Manipulating the activation barrier for $\text{H}_2(\text{D}_2)$ 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 to 523 K. Time-of-flight spectroscopy has been used to determine the translational energy distributions of associatively desorbing $\text{H}_2(\text{D}_2)$ molecules as a function of the potassium coverage and additional isotropic $\text{O}_2$ 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 such as $\text{O}_2$ or CO. Especially by choosing different isotropic CO pressures, the effective desorption barrier for hydrogen could be reversibly decreased and increased, which resulted in the equivalent changes of the mean kinetic energies of the desorbing $\text{H}_2$ molecules. © 2005 American Institute of Physics. [DOI: 10.1063/1.2121487]

I. INTRODUCTION

The influence of adlayers such as potassium on Ni, Rh, or Pd surfaces has been of great interest in catalysis since they often act as inhibitors as well as promoters in many surface reactions. Typical examples are the hindering of dissociative $\text{H}_2$ adsorption,$^{1-4}$ the adsorption and bond weakening/dissociation of $\text{CO}$ on Pt and Rh,$^{5-7}$ or the HCOOH stabilization on Pd by potassium.$^8$ Especially, the weakening/dissociation of CO on Pt and Rh,$^{5-7}$ or the bon monoxide.

II. EXPERIMENT

The experiments were carried out in an ultrahigh vacuum chamber, equipped with an Auger electron spectrometer (AES), low-energy electron-diffraction (LEED) optics, a differentially pumped inline quadrupole mass spectrometer (QMS), and a time-of-flight (TOF) spectrometer. An extractor ion gauge, a spinning rotor gauge, and a QMS further 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 such as 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.$^{12}$ The TOF data have been evaluated either by the least-squares fits of the Maxwellian distributions or by the momentum method,$^{13}$ if the spectra exhibited a non-Maxwellian behavior. All the 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 $\text{H}_2$ 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 Ref. 10. The permeation source was attached to a LN$_2$-cooled sample holder which allowed the positioning of the sample in front of all the analytical devices. A continuous flux of hydrogen could be achieved with this device by applying a proper backpressure.

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