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Interaction of CO with Pt_xAg_{1-x}/Pt(111) surface alloys: More than dilution by Ag atoms

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ABSTRACT

We have investigated CO adsorption on structurally well-defined Pt_xAg_{1-x}/Pt(111) surface alloys, combining temperature-programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRRAS) as well as density functional theory (DFT) based calculations. This is part of a systematic approach including previous studies of CO adsorption on closely related Pt(111)- and Pd(111)-based surface alloys. Following changes in the adsorption properties with increasing Ag content and correlating them with structural changes allow us to assign desorption features to specific adsorption sites/ensembles identified in previous scanning tunneling microscopy (STM) measurements, and thus to identify and separate contributions from different effects such as geometric ensemble effects and electronic ligand/strain effects. DFT calculations give further insight into the nature of the metal–CO bond on these bimetallic sites. Most prominently, the growth of a new CO desorption feature at higher temperature (~550 K) in the TPD spectra of Ag-rich surface alloys, which is unique for the group of Pt(111)- and Pd(111)-based surface alloys, is attributed to CO adsorption on Pt atoms surrounded by a Ag-rich neighborhood. Adsorption on these sites manifests in an IR band down-shifted to significantly lower wave number. Systematic comparison of the present results with previous findings for CO adsorption on the related Pt(111)- and Pd(111)-based surface alloys gains a detailed insight into general trends in the adsorption behavior of bimetallic surfaces.

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1. Introduction

Bimetallic catalysts, i.e., supported catalysts with bimetallic nanoparticles, have attracted considerable interest in recent decades as they often show an improved activity and/or selectivity compared with the individual components [1–4]. A number of specific effects such as the geometric ensemble effect [5,6], site-blocking effects [7], or the electronic ligand [8–10] and strain [11,12] effects have been put forward to explain the improved performance of these catalysts. As an example, it is well known that the dilution of an active metal (like Pd or Pt) with an inert metal (like Au or Ag) enhances the selectivity and long-term stability in selective hydrogenation or other reactions like, e.g., vinyl acetate synthesis on PdAu catalysts [13]. This was explained by the reduced availability of larger active metal ensembles, which enable or enhance competing reactions. It should be noted that in particular the older models were strictly based on the correlation of the reaction kinetics with the composition of the catalyst particles, and direct experimental verification of these effects was hardly possible.

In modern catalysis research, where relative rates are often calculated within the framework of the Sabatier principle, based on the adsorption

energies of the reaction educts, intermediates and products, and where the adsorption energies of the different species involved in a reaction are found to often vary in a correlated way between different catalyst materials [14], these adsorption energies are often calculated from the material or site dependent adsorption energies of a ‘descriptor’ species via the so-called scaling relations [15,16]. For bimetallic catalysts this means that various adsorption sites with different local compositions have to be considered for a comprehensive description of the reaction on these catalysts and for the identification of the active sites. Model studies along this way have been published recently for the electrocatalytic O₂ reduction on PtAu and PtRu bimetallic surfaces [17,18].

In an effort to better understand systematic trends in adsorption phenomena on bimetallic surfaces, we have investigated in previous years the adsorption of CO on structurally well-defined monolayer Pd_xAu_{1-x}/Pd(111) [19], Pd_xAg_{1-x}/Pd(111) [20–22] and Pt_xAu_{1-x}/Pt(111) [23] surface alloys, where the distribution of surface atoms was determined quantitatively by statistical evaluation of high resolution scanning tunneling microscopy (STM) images with chemical contrast [19,24–26]. Adsorption was investigated applying both experimental methods and density functional theory (DFT) based calculations. Completing this series of CO adsorption studies on closely related surface alloys, we here present results of a combined experimental and theoretical study on the interaction of CO with structurally well-defined Pt_xAg_{1-x}/Pt(111) surface alloys

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with systematically varied compositions. This is based on a detailed structural characterization by STM [27]. First experimental results on the formation of these surface alloys and characteristic electronic and CO adsorption properties at different stages of their formation were published recently [28]. An analysis of the structural stability of the Pt_xAg_{1-x}/Pt(111) surface alloys and related PtAg surfaces, based on STM data and DFT calculations, will be reported later [29].

Before entering into the presentation and discussion of our data, we will briefly summarize results from previous studies on the structural, electronic and adsorption properties of bimetallic PtAg surfaces and Pt_xAg_{1-x}/Pt(111) surface alloys. Although Pt and Ag are not bulk-miscible, it was already reported in the pioneering STM studies by Brune and Kern that intermixing of Ag deposits into a Pt(111) surface becomes possible upon heating; the onset of surface alloy formation was observed at ~620 K [30]. Further structural details including a quantitative description of the distribution of the two components in the surface alloy layer and of the abundance of small adsorption ensembles for varying compositions were recently derived in a detailed STM study [27]. In brief, this analysis showed a strong tendency towards phase separation in the surface alloy layer for the complete range of surface compositions [27]. The transfer of a measurable amount of Ag to the bulk upon annealing to temperatures below 850 K can be excluded on the basis of these measurements [27,30]. The electronic and adsorption properties of these surface alloys were studied by Strüber and Küppers using X-ray photoelectron spectroscopy (XPS) and temperature programmed CO desorption (CO TPD) measurements [31], respectively. In XPS, a uniform down-shift of the Ag(3d_{5/2}) binding energy (BE) by ~0.4 eV compared with Ag(111) is found for all Ag contents up to 1 ML already before surface alloy formation. After surface alloy formation, an additional shift is detected whose amount varies with Ag surface concentration and takes a maximum additional decrease of ~0.3 eV for vanishing Ag content [31]. Although no complete CO TPD series were reported, the measurements showed the occurrence of an additional TPD peak at ~570 K, which was preliminarily attributed to CO adsorbed on atoms of a Pt cluster embedded in a Ag surrounding [31].

In the following we report on the CO adsorption properties of Pt_xAg_{1-x}/Pt(111) surface alloys, which were prepared by deposition of sub-monolayer amounts of Ag on Pt(111) at room temperature and subsequent heating to higher temperature. After a short description of the experimental facilities and procedures (Section 2.1) and the computational details (Section 2.2), we will briefly summarize the most important structural characteristics of the Pt_xAg_{1-x}/Pt(111) surface alloys (Section 3.1.1), followed by the presentation of TPD and infrared reflection absorption spectroscopy (IRRAS) results for the CO adsorption on Pt_xAg_{1-x}/Pt(111) surface alloys with varying surface compositions (Sections 3.1.2 and 3.1.3). Section 3.2 comprises the results of systematic calculations of the CO adsorption energy on different relevant bimetallic surfaces. In Section 4.1 we discuss the experimental and computational results in a comprehensive way, focusing on trends in the CO adsorption properties induced by the varying local surface compositions. Finally, the data of the present study are compared with previous results on PtAu/Pt(111) [23], PdAg/Pd(111) [20–22] and PdAu/Pd(111) [19] surface alloys (Section 4.2).

2. Methods

2.1. Experimental part

The experiments were performed in an ultra-high vacuum (UHV) system (base pressure ~ 1 × 10⁻¹⁰ mbar) with facilities for TPD, IRRAS and XPS measurements, respectively. The system contains standard facilities for surface preparation, including an Ar⁺ ion sputter gun and a Ag evaporator. The Pt(111) sample, which was used as substrate for the bimetallic surfaces, could be cooled by liquid nitrogen to ~90 K and heated by resistive heating. The surface was cleaned before each experiment by a cycle of Ar⁺ sputtering (2 μA, 0.6 kV), oxygen treatment

(p_{O2} = 1 × 10⁻⁷ mbar, 900 K), and annealing to 1200 K. Subsequently, surface order and cleanliness were checked by CO TPD and XPS. Well-ordered and clean surfaces were identified by the absence of an additional feature at the high temperature edge of the main broad desorption peak in the CO TPD spectra, which is typical for desorption from defective surfaces [32,33], and the absence of any signal in the XP spectra not related to Pt. STM measurements on similarly prepared surfaces showed atomically smooth terraces (terrace width between 50 and 100 nm) separated by monoatomic steps [27].

In order to create the Pt_xAg_{1-x}/Pt(111) surface alloys, a sub-monolayer amount Ag was evaporated at room temperature (RT) from a resistively heated Knudsen cell (WA Technology), the deposition rate was ~0.05 monolayer (ML) min⁻¹ (one monolayer refers to the surface atom density of Pt(111)). During Ag deposition, the background pressure remained in the lower 10⁻⁹ mbar range. After Ag deposition the sample was heated to 850 K for 1 min to complete surface alloy formation. The Ag concentration was determined by XP spectra using Mg K_α radiation for excitation and a hemispherical analyzer (CLAM2, VG Scientific) with a pass energy of 25 eV for detail and 50 eV for survey spectra. The Ag coverage was calibrated by a combination of CO TPD and XPS measurements, for details see the Supporting information.

For CO TPD and IRRAS experiments, dosing was done by backfilling the chamber via a glass tube (inner diameter 8 mm) pointing towards the sample (opening ~ 50 mm away). Due to this construction, the actual pressure during dosing is ~1.8 times higher than what is measured at the ion gauge, the exposure values were corrected for this. For the CO TPD experiments, the sample was exposed at 90 K to doses sufficient to reach saturation, which was obtained independently of the surface composition after exposure to 13.5 L CO (1 L = 1.33 × 10⁻⁶ mbar s). Subsequently, a linear heating ramp of 4 K s⁻¹ was applied and the CO TPD spectra were recorded via a quadrupole mass spectrometer (Pfeiffer Vacuum, QMS 200). The mass spectrometer was shielded against desorption from edge areas or the sample holder by a cap with an aperture of 4 mm diameter [34]. Before a TPD run, the sample was positioned in front of the aperture, the distance between cap and sample was adjusted reproducibly by an electrical contact [35]. The IRRAS measurements were carried out at incidence and detection angles of 7° with respect to the surface plane using a mercury-cadmium-telluride (MCT) detector, the resolution was set to 4 cm⁻¹. Depending on the band intensities, between 1000 (for Pt(111)) and 4000 scans (for Ag-rich surfaces) were collected for one IR spectrum. Reference spectra of the CO_{ad} free surfaces were recorded after all CO was removed from the surface by heating to above the desorption temperature and subsequently cool-down to 200 K.

2.2. Computational details

Plane-wave DFT calculations were performed using version 5.3.3.4 of the VASP code [36], together with the Perdew–Burke–Ernzerhof (PBE) [37] and the revised-PBE (RPBE) [38] exchange–correlation functionals. The ionic cores are represented by projector augmented wave (PAW) potentials [39] as constructed by Kresse and Joubert [40,41]. The electronic one-particle wave functions are expanded in a plane-wave basis set up to a cutoff energy of 400 eV. This cutoff energy is expected to provide convergence better than 1 mRy (~13 meV) in eigenvalues for this kind of basis set. Spin polarization is not considered due to the non-spin-polarized nature of the system. Dipole moment correction is set up in order to account for effects derived of using asymmetric slabs. Scalar relativistic effects are already included from the parametrization at the basis set generation. Convergence criteria for the electronic self-consistency and the ionic relaxation are set to 1 · 10⁻⁴ and 1 · 10⁻⁵, respectively. A sufficiently large set of k-points was chosen in order to guarantee convergence.

First, the bulk energy (E_b) and bulk lattice parameter (d_b) of Pt and Ag were computed using an fcc unit cell and an 11 × 11 × 1 Γ-centered k-point grid. Values obtained using PBE/PAW for the bulk lattice parameters

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