

Abstract

Supported metal particles in the sub-nanometer regime frequently exhibit interesting functional properties such as catalytic activity, which can be highly size-dependent. In the emerging field of single-atom catalysis these effects are studied at the size limit, where the active phase is represented by isolated stable metal atoms on oxide supports or within surface alloys.

The present thesis is a surface-science study of metal adsorption at the magnetite $\text{Fe}_3\text{O}_4(001)$ surface on synthetic and natural single-crystal specimens prepared in ultra-high vacuum (UHV). The properties of the $\text{Fe}_3\text{O}_4(001)$ surface are investigated using scanning tunneling microscopy (STM), photoelectron spectroscopy (PES), low-energy electron diffraction (LEED), and density functional theory (DFT) calculations based on the WIEN2k program package. These experimental surface-science methods combined with DFT are also employed in the study of metal adsorption at this surface, performed in UHV as well as during exposure to low pressures of common reactant gases (2×10^{-10} mbar to 10^{-6} mbar of gases such as CO, O₂, NO).

Magnetite (Fe_3O_4) is a naturally abundant material, which finds application in energy technology as a catalyst or as a support material of active metal particles. The $\text{Fe}_3\text{O}_4(001)$ surface stabilizes isolated metal adatoms up to a temperature of 700 K and is thus a highly promising model system for the study of single-atom properties. The present thesis provides an overview of the adsorption properties of selected metals (Ag, Co, Cu, Mn, Ni, Pt, Rh, Ti, and Zr) at this surface and their interaction with gas molecules. As a first step, the structure of the $(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ reconstruction of the B-terminated (i.e., FeO_2 -terminated) $\text{Fe}_3\text{O}_4(001)$ surface is resolved via quantitative low-energy electron diffraction and *ab initio* thermodynamics. The stable reconstructed surface structure is based on a rearrangement in the subsurface layers, involving two subsurface Fe vacancies and one interstitial Fe atom per unit cell. This reconstruction creates a twofold coordinated adsorption site in each unit cell, which is the preferential site for metal atoms. In this site the adatoms bind strongly to surface oxygen and assume a cationic charge state. However, the adatom configuration does not correspond to the thermodynamic equilibrium; thus the adatoms can be destabilized by annealing to high temperatures. In this case the deposited metal atoms follow one of two observed pathways: incorporation or clustering. Metals that form stable spinel compounds (e.g. Ni in NiFe_2O_4) exhibit an energetic preference to enter the surface, filling the subsurface Fe vacancy and locally lifting the

reconstruction. The incorporation barrier varies for different chemical elements, leading to differences in the specific behavior. In most cases mild annealing is required to overcome the incorporation barrier (for Ni, Co, Mn, and Rh), whereas for example Ti and Zr are almost fully incorporated upon deposition at room temperature and Cu retains a partial coverage of adatoms even at 870 K. Noble metals (Au, Ag, Pt, and Pd), on the other hand, do not incorporate but form clusters once a critical number of interacting metal atoms is exceeded. The number of interacting metal atoms can be enhanced by high coverage or by increasing the mobility of the metal adatoms, for example thermally or chemically, via the formation of mobile metal-adsorbate complexes. The onset temperature of clustering for noble metals is found to be ≈ 700 K; close to the temperature where the surface reconstruction is lifted.

The combination of the experimental data with density functional theory calculations allows determining trends in the adsorption behavior. Thus, it is for example possible to ascribe a stronger metal-oxide bond to the $3d$ metals compared to the $4d$ and $5d$ metals, which are characterized by an increased strength of the metal-metal bond. Moreover, the concept of stable metal adatoms at the reconstructed $\text{Fe}_3\text{O}_4(001)$ offers the possibility to combine the specific chemical properties of different metals by co-deposition.

The prospective applications of single adatoms in catalysis encourage characterizing their interaction with reactive gas molecules such as CO, O_2 , and NO. Strong adsorption is found to stimulate the mobility of adatoms in various metal-gas combinations, such as Pt-CO, Rh-NO, and Rh- O_2 . For example Pt adatoms exposed to CO form stable, mobile carbonyl species, driving the formation of Pt clusters. When heated in UHV to 520 K, the smallest Pt clusters are destabilized and decay back to adatoms. In contrast, annealing the surface with Pt clusters at 550 K in reactive atmosphere (10^{-7} mbar CO, H_2 , or O_2) causes the clusters to activate the interaction between gas molecules and support. Under these conditions the Pt clusters mediate the oxidation of CO and H_2 via the extraction of lattice oxygen, and island growth via oxygen spillover in O_2 atmosphere.