Composition of the surface oxide on Pd(100) in an O_2 and CO environment

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The formation of oxides or thin oxide films (surface oxides) on transition metal surfaces during catalytic oxidation processes has recently gained more and more attention, since these oxidic phases may have some influence on the catalytic reactivity of the materials.

Focusing on the Pd(100) it was found that the oxidation of the Pd(100) surface leads to a $(\sqrt{5} \times \sqrt{5})R27^{\mathrm{o}}$ surface oxide structure, which was identified to be essentially a PdO(101) overlayer on Pd(100) [1]. In thermodynamic equilibrium with a pure O_2 gas phase this surface oxide represents the most stable phase over a wide range of environmental conditions, and this stability under high oxygen pressure was recently confirmed by *in-situ* surface X-ray diffraction (SXRD) measurements [2]. This suggests that the surface oxide may also play some role for the high-pressure CO oxidation catalysis at Pd(100).

To get a first insight into this catalytic reaction we investigate the stability range, the structure and composition of the surface oxide in equilibrium with an arbitrary O_2 and CO gas environment using density-functional theory and "constrained" atomistic thermodynamics, i.e. assuming the surface to be in equilibrium with the reactant gas phase [3,4]. In the resulting (T, p_{O_2}, p_{CO})-phase diagram, the stability range of the surface oxide indeed extends well over conditions representative of technological oxidation catalysis (ambient pressures, 300-500 K). In particular it also extends to the conditions employed in a recent reactor scanning tunneling microscopy (STM) study by Hendriksen and Frenken [5], reporting increased catalytic activity connected with oxide formation at the surface. To be more precise, the stable phase of the surface oxide under these conditions contains coadsorbed moderately bound CO, which might already point at possible reaction pathways.

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