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The adsorption properties of $PdZn_x$ alloy on Pd(1 0 0): Preparation and characterization

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Abstract

The formation of $PdZn_x$ alloy on Pd(1 0 0) and its characteristics were investigated by various methods, such as photoelectron, auger-electron, electron energy loss, thermal desorption spectroscopic methods and work-function measurement. The alloy was produced by the decomposition of diethyl zinc on Pd(1 0 0). The alloy surface reacts with O_2 and ZnO_x is formed. The reactivity of alloy to hydrogen is similar to that of K/Pd. The stability of adsorbed CO is lower than on clean Pd(1 0 0).
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1. Introduction

From an industrial point of view transition metals supported on ZnO are important catalysts. Some of them are in partially reduced form under working conditions. Alloy formation has been observed between Zn and the transition metal in several cases [1,2]. Great effort has been made to understand the real mechanism of these reactions on the above catalysts. Both Cu and Pd are active in methanol synthesis, but in some cases supported Pd was inactive [1,2]. The formation of stable, catalytically inactive alloy was considered on Pd containing automotive exhaust catalysts poisoned by Pb [3]. In the case of Pd/SnO_x, not only the chemical states of additives but also the Pd–Sn interaction could play a key role in the sensing process [4].

The alloy formation between evaporated Zn and transition metal single-crystal surfaces are discussed in [5] and references therein. It was found that a metal atom deposited on the surface of another metal can exhibit large perturbations in its electronic and chemical properties. Photoelectron spectroscopy methods revealed that d metals in contact with an sp metal have valence levels shifted toward higher binding energy with respect to those of their bulk position [5]. This is a consequence of d(s,p) rehybridization and charge transfer.

The primary aim of this work is to examine the interaction of Zn atoms with the Pd(1 0 0) surface. For this purpose we use a Zn precusor, diethyl zinc (DEZn) compound. The decomposition of adsorbed DEZn has been studied previously on Pd(1 0 0) and Rh(1 1 1) [6,7]. It has been found that the decomposition of DEZn is completed below 250 K. Apart from a small fraction of C_xH_y species the decomposition process is finished and metallic Zn is left on the surface above room temperature.

2. Experimental

The experimental setup and methods were described in detail in [6]; here we give only a short description. The experiments were carried out in a standard ultrahigh vacuum chamber equipped with facilities for photoelectron spectroscopy, an electron gun for Auger-electron spectroscopy (AES) and electron energy loss spectroscopy (EELS). Thermal desorption spectra (TDS) were followed by a multiplexed mass spectrometer. Changes in the work function ($\Delta\Phi$) were obtained by measuring the secondary electron cut-off in the photoelectron spectra with the sample at −9 V relative to ground.

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The Pd(1 0 0) single crystal was cut, polished and cleaned by standard methods which consisted of Ar^+ ion bombardment, annealing at 1100 K, and oxygen treatment at 700 K. The amount of oxygen, sulfur, phosphorus and carbon impurities on the cleaned surface were below the detection limit. DEZn was purified by freeze–pump–thaw cycles. DEZn was exposed at a constant pressure through a capillary while the sample was held at 300 K. The coverage was determined from the Zn($2p_{3/2}$) area, and simultaneously the carbon content left from the organic part of DEZn was also monitored by X-ray photoelectron spectroscopy (XPS); it was only 1–2% of a monolayer. Between two different experiments the sample was flashed to 1150 K twice and cleaned by standard methods and neither Zn nor carbon accumulation was found.

3. Results and discussion

After the adsorption of DEZn on the clean Pd(1 0 0) at 300 K a peak at 1021.1 eV with full-width at half-maximum (FWHM) 1.4 eV was detected by XPS. The area of this Zn($2p_{3/2}$) peak as a function of DEZn exposure shows a Langmuir-type uptake curve. At saturation its position is shifted to 1021.7 eV, and the FWHM slightly increased (1.65 eV). This peak can be identified as metallic Zn [1,2,5–7]. The Pd($3d_{5/2}$) XPS signal was also followed. The presence of Zn on the surface induced a new state of Pd separated by ~1.0 eV from the normal Pd peak at 335.2 eV. This XPS shift is in correlation with the enthalpy of the Pd–Zn alloy formation [5,8]. In our He I and He II excited ultraviolet photoelectron spectroscopic (UPS) studies we found similar trends with only a few differences between them. The presence of Zn atoms on the surface is confirmed by the Zn 3d peak at 9.6–9.7 eV (Fig. 1A and B). Due to the direct electronic interaction between the two metals, electron density close to the Fermi edge (at 0.5 eV) decreased and some re-structuring occurred in the Pd 4d band, with peaks at 2.85 eV in He I, 2.9–3.6 eV in He II excited UPS. The weak signals centered at 5.7, 8.0–8.2 and 13.2 eV are due to some adsorbed alkyl groups [6,7]. Their role in the interaction discussed here might be negligible, because their thermal instability is so low they vanished when the sample was heated up to 350 K. The presence of Zn on the Pd(1 0 0) surface decreases its work function by 1.0 eV at saturation exposure. EELS spectra, detected both in the secondary electron energy distribution ($N(E)$) and in the derivative ($dN(E)/dE$) mode, show a new peak at 12.5 eV with 300 eV primary electron energy. This can be interpreted as an electron transition from the Zn 3d orbital to the empty 4p above the Fermi level [6].

The effect of temperature on this metastable surface has been followed by XPS and EELS methods. The intensities of these Zn induced characteristic features plotted as a function of temperature (Fig. 2A) show more differences. The area of the Zn $2p_{3/2}$ signal shows a monotonous decrease between 400 and 1100 K, but it is constant at half-monolayer Zn up to 800 K. It is advantageous to compare

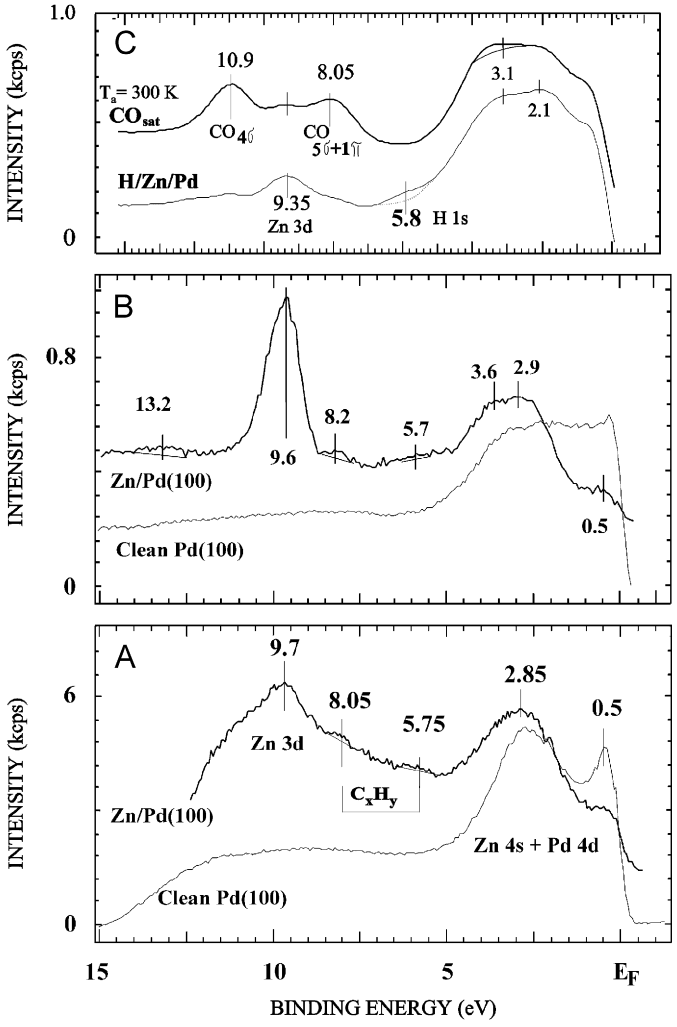

Fig. 1. He I (A) and He II (B) excited UPS spectra of clean Pd(1 0 0) and Zn/Pd(1 0 0) surfaces; (C) He II excited UPS of H/Zn/Pd(1 0 0) and CO/Zn/Pd(1 0 0) after saturation at 300 K with H_2 and CO, respectively. The Zn coverage was 25% of the maximum Zn coverage.

this with the corresponding Zn TDS spectra, presented in Fig. 2B. Apart from small Zn peaks below 600 K—which might come from the sample holder—Zn starts to desorb at 850 K. The Zn induced peak in EELS shows a rapid decrease at around 500 K. In the 500–850 K temperature range another alloy phase is present on the surface in which the electronic band structure has changed but EELS peak was not detected, although Zn is on the surface.

The electron and thermal desorption spectroscopic results support our conclusion that the interaction between these two metals is strong, i.e., alloy was formed in the top layer. In the XPS spectra the separation of the two Pd $3d_{5/2}$ states is quite high, 1.0 eV. The area of this new state is 39% of the total Pd peak. We may consider that those Pd atoms, which are surrounded by Zn atoms in the alloy, have modified binding energy. In this calculation, we neglect the layer thickness. The intensity ratio of Zn($2p_{3/2}$) to the "new" Pd($3d_{5/2}$) is 2. Taking into account the

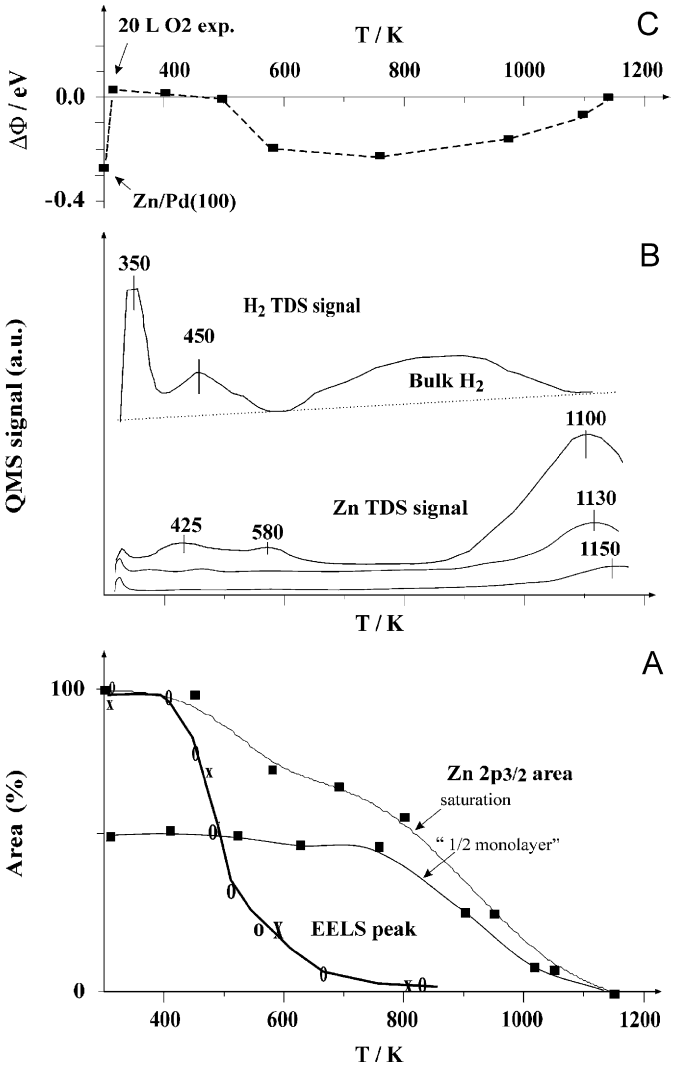

Fig. 2. (A) The relative intensities of Zn $2p_{3/2}$ and Zn-induced EELS peaks (peak-to-peak values in dN(E)/dE)) as a function of temperature; (B) Thermal desorption of Zn and H_2 from the Zn/Pd surface after saturation at 300 K by diethyl zinc. (C) Work function changes of the O_2/Zn/Pd(1 0 0) layer as a function of temperature with respect to the bare Pd surface.

sensitivity factors [9] and analyser transmission factors, the composition of this surface alloy N_{Zn}:N_{Pd} is 7.5. The Zn content is far above the value characteristic of Pd_5Zn_{21} [10]. The composition of this alloy changes at 500 K, close to the preparation temperature applied by Steinrück et al. [11]. This process ended up in a well-defined three-dimensional alloy. Based on the calculations of Chen et al. [12] the diffusion of Zn into the bulk finished at the 1:1 composition. Zn desorbtion starts above 800 K with T_p values from 1100 to 1150 K, slightly higher than in the case of Zn/Pd(1 1 1) [17]. According to Chen et al. [12] a Pd-rich interface was never formed between the topmost alloy layer and bulk Pd. In line of this consideration the experimental fact is that we never found any Zn accumulation.

The adsorption of CO on the alloy surface is both of technical importance as well as of academic interest, and can be used as a characterization method. The presence of Zn decreases the desorption peak temperature of CO. At its half-saturation Zn shifts this T_p value below room temperature. In the experiment presented in Fig. 1C, Zn coverage was only a quarter of the saturation and this surface was exposed to 15 L CO. Besides the Pd 4d and Zn 3d band, the CO-induced peaks at 8.05 and 10.9 eV are also shown on the He II excited UPS spectrum of the CO/Zn/Pd(1 0 0) layer (Fig. 1C), which can be assigned to the $5\sigma + 1\pi$ and 4σ orbitals [13]. Another feature at 3.1 eV also appeared, which can be regarded as a manifestation of a fractionally occupied 2π*-derived adsorbate resonance [14].

The adsorption and reaction of oxygen with Zn/Pd surface is briefly introduced. The alloy surface shows an enhanced activity because the uptake of oxygen increases by a factor of 2–3 compared with the bare Pd(1 0 0). This oxygen has two different chemical states well separated by 5 eV in the AES spectra, very likely one bonded to Pd, the other to Zn. The latter one is dominant, but its intensity decreases faster with temperature. Work function measurements show a dramatic change in the adsorbed layer at 500 K, and above 700 K, it is similar to the oxygen-free case (Fig. 2C). This means that with increasing temperature, oxygen desorbs and the surface tends to form a Zn/Pd alloy [1,16].

The interaction of hydrogen with Zn/Pd alloy was also examined. A weak signal at 5.8 eV in UPS (Fig. 1C) is one indication of adsorbed hydrogen [15]. The peaks in the H_2 TDS spectra (Fig. 2B) can be interpreted as follows: (i) some H_2 desorbs from the sample holder (T_{max} = 350 K); (ii) the chemisorbed hydrogen desorbs with $T_p = 450$ K; stabilization by Zn is evident. (iii) the broad peak between 600 and 1100 K is the release of dissolved H_2. Similar desorption spectra were found when hydrogen was adsorbed at 300 K on the K/Pd(1 0 0) interface [17]. In this context the Zn/Pd layer is very similar to K/Pd.

4. Conclusions

The advantage of the application of DEZn is the preparation of an oxygen-free Zn layer. The as-prepared layer—which has a characteristic EELS feature—is not stable thermodynamically. A new alloy phase was formed at 500 K, which starts to decompose above 850 K. Compared with bare palladium, the alloy surface has an enhanced reactivity towards O_2, and on the contrary, weaker reactivity to CO. Zn enhances the diffusion of hydrogen into palladium.

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