Anomalous Surface Segregation of the *Less* Reactive Bimetallic Alloy Component Driven by CO Adsorption

Klas J. Andersson[1], Federico Calle-Vallejo[2], Jan Rossmeisl[2] and Ib Chorkendorff[1]*
[1] *Center for Individual Nanoparticle Functionality, Technical University of Denmark, DK-2800 Lyngby, Denmark*
[2] *Center for Atomic-Scale Materials Design, Technical University of Denmark, DK-2800 Lyngby, Denmark*

*ibchork@fysik.dtu.dk

Introduction

Bimetallic alloys offer a way of tuning electronic structure and catalytic properties of metal surfaces [1]. Crucial to the catalytic performance of an alloy surface is its composition and structure. The bonding of adsorbates may induce changes in local atomic composition and surface structure, changing activity and selectivity of the catalyst. Capitalizing on such effects for catalyst preparation means greater flexibility in alloy surface design for low temperature applications. The expected response to adsorbates is that the more reactive alloy component, forming the strongest chemical bond with the adsorbates, segregates to the surface. Counter-intuitive to this picture and all prior observations in the literature, we show that CO adsorption at elevated pressure and temperature induces surface segregation of the *less* reactive alloy component Cu, switching a CuPt *near-surface* alloy (NSA) [2] to a novel self-organized CuPt *surface* alloy. As strongly indicated by experiments and confirmed by density functional theory (DFT) calculations, the Cu surface segregation is rationalized by the vastly stronger Pt-CO bond when Cu is present in the first surface layer of Pt.

Materials and Methods

All experimental studies were carried out in a combined ultra-high vacuum (UHV) / high pressure cell system encompassing a polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) set-up [3]. A Pt(111) single-crystal surface was dosed with 1/3 to 3 monolayers (ML) of Cu. Annealing above 500 K in UHV generated a CuPt NSA [2] under UHV conditions. After characterization, the samples were subjected for 10 minutes to a CO pressure of 2 mbar at a fixed temperature in the range 300 to 723 K, and subsequently allowed to cool down to room temperature for another 10 minutes in the CO atmosphere before CO evacuation. Samples were characterized in-situ by means of PM-IRAS and ex-situ under UHV, before and after treatment, by PM-IRAS, XPS, He^+-ISS, TPD and LEED. On the theoretical side, DFT calculations were performed in a slab-geometry utilizing plane-waves, ultra-soft pseudopotentials and periodic boundary conditions.

Results and Discussion

The CuPt NSA was found not to be stable in the CO atmosphere at temperatures above 473 K. Instead of weakened Pt-CO bonding compared to pure Pt(111) as when Cu is located in the 2nd layer of the NSA [2], drastically increased CO bonding was observed with up to 1/3 ML CO desorbing at a temperature as high as 580 K. Accompanying this change in surface properties was a large Cu surface segregation, evident from XPS and ISS data. The changes were completely reversible upon desorbing the CO by heating above 673 K in UHV. The Cu content needed to saturate the new surface alloy is ~2/3 ML Cu, leading to a CO saturation coverage of ~1/3 ML and an observed $(\sqrt{3}\times\sqrt{3})R30°$-LEED pattern. The observed ~25 cm^{-1} IR peak redshift for atop CO on Pt-sites and narrow FWHM compared to CO on pure Pt(111) strongly suggest significantly reduced lateral (repulsive) interaction between CO molecules adsorbed atop Pt sites and hence a well-ordered surface with well-defined, well-dispersed and isolated Pt-sites. DFT calculations reproduce the experimental observations and confirm that the vastly increased Pt-CO binding energy with 2/3 ML Cu in the 1st layer of Pt rationalizes the observed Cu surface segregation. All results are combined and summarized as an illustration in Figure 1.

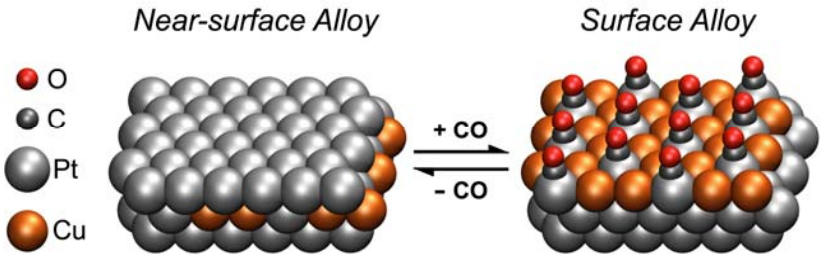

Figure 1. (color) Illustration of the CuPt near-surface alloy (left), CO-induced Cu surface segregation and the novel self-organized surface alloy (right) as a result of this.

Significance

An important consequence of our results is that it adds to the promise of using molecular adsorbate-induced surface changes as a tool for selective and dynamical engineering of alloy surfaces for catalysis [4]. Earlier indications of increased Pt-group metal bonding to CO with Cu or Ag present in its 1st layer [5-8], suggest our results at elevated temperature and CO pressure may extend to a range of coinage (Cu, Ag)/Pt-group bimetallic surface alloys.

References

1. Sinfelt J., *Bimetallic Catalysts: Discoveries, Concepts and Applications*, WILEY, New York, 1983.
2. Knudsen J., Nilekar A.U., Vang R.T, Schnadt J., Kunkes E.L., Dumesic J.A., Mavrikakis M., Besenbacher F., *J. Am. Chem. Soc.* 129, 6485 (2007).
3. Schumacher N., Andersson K., Grabow L.C., Mavrikakis M., Nerlov J., Chorkendorff I., *Surf. Sci.* 602, 702 (2008).
4. Nerlov J., Chorkendorff I., *J. Catal.* 181, 271 (1999).
5. Hager T., Rauscher H., Behm R.J., *Surf. Sci.* 558, 181 (2004).
6. Gonzalez S., Illas F., *Surf. Sci.* 598, 144 (2005).
7. Sakong S., Mosch C., Groß A., *Phys. Chem. Chem. Phys.* 9, 2216 (2007).
8. Inderwildi O.R., Jenkins S.J., King D.A., *Surf. Sci.* 601, L103 (2007).