

PdZn/Pd(111) surface alloys as model catalysts for methanol steam reforming

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Introduction

Pd supported on ZnO has recently raised great interest as a catalyst for methanol steam reforming. Different from unsupported Pd, Pd-ZnO shows high selectivity and good conversion towards CO₂ and hydrogen [1]. The difference is attributed to the formation of a PdZn alloy under reaction conditions, but there is still limited knowledge on the exact surface structure/composition and reaction mechanism(s).

To get further insight, we have investigated the adsorption and interaction of CO and methanol with a well-defined model PdZn/Pd(111) 1:1 surface alloy, using XPS (X-ray Photoelectron Spectroscopy) and PM-IRAS (Polarization-Modulation IR Reflection Absorption Spectroscopy).

Experimental

The experimental setup combines UHV (ultrahigh vacuum) facilities for the preparation and characterization of model catalysts by XPS and LEED (Low Energy Electron Diffraction) with the possibility of *in situ* surface spectroscopy by PM-IRAS. PM-IRAS is well suited for *in situ* investigations of gas-surface interactions, since it allows to detect surface adsorbed molecules/species even under atmospheric pressure [2].

PdZn 1:1 surface alloys were prepared by physical vapor deposition of Zn onto a Pd(111) single crystal substrate at 77 K and subsequent annealing at 550 K. A well ordered LEED pattern was obtained, in agreement with recent STM and DFT studies suggesting a coexistence of 3 rotational domains of a (2x1) structure [3,4,5]. XPS detected alloy related features at a binding energy of 335.6 eV (Pd 3d_{5/2}) and 1021.0 eV (Zn 2p_{3/2}).

Results and discussion

After an exposure of 10 L CO at 77 K no CO adsorption was observed. The adsorption energy of CO on the PdZn alloy is apparently rather low, which explains the absence of CO adsorption in previous studies [6]. Nevertheless, as shown in Figure 1, with a background CO pressure of 1x10⁻⁶ mbar at 200 K a band at 2058 cm⁻¹ was observed by PM-IRAS. This band is attributed to CO linear adsorbed on top of Pd atoms. Increasing the CO pressure to the mbar regime shifted the band to 2070 cm⁻¹ due to higher coverage, but no additional features were obtained in the region between 1950 cm⁻¹ to 1800 cm⁻¹, indicating the absence of any bridge or hollow bound CO species. The

vibrational frequencies are in good agreement with literature IR data reported for powder catalysts [7], showing the relevance of our model system.

In contrast to pure Pd, no carbonaceous deposits are detectable with XPS when the PdZn surface alloy is exposed to methanol at 300 K. This may possibly be explained by missing adsorption sites for flat-lying, bridge bound formaldehyde species which are a likely precursor for C-O bond cleavage. PM-IRAS studies of methanol adsorption are currently performed to examine the effect of alloy formation on available adsorption sites for methanol and possible intermediates.

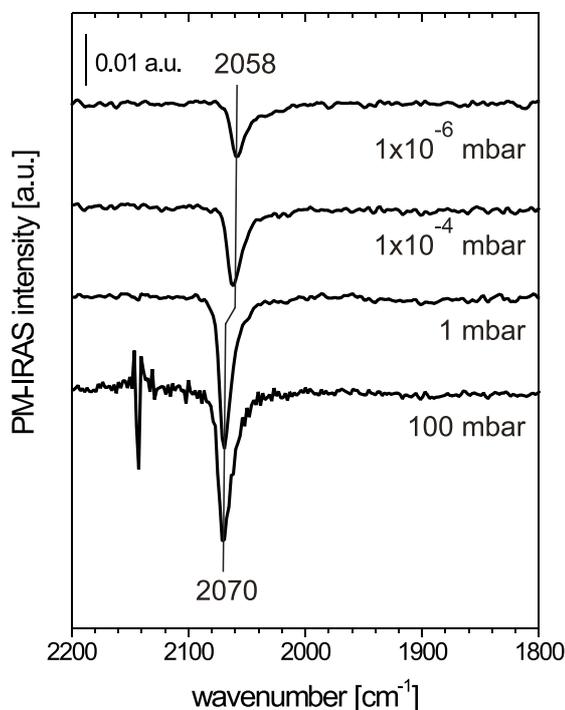


Figure 1: PM-IRAS spectra of CO adsorbed on PdZn/Pd(111) at 200 K

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