Oxidation over Pd Model Surfaces - a Near-Ambient Pressure XPS and DFT Study

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Introduction

Palladium is a versatile oxidation catalyst, among others finding applications in CO removal from car exhaust [1] and total oxidation of hydrocarbons [2]. Furthermore, Pd and its alloys have high solubility, permeability and selectivity for hydrogen, making them suitable as hydrogen separation membrane materials [3].

In the present work, we have investigated single crystal surfaces of Pd(100) and Pd75Ag25(100) as model systems for addressing oxide formation during CO and H2 oxidation reactions at Pd surfaces as well as the influence of Ag as alloying element on these reactions under near ambient, oxygen rich conditions.

Materials and Methods

Experimentally, near ambient X-ray photoelectron spectroscopy (HP-XPS) in combination with quadropole mass spectrometry (QMS) have been applied for characterization of Pd(100) and Pd75Ag25(100) under exposure to mixtures of O2 and CO or/and H2. The experiments were performed at beamline I511-1 of the MAX IV Laboratory [4]. Density functional theory calculations [5,6] have been performed to investigate the CO oxidation paths over Pd(100) and Pd75Ag25(100). The first principles results are used to construct a mean-field microkinetic model.

Results and Discussion

O 1s core level spectra recorded during CO oxidation over Pd(100) are presented in Fig. 1. The different contributions to the spectra are marked in the right panel. The activation energy for CO oxidation over this surface was determined to be 1.0 eV, while a value of 1.1 eV was obtained for Pd75Ag25(100). CO inhibition of the reaction is observed at low temperatures for both surfaces upon CO oxidation. At temperatures higher than 185 °C, the characteristic (√5 × √5) R27° surface oxide [7] is the highly active surface in the reactions over Pd(100), as also previously reported [8, 9], and mass transfer limitations in the gas phase come into play. In the case of Pd75Ag25(100), however, chemisorbed oxygen only is observed when the surface is highly active. The ordered oxide is not observed despite its occurrence after O2 exposure at UHV conditions [10]. Moreover, interesting kinetic effects, such as reversed hysteresis are observed at elevated temperatures. This can according to the first principles based kinetic simulations be attributed to changes in the surface composition and therefore the reactivity. Alloying Pd by Ag is, thus, found to have significant effects on the oxidation reactions. In the case of simultaneous oxidation of CO and H2, the CO oxidation reaction determines the overall reaction behavior.

Figure 1. CO oxidation over Pd(100) at 0.7 mbar total pressure and O2:CO ratio 10:1. Left: The O 1s core level region recorded as a function of sample temperature along with the corresponding QMS data for O2, CO and CO2. Right: Decomposition of O 1s core level spectra at two different stages (marked with dashed lines in the left part) during the CO oxidation experiment, at low (lower panel) and high activity (upper panel) towards CO2 formation.

Significance

Simultaneous HP-XPS and QMS experiments in conjunction with first principles based microkinetics has been applied to elucidate the nature of the active Pd surface during CO oxidation, both in terms of surface oxygen species and with respect to the surface composition of Pd alloyed with Ag.

References