

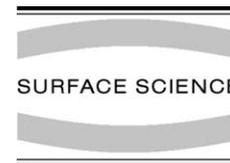


ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

SCIENCE @ DIRECT®

Surface Science 600 (2006) 78–94



[www.elsevier.com/locate/susc](http://www.elsevier.com/locate/susc)

## Electronic properties of thin Zn layers on Pd(1 1 1) during growth and alloying

Andreas Bayer<sup>a</sup>, Ken Flechtner<sup>a</sup>, Reinhard Denecke<sup>a,\*</sup>,  
Hans-Peter Steinrück<sup>a</sup>, Konstantin M. Neyman<sup>b,c</sup>, Notker Rösch<sup>d</sup>

<sup>a</sup> *Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany*

<sup>b</sup> *Institució Catalana de Recerca i Estudis Avançats (ICREA), 08010 Barcelona, Spain*

<sup>c</sup> *Departament de Química Física i Centre especial de Recerca en Química Teòrica, Universitat de Barcelona i Parc Científic de Barcelona, c/Marti i Franques, 1, 08028 Barcelona, Spain*

<sup>d</sup> *Department Chemie, Theoretische Chemie, Technische Universität München, 85747 Garching, Germany*

Received 15 July 2005; accepted for publication 29 September 2005

Available online 10 November 2005

---

### Abstract

The growth and alloying of thin Zn layers on Pd(111) was investigated using X-ray and ultraviolet photoelectron spectroscopy as well as low energy electron diffraction and correlated with density functional calculations. At 105 K, the formation of a pseudomorphic Zn monolayer is observed. Upon heating this layer to 550 K or upon deposition of 1 ML at 550 K, an ordered  $p(2 \times 1)$  PdZn surface alloy with a Pd:Zn ratio of  $\sim 1:1$  is formed, with a characteristic Pd  $3d_{5/2}$  peak at a binding energy of  $\sim 335.6$  eV. For deposition of 3 ML Zn at 550 K or by heating 3 ML, deposited at low temperature, to 500 or 600 K, a PdZn alloy with a Pd:Zn ratio of again  $\sim 1:1$  is found in the surface region, with a Pd  $3d_{5/2}$  peak at  $\sim 335.9$  eV; the direct preparation at 550 K leads to a more homogeneous and better ordered alloy. The valence band spectrum of this alloy with a low density of states at the Fermi level and pronounced maxima due to the “Pd 4d” band at  $\sim 2.4$  and  $3.9$  eV closely resembles the spectrum of Cu(111), in good agreement with the calculated density of states for a PdZn alloy of 1:1 stoichiometry. The shift of the “Pd 4d” band to higher binding energies as compared to Pd(111) indicates a charge transfer from Zn to the Pd 4d levels. Overall, the similarity between the ultraviolet photoelectron spectra for the PdZn alloy and for Cu(111) is taken as explanation for the similar chemical activity of both systems in methanol steam reforming.

© 2005 Elsevier B.V. All rights reserved.

*Keywords:* Photoelectron emission; Alloys; Metallic films; Palladium; Zinc; Growth; Density functional calculations

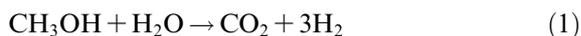
---

\* Corresponding author. Tel.: +49 9131 85 27320; fax: +49 9131 85 28867.

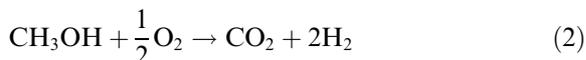
E-mail address: [reinhard.denecke@chemie.uni-erlangen.de](mailto:reinhard.denecke@chemie.uni-erlangen.de) (R. Denecke).

## 1. Introduction

Presently, much attention is focused on the production of hydrogen as energy carrier. In combination with fuel cells it can be used as clean and efficient source of electric power for both mobile and stationary applications [1,2]. Oxidative methanol reforming is regarded as one of the most promising techniques for the mobile supply of hydrogen [3,4]. Thereby, endothermic steam reforming of methanol ( $\Delta H^0 = +131.0$  kJ/mol)



is combined with exothermic partial oxidation of methanol ( $\Delta H^0 = -154.8$  kJ/mol)



to achieve an almost thermoneutral overall reaction [3].

Highly active and selective catalysts for oxidative methanol reforming are mainly based on Cu [5], Cu/ZnO [6–10], and Pd/ZnO [11–19]. Recently, the latter catalyst system has attracted particular attention as it exhibits superior long-term and thermal stability under real catalytic conditions compared to the commercially used Cu/ZnO catalysts [3,4]. Pd supported on  $\text{In}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  shows similar high activity and selectivity [20]. In contrast, on unsupported pure Pd catalysts methanol is predominantly decomposed to hydrogen and carbon monoxide, resulting in poor selectivity for the steam reforming of methanol [11,17]. The very strong enhancement in catalytic activity towards steam reforming of methanol on Pd/ZnO, Pd/ $\text{In}_2\text{O}_3$ , and Pd/ $\text{Ga}_2\text{O}_3$  catalysts is ascribed to the formation of PdZn, PdIn, and PdGa alloys, respectively, by reduction of the powder catalysts at elevated temperatures [12,15–18,20]. X-ray diffraction measurements show patterns characteristic for these alloys [3,12,15–17,19]. In the case of Pd/ZnO catalysts, crystallites with predominantly PdZn(111) and PdZn(200) surfaces form [3,18]. Results of studies by X-ray photoelectron spectroscopy (XPS) also confirm the formation of PdZn alloys [18,21]. Furthermore, it is well known that Pd and Zn are miscible and thus form alloys with a large range of relative compositions [22,23].

The similar catalytic performance of PdZn- and Cu-based catalysts in methanol steam reforming [3,4,14,17,18] has been suggested to originate from similar electronic structures [24]. In a very simplified model, mixing of the electron configurations of Pd( $4d^{10}$ ) and Zn ( $3d^{10}4s^2$ ) atoms results in an average configuration of  $d^{10}s^1$ , the electron configuration of Cu. The 4d band of bulk Pd is not completely filled, yielding an electron configuration of  $4d^{9.5}5s^{0.5}$  [25,26]. Recent calculations based on density functional theory (DFT) revealed that the density of states of the valence band region of PdZn alloys resembles that of metallic Cu [24,27,28]. In addition, these calculations identified the PdZn(111) surface as the most stable one.

Therefore, we have studied the growth and alloy formation of Zn on a Pd(111) single crystal surface using high resolution XPS, ultraviolet photoelectron spectroscopy (UPS), and low energy electron diffraction (LEED). Contrary to most previous investigations on powder catalysts, we used a single crystal as it is a well-defined model system. Core- and valence-level photoelectron spectroscopy allowed for observing changes in the electronic structure and chemical composition of the system Zn/Pd(111) due to mixing/alloying. LEED patterns served for the identification of ordered alloy structures. Results of DF calculations assisted in the assignment.

## 2. Experimental setup and data analysis

The experiments were performed in a two-chamber UHV system (Scienta ESCA 200), which is described in detail elsewhere [29]. The  $\mu$ -metal shielded *analyzer chamber* is equipped with a 200 mm electron energy analyzer, a monochromatized X-ray source (Al  $K_{\alpha}$ ), and a He-discharge lamp. The *preparation chamber* is equipped with a sputter-gun, a two-grid back-view LEED system, and a quadrupole mass spectrometer (QMS) for residual gas analysis and recording of temperature programmed desorption (TPD) spectra. A home-built Knudsen cell is used for evaporating Zn at a constant flux by resistively heating a Mo crucible with pieces of Zn wire (MaTeck, purity 99.99%) inside. Gases like CO (Linde, purity 99.97%) can

Download English Version:

<https://daneshyari.com/en/article/5426660>

Download Persian Version:

<https://daneshyari.com/article/5426660>

[Daneshyari.com](https://daneshyari.com)