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Growth and decay of the Pd(1 1 1)–Pd_5O_4 surface oxide: Pressure-dependent kinetics and structural aspects

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Abstract

Growth and decomposition of the Pd_5O_4 surface oxide on Pd(1 1 1) were studied at sample temperatures between 573 and 683 K and O_2 gas pressures between 10^{-7} and 6×10^{-5} mbar, by means of an effusive O_2 beam from a capillary array doser, scanning tunnelling microscopy (STM) and thermal desorption spectrometry (TDS). Exposures beyond the p(2 × 2)O adlayer (saturation coverage 0.25) at 683 K (near thermodynamic equilibrium with respect to Pd_5O_4 surface oxide formation) lead to incorporation of additional oxygen into the surface. To initiate the incorporation, a critical pressure beyond the thermodynamic stability limit of the surface oxide is required. This thermodynamic stability limit is near 8.9×10^{-6} mbar at 683 K, in good agreement with calculations by density functional theory. A controlled kinetic study was feasible by generating nuclei by only a short O_2 pressure pulse and then following further growth kinetics in the lower (10^{-6} mbar) pressure range.

Growth of the surface oxide layer at a lower temperature (573 K) studied by STM is characterized by a high degree of heterogeneity. Among various metastable local structures, a seam of disordered oxide formed at the step edges is a common structural feature characteristic of initial oxide growth. Further oxide nucleation appears to be favoured along the interface between the p(2 × 2)O structure and these disordered seams. Among the intermediate phases one specifically stable phase was detected both during growth and decomposition of the Pd_5O_4 layer. It is hexagonal with a distance of about 0.62 nm between the protrusions. Its well-ordered form is a $(\sqrt{67} \times \sqrt{67})R12.2^\circ$ superstructure.

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Isothermal decay of the Pd_5O_4 oxide layer at 693 K involves at first a rearrangement into the $(\sqrt{67} \times \sqrt{67})R12.2^\circ$ structure, indicating its high-temperature stability. This structure can break up into small clusters of uniform size and leaves a free metal surface area covered by a $p(2 \times 2)O$ adlayer. The rate of desorption increases autocatalytically with increasing phase boundary metal-oxide. We propose that at close-to-equilibrium conditions (693 K) surface oxide growth and decay occur via this intermediate structure.

Keywords: Palladium; Oxidation; Surface oxide; Thermal desorption spectroscopy; Scanning tunnelling microscopy; Nucleation; Phase growth; Autocatalytic decomposition

1. Introduction

Catalytic combustion of hydrocarbons on Pd catalysts has received extensive attention due to the growing interest in power generation with gas turbines [1,2] and due to the need for removing small amounts of methane from emissions of fuel engines [3]. Because of the lower operating temperature catalytic combustion lowers NO_x emissions, but a number of problems remain associated with the activity, stability and durability of the supported Pd catalysts. The complex kinetic behaviour of oxidation and reaction is connected with a pronounced kinetic hysteresis between formation and decay of the PdO bulk oxide phase. This redox hysteresis, playing a crucial role in all attempts to sustain and control catalytic activity, has been an important topic in the literature [4–6]. It is known that the surface and bulk properties of the O/Pd system are quite variable and that both morphology and catalytic activity are a function of oxygen pressure and temperature [7–9]. The bulk PdO phase is stable at low temperature and decomposes into metallic Pd and oxygen upon heating. On the other hand, palladium oxide is known for its high overall catalytic activity in the low-temperature regime and is expected to show a better catalytic performance than the metal in low-temperature combustion [7,10].

The two-dimensional Pd_5O_4 surface oxide phase on Pd(1 1 1) can be regarded as a well-defined intermediate state between chemisorbed oxygen on Pd metal and PdO bulk oxide. In a recent study [11] its structure was resolved by scanning tunneling microscopy (STM), surface X-ray diffraction (SXRD), high resolution core level spectroscopy (HRCLS), and density functional calculations (DFT). A combination of these methods revealed a purely two-dimensional incommensurate structure without resemblance to bulk oxides of Pd. In [11] it is also demonstrated how the atomic arrangement of a non-trivial incommensurate surface can be determined by molecular dynamics in a case where experimental techniques alone do not give a solution. In this computational work, the structure was resolved by an extensive search of the configuration space by first melting and then crystallizing Pd_xO_y overlayers of different composition on a Pd(1 1 1) substrate, the only experimental input being the periodicity of the overlayer, as determined by LEED and STM. SXRD and HRCLS measurements and the perfect agreement of the simulated STM image with experiment confirmed the structure. In particular, the presence of differently coordinated *coplanar* O and Pd atoms within the 2D structure were clearly resolved in the HRCLS experiments and allowed for a safe distinction of Pd_5O_4 from any crystallographic plane of bulk PdO that would exhibit a chemically uniform environment of all Pd and O atoms. Moreover, the oxygen coverage calculated from the Pd_5O_4 structure in [11] could be verified in the present work by TPD calibration (section 2.1). The stoichiometry corresponds to a mean oxygen coverage of $1/\sqrt{3} = 0.58$ monolayers oxygen, referenced to bulk terminated Pd(1 1 1). The catalytic properties of Pd_5O_4 are still unknown, but may be very important for approaching microscopic understanding of the kinetic hysteresis between oxidation and reduction. In the present work we report new kinetic and structural aspects of the formation and decay of this surface oxide phase. Surface phase growth and decay are important factors in kinetic rate oscilla-