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INTERACTION OF H_2 (D_2) AND POTASSIUM WITH Ag(111) AND Ag(110)

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Adsorption and coadsorption of H_2 (D_2) and potassium on the single–crystal silver surfaces (111) and (110) have been studied using thermal desorption spectroscopy, work function measurements and LEED. Atomic hydrogen was used to cover the silver surfaces, since a very high activation barrier makes molecular adsorption impossible. From the Ag(111) surface hydrogen desorbs in a single peak with a close to second order reaction and a desorption energy of 29.4 kJ/mol. Hydrogen desorption from Ag(110) is characterized by two overlapping desorption peaks which are very sensitive to small amounts of water coadsorption. Upon hydrogen saturation (0.65 ML) on Ag(111), the work function increases by 240 meV. Coadsorbed potassium shifts the desorption temperature for H_2 dramatically by 250 K to higher temperature on both surfaces. Simultaneous desorption of hydrogen and potassium on both silver surfaces with a ratio of 1 K-atom to $4H_2$ molecules indicates the formation of a potassium–hydrogen complex in the coadsorbate.

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1. Introduction

Hydrogen adsorption on noble metal surfaces has recently attained considerable interest. Due to the relatively high activation barrier caused by the filled d–band, virtually no dissociative adsorption of hydrogen molecules at room temperature can be observed on these surfaces. The most efficient way to cover noble metal surfaces with hydrogen is to use beams of atomic hydrogen [1]. Nevertheless, information concerning the interaction of molecular hydrogen with noble metal surfaces can still be gathered by studying the desorption kinetics using thermal desorption spectroscopy. In this paper we report on the hydrogen–silver adsorption system and the influence of potassium coadsorption on the hydrogen adsorption and desorption kinetics. Apart from some theoretical work on the hydrogen-silver system [2], only a few reports deal with the experimental study of the specific adsorption systems H_2-Ag(111) [3 – 5] and H_2-Ag(110) [6]. From the experimental data available, one can see that considerable differences in the results exist. Obviously, small changes in the surface structure and/or minute amounts of impurities seem to have a significant influence on the desorption kinetics. The aim of the present work is to study the hydrogen–silver system in more detail.

2. Experimental

Single crystal planes (110) and (111) of silver were oriented with a precision goniometer polishing device [7] to within $\pm 0.3^\circ$, as checked in a Laue apparatus. They were subsequently polished with SiC and diamond paste. After the last polishing step involving 1 μm diamond paste as well as 0.05 μm alumina, an electropolishing procedure was applied. Thin platinum wires (0.2 mm in diameter) for resistive sample heating were attached to the back side of the crystals using gold soldering. In the same way a NiCr-Ni thermocouple was attached to the sample.

Upon introduction of the sample into the ultrahigh-vacuum chamber, the crystal surface was cleaned by extended Ar^+ sputtering (1-2 keV) at room temperature and subsequent annealing at 800 K for several minutes [8]. Surface cleanliness was checked by Auger spectroscopy and surface crystallography was monitored by LEED. Work function measurements were performed with a retarding field method. Modulation of the electron beam gun and detection of the sample current using a lock-in amplifier allowed work function measurements during desorption experiments [9].

Dosing of the sample was carried out using the fraction of atomic hydrogen effusing from a Knudsen source at 1600 K. At this temperature a few percent of the hydrogen molecules are dissociated [10]. No attempt to calibrate the effective exposure to atomic hydrogen was made. However, calibration of the absolute coverage was performed by comparing the desorption spectra with a standard desorption spectrum from a tungsten filament [11]. With this calibration method absolute coverages can be measured with an accuracy of 5–10 % . The sample temperature during adsorption was held at about 100 K to avoid premature desorption due to the low desorption energy. Temperature programmed desorption was performed with a heating rate of 3 K/s using a computer controlled regulation circuit. Hydrogen desorption was monitored with a mass spectrometer in the isotropic mode. Potassium was evaporated using a commercial SAES getter source and potassium desorption spectra were recorded with an in–line mass spectrometer.

3. Results and discussion

3.1. $H_2(D_2)/Ag(111)$

A typical set of desorption spectra for hydrogen from Ag(111) can be seen in Fig. 1. The spectra shift to lower temperature with increasing coverage and the spectra are close to symmetric. These features are characteristic for second–order desorption. The evaluation method by Parker et al. [12], which allows the determination of the reaction order by a simple fit procedure, yields a desorption order of 1.7 ± 0.3. Analysis of the spectra using the method by King [13] leads to the coverage independent desorption energy of 29.4 ± 3 kJ/mol. An alternate evaluation of the desorption spectra using the leading edge analysis by Habenschaden and Küppers [14] yields basically the same results. At very high coverages (curves g–i) the desorption spectra show a rather unorthodox behaviour; they cross each other at the trailing tail of the desorption curves. In a set of desorption spectra of this type one can always find two spectra where at a specific temperature the momentary coverages are the same, but the desorption rates are different. This means the desorption rate is not a state function of the momentary coverage and temperature, but is also a function of the initial coverage. In other words, full quasi–equilibrium does not exist during desorption. A similar desorption behaviour has been observed for the system H_2–Cu(100) [15]. Most likely, the surface is changed upon adsorption of large amounts of hydrogen to yield a slightly lower effective desorption energy. This is probably due to the surface reconstruction or local displacement of surface atoms. These changes are apparently not restored immediately during desorption, giving rise to a shift of the total desorption spectrum to lower temperatures. Only after complete removal of the adsorbed hydrogen will the surface reconstruction be lifted. In this coverage regime standard evaluation methods using the full set of spectra [13] are no longer applicable.

The saturation hydrogen coverage on the Ag(111) surface was calibrated to 0.65 ± 0.05 ML using the tungsten filament standard spectrum [11]. This value is in very good agreement with the result of Lee et al. [4]. The work function increases linearly with increasing hydrogen coverage and results in a maximum work function change of 240 ± 10 meV at a coverage of 0.65 ± 0.05 ML. Applying the Helmholtz equation $\Delta\Phi = \mu N_s \Theta/\epsilon_0$, with the density of the Ag(111) surface $N_s = 1.38 \times 10^{15}$ atoms/cm^2 and the vacuum permittivity $\epsilon_0 = 8.8 \times 10^{14}$ As/Vcm, one obtains a dipole moment of $\mu = 0.07$ D [16]. Typically, the dipole moments caused by hydrogen atoms on metal surfaces are below 0.05 D. Therefore the result of $\mu = 0.07$ D suggests some surface reconstruction taking place during adsorption of hydrogen leading to a higher effective dipole moment.

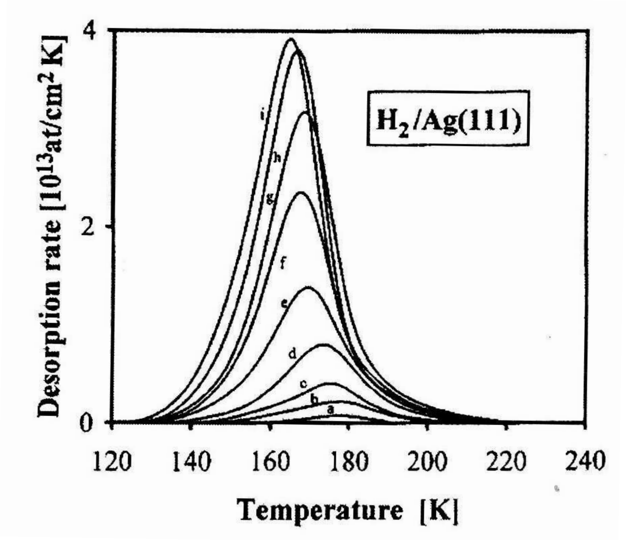

Fig. 1. Thermal desorption spectra for hydrogen recombinatively desorbing from Ag(111)*. The curves* a *through* i *represent increasing atomic hydrogen exposures. Adsorption temperature: 100* K*, heating rate* $\beta = 3$ K/s.

3.2. H_2+ *Potassium/*Ag(111)

The desorption kinetics of hydrogen undergoes dramatic changes on a potassium precovered Ag(111) surface. Figure 2 shows hydrogen (curve a) and potassium (curve b) desorption spectra for 0.7 ML hydrogen adsorbed on a 1.5 ML potassium precovered surface. The spectra for the same species adsorbed separately on the silver surface are included for comparison (H_2: curve c and K: curve d). In the case of coadsorption the hydrogen desorption peak is shifted by 250 K compared with the clean surface and appears as a single peak at 420 K (curve a). Part of the potassium multilayer still desorbs at about 320 K, but a well pronounced second potassium desorption peak shows up concomitantly with the hydrogen desorption peak (curve b). A calculation of the absolute amount of potassium atoms and hydrogen molecules desorbing simultaneously yields a ratio of K:H_2 = 1:4. This demonstrates clearly that a hydrogen potassium complex is formed, mostly with potassium atoms in the multilayer as deduced from the decrease of the K multilayer peak. Nevertheless, no KH_x complex could be detected in the mass spectrometer. This means that the complex must be very unstable and decomposes during or immediately after desorption.

A comparison of our data for hydrogen-potassium coadsorption with the data by Zhou et al. [3] for the hydrogen-chlorine coadsorption system shows the opposite influence of electropositive and electronegative coadsorbates on the energetics and kinetics of hydrogen desorption. Whereas preadsorbed potassium increases the desorption temperature and the saturation coverage of hydrogen, preadsorbed chlorine decreases the desorption temperature and the saturation coverage for hydrogen. Attractive forces between hydrogen and potassium stabilize the adsorbate, whereas repulsive interaction forces between chlorine and hydrogen destabilize the adsorbate. This influence of electronegative and electropositive coadsorbates on hydrogen adsorption has been investigated in some detail for the H_2 + K and H_2 + O on Ni(111) [17]; the results confirm the above conclusions.

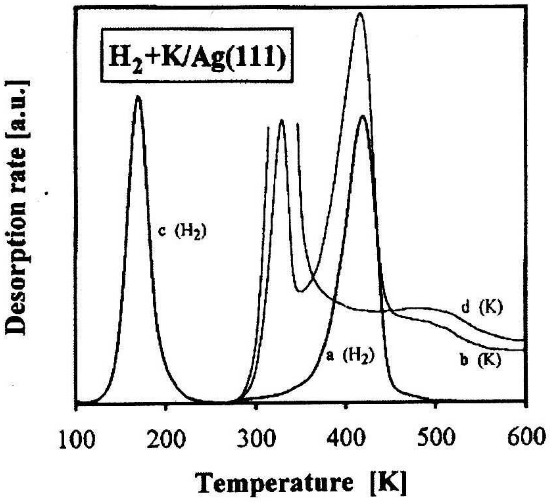

Fig. 2. Desorption spectra for hydrogen and potassium from Ag(111). (a) *Desorption of hydrogen (0.7* ML*) from a potassium precovered surface* (1.5 ML), (b) *Potassium desorption from the coadsorbed layer,* (c) *Desorption of pure hydrogen* (0.5 ML), (d) *Desorption of pure potassium* (1.5 ML).

3.3. $H_2(D_2)$/Ag(110)

Similar to the Ag(111) surface, no molecular adsorption of hydrogen (deuterium) could be detected on Ag(110). Therefore, atomic hydrogen (deuterium) from a hot Knudsen source was used again to cover the surface. A typical set of desorption spectra for deuterium is depicted in Fig. 3. Two desorption peaks can be recognized, the higher one slightly shifted to lower temperature with increasing coverage, whereas the lower desorption peak remains nearly unchanged with coverage. A shoulder at the high temperature side of the spectrum even suggests a third desorption peak. At saturation coverage (which was determined to be 0.95 ML, using the calibration method described above) the two peaks are located at 155 K and 165 K. Since the overlap of both peaks is rather pronounced, we abstained from an evaluation of the desorption energies using the peak shape. It should be mentioned that it was very difficult to get reproducible results for this adsorption system. Small changes in the experimental procedure (surface preparation, annealing time) altered the shape of the desorption spectra. In particular, concomitant adsorption of small amounts of water had a significant influence on the desorption spectra.

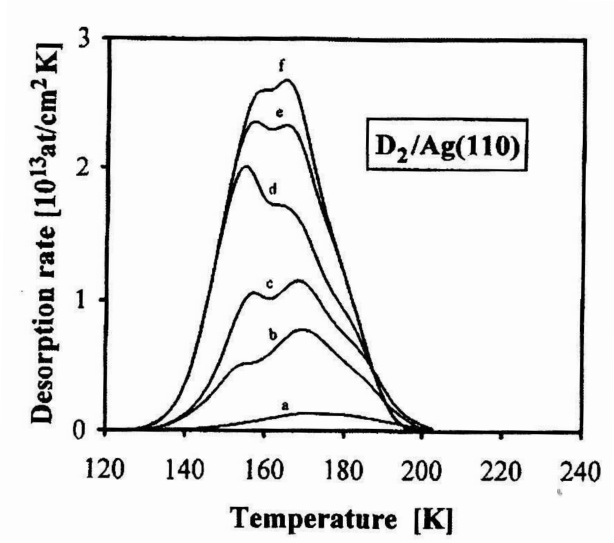

Fig. 3. Thermal desorption spectra for deuterium recombinatively desorbing from Ag(110). *The curves* a *through* f *represent increasing atomic deuterium exposures. Adsorption temperature: 100* K, *heating rate* $\beta = 3$ K/s.

3.4. H$_2$ + *Potassium/*Ag(110)

Potassium adsorption on and desorption from the clean Ag(110) surface is comparable with the Ag(111) case. A broad desorption peak for the monolayer, ranging from 350 K to over 600 K, and a sharp desorption peak for the multilayer located at 320 K were observed. Similarly, the hydrogen desorption peak changed dramatically upon potassium coadsorption. In Fig. 4 hydrogen desorption spectra for different amounts of preadsorbed potassium can be seen (curves a through c). For all spectra the same hydrogen exposure was used, which produced 0.8 ML of adsorbed hydrogen on the clean surface. With increasing potassium precoverage the hydrogen desorption peaks broaden and shift to higher temperature. At high potassium precoverage the hydrogen desorption spectra sharpen again until, at a more than one monolayer potassium precovered surface, a very sharp hydrogen desorption spectrum appears at 420 K. In Fig. 4 also the desorption spectrum of pure potassium (curve d) and of potassium coadsorbed with hydrogen (curve e) is shown.

The ratio of potassium atoms to hydrogen molecules desorbing simultaneously in the peak around 420 K is 1: 4.5. For this calculation a potassium monolayer density of 0.45×10^{15} atoms/cm^2 (0.54 ML) was assumed. This calibration was done by comparing the potassium desorption spectra with the well defined potassium spectra from Ni(111) [17]. It is interesting to note that the amount of adsorbed potassium atoms in the monolayer is practically the same on both silver surfaces (111) and (110). Furthermore the saturation coverage of hydrogen on the fully potassium covered silver surfaces is also nearly the same (about 0.95×10^{15} H atoms/cm^2). And finally also the part of potassium which desorbs simultaneously with hydrogen (about 20 % of the potassium monolayer) is the same for both surfaces.

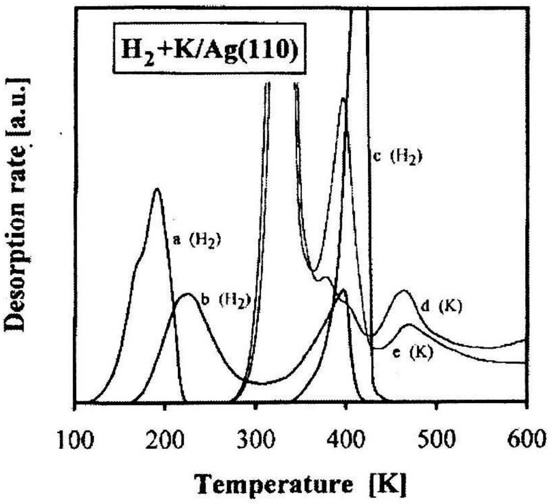

Fig. 4. Desorption spectra for hydrogen and potassium from Ag(110). (a) *Desorption of pure hydrogen (0.8* ML*),* (b) *Hydrogen desorption after 0.8* ML *potassium precoverage,* (c) *Hydrogen desorption after* 1.8 ML *potassium precoverage,* (d) *Desorption of pure potassium (1.8* ML*),* (e) *Potassium desorbing from a coadsorbed layer (1.8* ML *potassium, 1.1* ML *hydrogen).*

4. *Summary*

We have studied the desorption kinetics of hydrogen (deuterium) from clean and potassium covered Ag(111) and Ag(110) surfaces using temperature programmed desorption and work function measurements. Atomic hydrogen was used to cover the silver surfaces since a rather high activation barrier for dissociative adsorption exists. We found that hydrogen desorbs from the Ag(111) surface in form of a single peak close to a second order reaction, with a coverage independent desorption energy of 29.4 kJ/mol. A rather large change of the work function by 240 meV upon hydrogen saturation (0.65 ML) points to some surface atom displacements caused by the adsorbate. Preadsorbed potassium shifts the hydrogen desorption peak by 250 K to higher temperature, and simultaneous desorption of hydrogen and potassium can be observed. This is explained by decomposition of a potassium–hydride complex. For the hydrogen (deuterium)–Ag(110) system two desorption peaks were observed. The saturation coverage is 0.95 ML. It could be shown that the shape and temperature position of the peaks were drastically affected by small amounts of water coadsorbed from the residual gas. Preadsorbed potassium on Ag(110) influenced hydrogen desorption in a similar way as for the hydrogen–Ag(111) case:

Concomitant desorption of potassium and hydrogen indicating decomposition of a potassium hydride complex.

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INTERAKCIJA H_2 (D_2) I KALIJA SA Ag(111) I Ag(110)

Adsorpcija i koadsorpcija H_2(D_2) i kalija na monokristalnim (111) i (110) površinama srebra proučavane su termalnom desorpcijskom spektroskopijom, mjerenjima izlaznog rada i LEED. Sa Ag(111) površine vodik desorbira s jednim vrhom s desorpcijskom energijom 29.4 kJ/mol. Desorpcija vodika sa Ag(110) ima dva preklopljena desorpcijska vrha koji su vrlo osjetljivi na male količine adsorbirane vode. Koadsorbiran kalij pomiče desorpcijsku temperaturu naviše za 250 K na obje površine. Istovremena desorpcija vodika i kalija s obje površine srebra ukazuje na stvaranje kompleksa kalij–vodik u koadsorbatu.