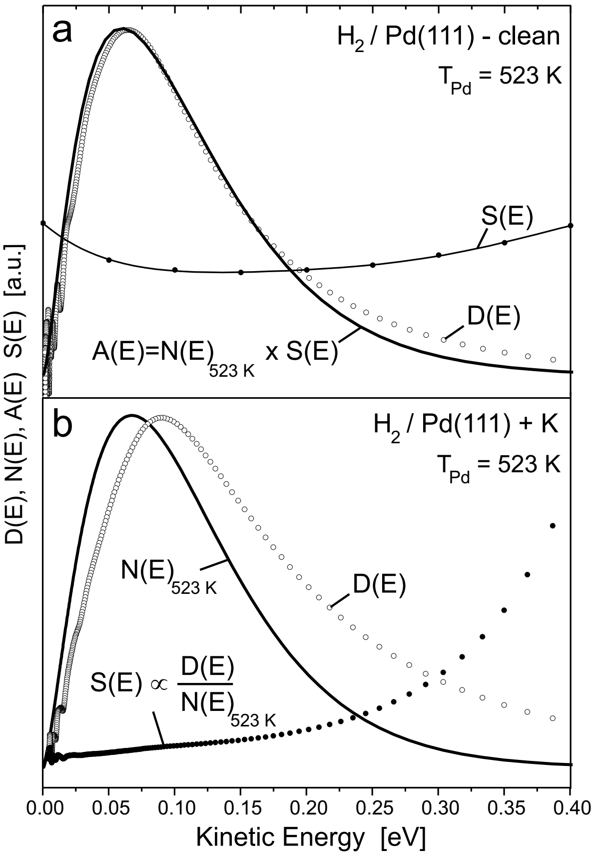

FIG. 3: Evaluation of the adsorption and desorption flux distribution for hydrogen on clean and potassium covered Pd(111), invoking detailed balancing considerations. For details see text.

B. Angular distribution: H_2 desorption from K/Pd(poly)

Because of the large distance between the sample and the detector (870 mm) and the small aperture of the QMS detector (5 mm) the TOF unit also serves as an excellent directional detector. Consequently, one should be able to measure the angular distribution of the desorbing flux $\Phi_{H_2}(\theta)$ directly by tilting the permeation source with respect to the detection direction [17]. In our case, however, the applied sample holder did not offer this possibility. Nevertheless, as a first approximation the angular distribution can be obtained from the ratio between the flux in normal direction $\Phi(0°)$ and the total desorption flux Φ_{tot}, if we assume an angular desorption flux distribution in the form of $\Phi(\theta) = \Phi(0°) \cdot \cos^n(\theta)$, as it is often done in the literature [19]. It can easily be shown that in this case the exponent n can be obtained directly from the following equation: $\Phi(0°)/\Phi_{tot} = (n + 1)/2\pi$.

Therefore, the ratios between the desorption flux into normal direction $\Phi_{H_2}(0°)$ and the corresponding total flux $\Phi_{H_2,tot}$ into the hemisphere have been measured for the clean and the potassium covered polycrystalline Pd surface. Due to influences like the finite chopper-gate-function and the velocity dependent sensitivity of the detector (QMS), the areas under the measured TOF spectra are not directly proportional to the incoming flux as such. Therefore, these influences have to be taken into account properly to evaluate values proportional to the incoming normal flux $\Phi(0°)$. Since the desorption from the clean palladium surface has been shown to be thermalized, the angular distribution can be described by $\Phi(\theta) = \Phi(0°) \cdot \cos(\theta)$ with $n = 1$. If the ratio $\Phi(0°)/\Phi_{tot}$ for this case is taken as a reference, the value n of the angular distribution for the potassium covered palladium surface can be calculated. For H_2 permeation/desorption from the K-covered polycrystalline palladium surface at 523 K a value of $n = 3.8$ has been obtained, which signifies a quite strongly forward focused distribution. This finding is in good agreement with the obtained hyperthermal flux if we assume normal energy scaling for the desorption process. According to Ref. [20] an angular distribution $\Phi(\theta) = \Phi(0°) \cdot \cos^n(\theta)$ should lead to a mean kinetic energy in the form of $\langle E_{kin}\rangle = (n+3)/2 \cdot kT_{surf.}$. Since $\langle E_{kin}\rangle = 2kT_{out} = mkT_{surf.} = (n + 3)/2 \cdot kT_{surf.}$, one can easily see that the value $m = 3.4$, as obtained from the TOF measurement, corresponds perfectly to $n = 3.8$ as obtained from the angular measurement.

C. Potassium coverage dependence of the desorption barrier for H_2 (D_2)

Sticking coefficient measurements for dissociative H_2 adsorption on potassium covered Pd(110) [1] and Pd(100) [4] surfaces revealed a linear decrease of the initial sticking probability $S^0_{H_2}$ for increasing potassium coverages. $S^0_{H_2}$ could be completely reduced on Pd(100) for coverages exceeding $\Theta_K = 0.25$ ML ($= 3.3 \times 10^{14}$ K-atoms/cm^2). These results were supported by additional theoretical investigations finding K-induced energy barriers in the entrance channel for dissociative H_2 adsorption [2]. Long-range electronic effects and not just simple site blocking have been identified as the primary cause of this behaviour. Permeation experiments can serve as an excellent means to measure the developement of such barriers. In Fig. 4, the change of the mean kinetic energy, expressed as $T_{out} = \langle E_{kin}\rangle/2k$, is presented as a function of the potassium coverage Θ_K for isothermal permeation/desorption of H_2 at $T_{Pd} = 523K$ (D_2 at $T_{Pd} = 500K$).

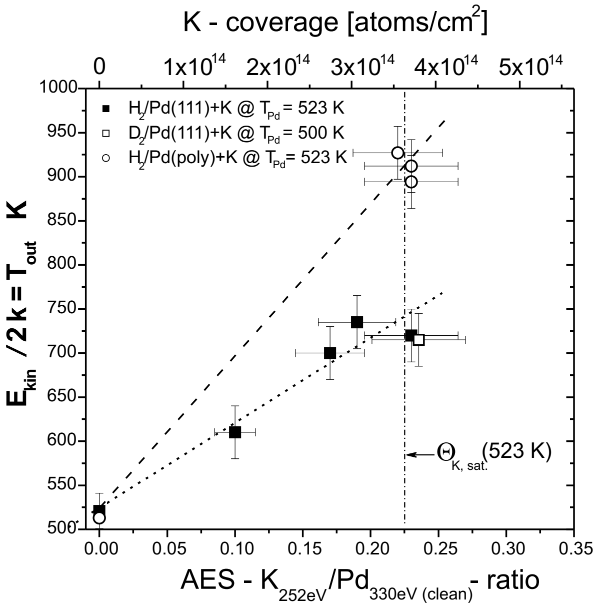

FIG. 4: Mean kinetic energy $\langle E_{kin}\rangle$ of permeating/desorbing H_2 (D_2) as a function of the potassium coverage Θ_K. $\langle E_{kin}\rangle$ is expressed as T_{out} according to $T_{out} = \langle E_{kin}\rangle/2k$.

The data for the case H_2/Pd(111) in Fig. 4 clearly show that the mean kinetic energy of recombinatively desorbing hydrogen molecules increases linearly with increasing potassium coverage. No isotope effect between H_2 and D_2 desorption could be observed within the experimental error. However, as already reported in section III A, the activation effect is much stronger on the polycrystalline surface. Fig. 4 further demonstrates that even at low coverages, where the surface still exhibits sufficient potassium-free areas, a significant influence on the desorption barrier can be found. This is in accord with the postulated long-range effect of adsorbed potassium. Thus, the present results support the picture of altered electronic densities within large areas around each of the adsorbed potassium atoms, that start to overlap more and more with increasing coverage (as described in [1]) and to simultaneously increase the effective desorption barrier.

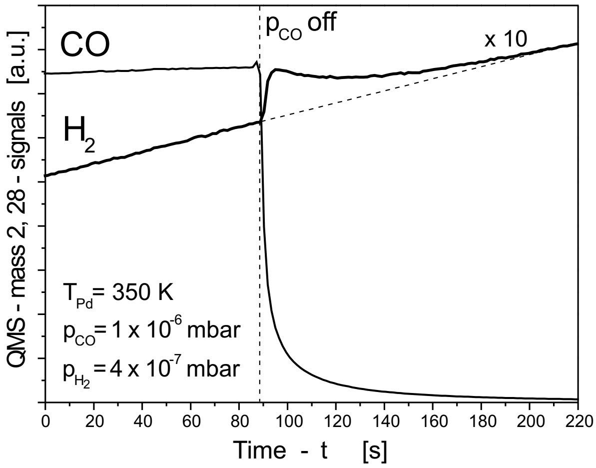

FIG. 5: Temporal evolution of the QMS mass signals (H_2 and CO) during hydrogen permeation/desorption from a clean polycrystalline palladium sample in CO atmosphere. The isotropic CO exposure is terminated at $t \approx 90$ s.

D. Site blocking by adsorbed CO

Contrary to the long-range electronic effect of adsorbed potassium, pure site blocking has been found for CO coadsorption during hydrogen permeation/desorption experiments. It was found that the kinetic energy distribution for desorption from a palladium surface at $T_{Pd} = 350K$ did not suffer any changes if the sample was simultaneously exposed to a constant isotropic CO pressure in the order of $p_{CO} = 1 \times 10^{-6}$ mbar. At this sample temperature, a quite high CO equilibrium coverage can be established on the sample surface during permeation (the desorption peak maximum of CO occurs at ~480 K according to Refs. [21–23]).

Direct evidence for the existence of a certain CO coverage under these conditions comes from a characteristic change in the hydrogen permeation flux signal after a sudden decrease of the CO partial pressure on the front side of the permeation source (see Fig. 5). Right after the CO exposure is terminated, the constant hydrogen flux signal is superimposed by a temporal increase with a long trailing edge (over a time-period of ~ 100 sec.) which is significant for a diffusion limited process. The release of hydrogen from sub-surface layers, that accumulated due to a reduction of the accessible area for out-diffusion during the CO exposure seems to be a reasonable interpretation for the observed behaviour in Fig. 5. The question remains why hydrogen can desorb without excess energy from this CO covered surface? As known from literature CO molecules can change from on-top to bridge sites at high coverage. Furthermore, coadsorption experiments of hydrogen and CO have shown that separate islands of the two species are formed on a Pd(111) surface [24, 25]. Therefore we suggest that the surfacing hydrogen locally displaces CO molecules thus enabling associative desorption from "clean" surface areas. As no change in the hydrogen TOF-spectra has been observed, the adsorbed CO can only act as site-blocking entity. This would be also in accordance to the already known diminuation of the amount of adsorbed hydrogen on CO precovered surfaces as well as to the transfer of adsorbed H atoms into subsurface sites by CO coadsorption [23, 24].

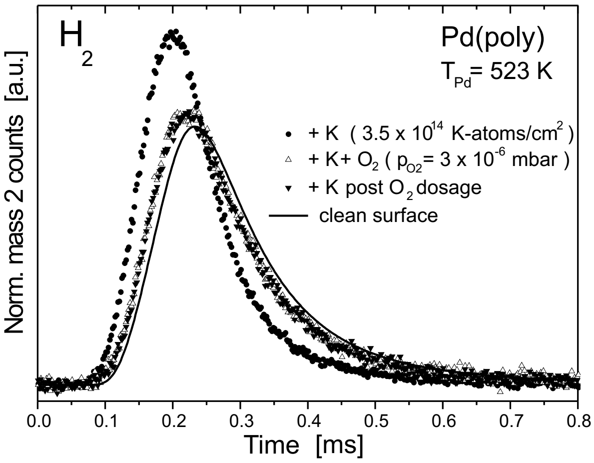

FIG. 6: Oxygen induced changes in the TOF distributions of permeating/desorbing H_2 from a potassium activated palladium surface. The mean kinetic energies of the H_2 spectra, expressed by $T_{out} = \langle E_{kin} \rangle / 2k$ are as follows: $T_{out} \approx 900$ K (full circles); $T_{out} \approx 660$ K (open triangles); $T_{out} \approx 670$ K (full triangles) and $T_{out} \approx 523$ K (black line) for the reference spectrum of the clean surface. All data are normalised to the same area.

E. Coadsorption of O_2 + K

Based on our previous experiments using permeating hydrogen for water formation on palladium surfaces [10], the TOF distributions of desorbing H_2 from potassium covered palladium surfaces during simultaneous O_2 exposure have been studied in more detail. Again, a continuous hydrogen permeation flux of about 1×10^{16} H_2-molecules/sec through the potassium saturated palladium samples has been established. The sample temperatures have generally been in the range between 450 K and 523 K and kept constant during each experiment. In the following, the K-saturated sample front side was exposed to an isotropic oxygen pressure of $p_{O_2} \approx 3 \times 10^{-6}$ mbar. Immediately after increasing the oxygen partial pressure a simultaneous reduction of the H_2-related partial pressure signal has been observed, as a part of the permeating hydrogen reacts with adsorbed oxygen towards water [10] (the hydrogen flux was too large for a total conversion into water under these conditions).

The more interesting change, though, has been observed in the kinetic energy distribution of the desorbing H_2 molecules. TOF measurements have been performed for H_2 desorption from the initially K-covered surface (as in section III A) before, during the water formation pro-

TABLE I: Mean kinetic energies $\langle E_{kin} \rangle$ of permeating/desorbing H_2 molecules from palladium surfaces. $\langle E_{kin} \rangle$ is expressed in form of a temperature T_{out} in [K], according to $T_{out} = \langle E_{kin} \rangle / 2k$.

perm./desorp.- conditions	**Pd(111)** $T_{Pd} = 523K$	**Pd(poly)** $T_{Pd} = 450K$	**Pd(poly)** $T_{Pd} = 523K$
clean	523	450	523
K covered	700-735	880	900-930
+K +O_2	600	550	660
+K post O_2	600	550	670
+K +CO	650	750	750
+K post CO	710	750	840

cess and again right after the oxygen exposure. Figure 6 and Table I summarise the results of these time-of-flight measurements. As described in the previous section, the desorption from the potassium saturated surface shows a clear hyperthermal distribution (full circles in Fig. 6). But as soon as additional oxygen is supplied, the H_2-TOF distribution is radically changed resulting in a new distribution with a much lower mean kinetic energy (open triangles in Fig. 6), close to the value obtained from the clean surface (black line). This altered distribution remains even if the oxygen is finally removed from the surrounding gas phase (inverted triangles in Fig. 6). The effective desorption barrier for recombinative desorption of H_2 is thus significantly and permanently changed, although the actual potassium coverage remained the same (as confirmed by AES). All of the described effects occur on both, the Pd(111) and the polycrystalline palladium surface, respectively. But as the absolute changes of the TOF distributions were smaller for the single crystal (see Tab. I), only the results for the Pd(poly) surface are shown in Fig. 6.

The interaction of oxygen and potassium on transition metals has already been investigated in quite a few recent studies, where it was found that a dense potassium-oxide structure can be formed on the surface [26, 27]. An important aspect of this oxide formation process constitutes the diminuation of the distances between potassium atoms in the oxide compared to the initially pure potassium layer. The transformation of the homogeneous K-layer into compressed oxide islands has been explained by an oxygen induced metallic-to-ionic transition of the adsorbed potassium atoms [14, 28]. It could be shown that oxygen exposure of the Pd(111) surface, prior to evaporation of potassium, leads to a higher K-coverage than without the oxygen pre-coverage at the same sample temperature. This corroborates the fact that a potassium oxide layer on Pd(111) incorporates more K-atoms per unit area than the pure K-adlayer. Hence, due to formation of a condensed oxide-phase with reduced potassium interdistances, potassium(-oxide)-free areas will be formed under the above presented conditions, where (i) water formation can take place and (ii) the excess hydrogen can desorb with a significantly reduced desorption barrier. These dense oxide structures, once formed, remain unchanged at sample temperatures between 450 K and 523 K even after terminating the oxygen supply.

F. Coadsorption of CO + K

The same experiments as described in section III E have been performed with isotropic carbon monoxide exposure under similar pressure and hydrogen flux conditions and in the same temperature range. Exemplary results for TOF distributions of permeating/desorbing hydrogen, before, during and after CO co-exposure at $T_{Pd} = 523$ K are presented in Figure 7 and Tab. I. Again, similar to the effect of O_2 dosing, the effective barrier for hydrogen desorption is significantly reduced (open triangles in Fig. 7) as soon as the CO pressure is supplied to the K-saturated sample. The CO induced decrease of the effective desorption barrier is found to be somewhat less pronounced compared to the oxygen induced changes. If CO is dosed at a sample temperature of 450 K the resulting configuration of the K-CO layer also remains intact in absence of the isotropic CO pressure. This is indicated by an irreversible reduction of the desorption barrier (the H_2 TOF spectra during and after CO exposure are identical; see Tab. I). Only upon heating to about 523 K, the adlayer could again be completely reactivated, leading to H_2 TOF spectra similar to the one presented in Fig. 7 (full circles).

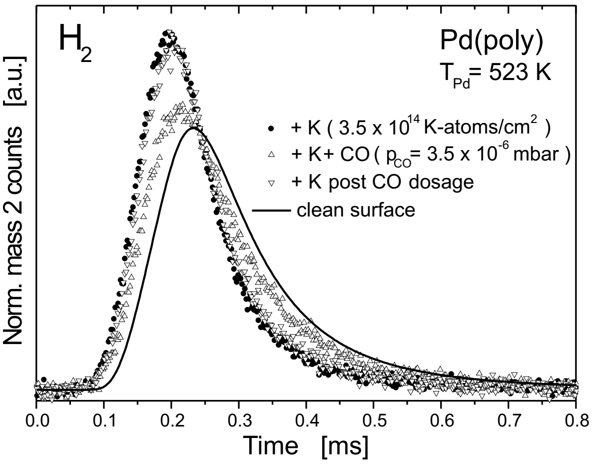

FIG. 7: CO induced changes in the TOF distributions of permeating/desorbing H_2 from a potassium activated palladium surface. The mean kinetic energies of the H_2 spectra, expressed by $T_{out} = \langle E_{kin} \rangle / 2k$ are as follows: $T_{out} \approx 930$ K (full circles); $T_{out} \approx 750$ K (open triangles); $T_{out} \approx 840$ K (inverted triangles) and $T_{out} \approx 523$ K (black line) for the reference spectrum of the clean surface. All data are normalised to the same area.

For the CO exposure experiments performed at $T_{Pd} = 523$ K, however, it could be found that the reduced effective desorption barrier (open triangles in Fig. 7) immediately returns almost up to its initial height at the moment when the CO exposure is terminated (inverted triangles). Again, similar results have been observed on the Pd(111) and the polycrystalline surface but the absolute changes in the energy distributions were larger on the Pd(poly) sample (see values in Fig. 7).

The different behaviour of reversibility of the CO induced barrier reduction for the different sample temperatures can be attributed to the desorption temperature (adsorption energy) of CO on palladium. We suppose that after the CO exposure at 450 K enough CO molecules remain adsorbed on the surface, keeping-up the special K-CO configuration that minimises the desorption barrier for hydrogen. At sample temperatures around 523 K, however, due to more rapid thermal desorption no significant CO coverage could be established without an appropriate CO pressure, even in presence of a K-adlayer.

In section III D we have described that a pure adlayer of CO on clean palladium surfaces does not induce a significant barrier for H_2 adsorption nor is there any evidence for reactions between hydrogen and CO under these conditions. It is also known from the literature that potassium adlayers might induce CO dissociation [7] or initiate the formation of formate or carbonate species [29], but no evidence for one of these reactions to happen at larger scale could be found in the present case. This comprised the absence of detectable carbon or oxygen accumulations on the palladium surfaces or additional CO_2 or H_2O desorption, correlated with the CO pressure or the hydrogen flux. Finally, as the desorption barrier was shown to be reversible, no O+K-adlayers from dissociated CO were formed, which would remain stable after the CO exposure. Only on Pd(poly), where the regeneration of the initial barrier was not as complete as on Pd(111) some CO dissociation might have occurred.

Concerning the reduction of the effective H_2-desorption barrier by CO we think that a similar demetallisation-effect, as found for the O_2 coadsorption experiments, might be the appropriate explanation for the observed behaviour. The interaction of CO molecules with the adsorbed K-atoms reduces their effective atomic radius (from metallic to ionic), thus inducing the formation of more compact CO-K domains and K-depleted areas with reduced desorption barrier. Carbon-monoxide induced demetallisation of an adsorbed potassium layer has also been observed for CO adsorption on K/Pt(111) [5] and by He-scattering experiments on K/Cu(100) [28]. For the CO-K domains, a combined DFT and LEED(IV) study proposed a $(\sqrt{3} \times \sqrt{3})R30°$-(K+CO) structure on Pt(111) [30]. This structure may serve as an example for similar compact CO-K domains that developed on the palladium surfaces in this study. Hydrogen coming from subsurface layers then may primarily desorb via those paths with reduced barriers, e.g. the K-depleted domains.

As a consequence, at sample temperatures above the desorption temperature of CO on K covered palladium, the CO equilibrium coverage and consequently the effective hydrogen desorption barrier can easily be controlled by the surrounding CO partial pressure. The resulting mean kinetic energies $\langle E_{kin} \rangle$ could be continuously adjusted between $\langle E_{kin} \rangle = 2kT_{out} = 0.16$ eV ($T_{out} = 930$ K) at $p_{CO} \approx 1 \times 10^{-10}$ mbar and $\langle E_{kin} \rangle = 0.13$ eV ($T_{out} = 750$ K) at $p_{CO} \approx 3.5 \times 10^{-6}$ mbar on the K-modified polycrystalline palladium surface.

IV. SUMMARY & CONCLUSION

We have investigated the hydrogen (deuterium) permeation and desorption from Pd(111) and polycrystalline palladium by time-of-flight spectroscopy. Desorption from the clean palladium surfaces has been found to result in a thermalized flux, which means that there exists no activation barrier for adsorption. However, hyperthermal H_2 (D_2) desorption has been observed on both surfaces covered with potassium, indicating the existence of an activation barrier for adsorption. The mean kinetic energy of desorbing H_2 was found to increase linearly with the applied potassium coverage. At the same time, the angular distribution changed from a cosine distribution to a forward-focused distribution ($cos^{3.8}\theta$).

Coadsorption of O_2 on the K-covered surfaces reduced the effective H_2 desorption barrier due to the formation of dense potassium-oxide structures separated by areas of less K-coverage. This change of the desorption barrier was irreversible.

Coadsorption of CO at 523 K lead to a reversible transfer of the homogeneous K-overlayer into denser CO-K structures separated by areas with a reduced H_2 desorption barrier. The effective mean barrier height for recombinative hydrogen desorption could therefore be reversibly varied within a certain range, simply by adjusting the surrounding CO pressure.

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