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On the stability of the CO adsorption-induced and self-organized CuPt surface alloy

K.J. Andersson, I. Chorkendorff *

Center for Individual Nanoparticle Functionality (CINF), Department of Physics, Technical University of Denmark, Fysikvej 312, DK-2800 Kgs. Lyngby, Denmark

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ABSTRACT

The stability of the recently discovered CO-induced and self-organized CuPt surface alloy was explored at near ambient pressures of O_2 (200 mbar) at room temperature, in a $CO + H_2$ mix ($P_{tot} = 220$ mbar, 4% CO) from room temperature to 573 K, as well as in a $CO + H_2O$ mix ($P_{tot} = 17$ mbar, 50% CO) from room temperature to 673 K. No indications of substantial changes in surface structure were observed under the latter conditions compared to CO alone whereas the O_2 oxidation resulted in CO removal and the build-up of an ultrathin CuO_x-film. However, the oxidized CO/CuPt surface alloy could be regenerated by reducing the CuO_x in 100 mbar CO for 10 min at room temperature. The results show, amongst others, the stability of the CuPt surface alloy in various environments containing CO and how a novel coinage/Pt-group bimetallic surface alloy catalyst induced by CO adsorption can be reactivated before use in applications such as electrochemistry at ambient temperatures.

1. Introduction

Recent microkinetic modeling of the water-gas shift (WGS) reaction, $CO + H_2O \rightarrow H_2 + CO_2$, under industrial conditions on a range of metals suggests a volcano-type maximum in activity by increasing the CO and O adsorption energies on Cu [1]. In subsequent works [2,3] such a more reactive Cu surface, induced by an 8% stretching of the Cu lattice by growing it on a Pt(111) surface, was probed by its interaction with CO_2 and H_2. Although several interesting phenomena were observed, such as formation of tridentate carbonate at Cu steps and defects, significantly reduced formate stability compared to defect-free and unstrained Cu and a possible pathway to methanol formation via hydrogenation of the tridentate carbonate at step-sites, the Cu overlayer was not stable above 460 K, forming instead a CuPt near-surface alloy.

The near-surface alloy (NSA) was earlier shown to have Cu preferentially located in the 2nd layer of Pt, [4] and suggested to be a promising WGS catalyst. Amongst its properties was a reduced Pt-CO bonding, [4] proposed to alleviate possible CO-poisoning problems of Pt-based WGS catalysts.[1] However, experiments in our laboratory [5] showed that the CuPt NSA is not stable in a CO atmosphere at temperatures above 473 K. Instead of weakened Pt-CO bonding compared to pure Pt(111) as observed for the NSA [4], drastically increased CO bonding by about 0.7 eV was observed with 1/3 ML CO desorbing at a temperature as high as 580 K. [5] Accompanying this change in surface properties was a large Cu surface segregation and the development of a well-ordered surface structure of $(\sqrt{3} \times \sqrt{3})R30°$ periodicity. Along with a number of other in-situ and ex-situ data, combined with extensive density functional theory (DFT) calculations, it was concluded that the CuPt NSA with Cu preferentially located in the 2nd layer of Pt [4] was reversibly transformed via CO adsorption into a novel self-organized CO/CuPt *surface alloy* with Cu in the 1st surface layer [5]. This is illustrated in Fig. 1.

Despite the facts that, 1) CO binds much weaker to Cu than Pt and, 2) having Cu located in the 2nd layer of Pt was previously found to be energetically favorable [4], Cu segregates from the 2nd to the 1st layer at elevated temperature in an atmosphere of CO. The result may at first seem counter-intuitive. However, the driving force for this transformation was shown to be due to the vastly increased binding energy of CO to surface Pt atoms modified by Cu neighbors in the 1st surface layer. [5] The effect that Cu has on Pt in the 1st layer appears common with other coinage- (Cu, Ag)/Pt-group metal systems,[6–9] and suggests similar CO-induced surface alloys could be formed in such systems.

Capitalizing on adsorption-induced effects such as those above for preparation of novel catalysts means greater flexibility in alloy surface design for, e.g., low temperature applications. Indeed, CO adsorption was recently used by Mayrhofer et al. to drive surface segregation and enrich the surface layer of PtCo nanoparticles with Pt [10], in this way activating their electrocatalyst. In a subsequent paper, [11] the degradation of the catalyst under more oxidizing conditions was also shown.

Very promising results have been obtained using CuPt alloys for the electrocatalytic oxygen reduction reaction (ORR). [12,13] The CuPt

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* Corresponding author. Tel.: +45 45 25 31 70; fax: +45 45 93 23 99.
E-mail address: ibchork@fysik.dtu.dk (I. Chorkendorff).

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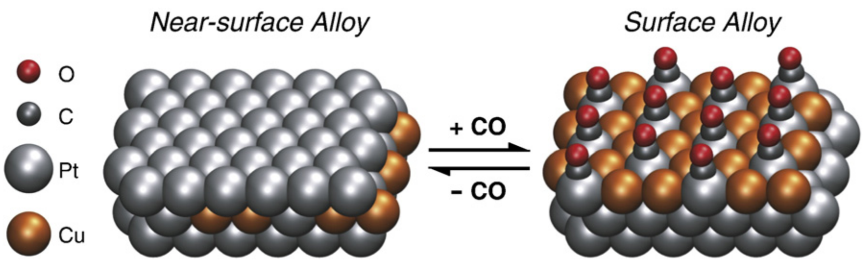

Fig. 1. Illustration of the CuPt NSA (left), CO-induced Cu surface segregation and the novel surface alloy (right) as a result of this.

surface alloy we have generated may be of relevance to electrocatalytic applications, besides being an interesting WGS catalyst candidate for situations where the WGS activity scales with increasing adsorption strength of CO, e.g., when supported on a redox-active carrier material. [14] A particularly interesting area here is methanol oxidation and CO_2 reduction where Cu has shown unique reactivity at ambient conditions albeit at high overpotentials [15].

For practical purposes, a frequent fundamental requirement is that a catalyst should be stable towards oxidation from exposures to ambient air. If deactivation occurs, or deliberately has been induced in a controlled fashion to protect the catalyst prior to ambient air exposure, simple methods for its reactivation are necessary before use. Here we explore the stability of the novel CO/CuPt surface alloy at near ambient pressures. We show that it is stable in various CO-containing environments at elevated temperatures and that it can be reactivated by a room temperature CO exposure after oxidation in ambient air.

2. Methods

The combined ultra-high vacuum (UHV) and high-pressure cell setup, as well as the preparation of the Pt(111) single crystal have been described in detail elsewhere [2]. Briefly, the setup used is an UHV chamber (1×10^{-10} Torr base pressure) connected to, and separated from, a high-pressure cell (HPC) as described in [16,17]. The setup is equipped with standard UHV surface science techniques as well as in-situ polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) [18–21], an FT-IR method which utilizes different polarizations of the radiation to distinguish between adsorbates on the sample surface and the gas phase. The p-polarized radiation orthogonal to the surface can be absorbed via vibrational excitation of surface species whereas the parallel s-polarized radiation cannot. The obtained surface spectra presented here are the difference between the reflectivities of the two polarizations normalized with their sum, *i.e.*, p-s/p + s. A background subtraction procedure was employed between 2000 and 2150 cm^{-1} removing both intrinsic and extrinsic background contributions to the surface spectra.

Cu was deposited on the clean and well-ordered Pt(111) crystal through physical vapour deposition with a rate of 0.2 ML / min at a substrate temperature of 425 K; the sample heating utilized in the setup was direct resistive heating through a U-shaped W-wire on which the sample was mounted. The CO/CuPt surface alloy used in this work was generated by deposition of 2/3 ML Cu on Pt(111), annealing in 2 mbar CO at 673 K for 10 min, and a subsequent 10 min cool down to room temperature before evacuating the CO [5].

The N60 grade CO used was passed over an active carbon filter and a Cu coil based liquid nitrogen cooling trap, and subsequent gas lines up to the Ni-free steel (Arne) HPC were also made of Cu; the N55 grade O_2 was used as is whereas the N60 grade H_2 for use in the HPC was passed over a reduced Cu catalyst. The Milli-Q H_2O used was stored in a glass container and was initially cleaned by multiple freeze-pump-thaw cycles and finally by direct distillation before use. No surface contaminants were observed by X-ray photoelectron spectroscopy (XPS), He^+ ion scattering spectroscopy (ISS), low energy electron diffraction (LEED) and IR before, during or after experiments. In particular, possible Ni impurities from Ni-carbonyl [22] ($Ni(CO)_4$) were consistently measured to be ≤ 0.005 ML as judged by XPS.

3. Results and discussion

We focus initially our attention to the deactivation and reactivation of the CO/CuPt surface alloy after exposure to conditions very closely simulating the oxidative potential of ambient air. Shown in Fig. 2 are PM-IRRAS spectra of the C–O stretch region for atop site adsorbed CO during various stages of 200 mbar O_2-exposure and CO-reactivation at room temperature (RT); at no instance was a CO site occupancy other than atop adsorption observed. Comparing the spectrum of the starting CO/CuPt surface alloy under UHV conditions, it is apparent that in 200 mbar O_2 the adsorbed CO reacts away rapidly. Beyond 10 min, CO was no longer observed on the surface by IR. However, a total O_2-exposure time of 40 min was employed to ensure complete CO removal. When exposing the oxidized surface to 100 mbar CO at room temperature, CO was observed to readsorb quickly. The spectrum in 100 mbar CO did not change beyond the first spectrum (~10 min). As can be observed in Fig. 2, upon evacuation of the CO from the HPC down to UHV the IR peak intensity increases and the peak position shifts to higher wavenumber back to that of the original CO/CuPt surface alloy under UHV conditions (2069 cm^{-1}). This was also observed in other similar experiments. The IR observations suggest that CO can be readsorbed in a state very similar to the starting CO/CuPt surface alloy and hence that CO indeed reactivates the surface after exposure to the oxidizing conditions in ambient air. However, the lower peak intensity compared to the starting surface also suggests some difference, such as a lower CO coverage or a degree of direct CO–CO interactions. CO–CO interactions

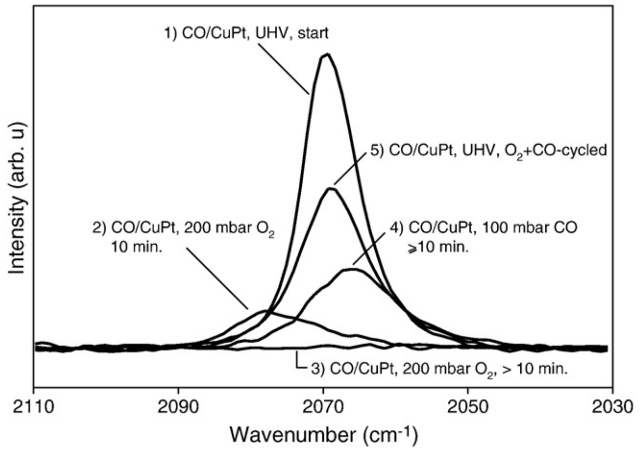

Fig. 2. PM-IRRAS spectra of atop adsorbed CO (C-O stretch region) obtained at room temperature, 2 cm^{-1} resolution. The shown spectra are in order of treatment: (1) starting CO/CuPt surface alloy in UHV, (2,3) during oxidation in 200 mbar O_2, (4) during reduction in 100 mbar CO, and (5) after subsequent CO evacuation down to UHV.