

O 73: Symposium: Bimetallic Nanosystems: Tuning Physical and Chemical Properties II (Invited Speakers: André Fielicke, Thomas Risse, Jürgen Behm)

Time: Thursday 14:00–17:30

Location: MA 005

Invited Talk

O 73.1 Thu 14:00 MA 005

Doped clusters in light of an IR-FEL — ●ANDRÉ FIELICKE¹, PHILIPP GRUENE¹, GERARD MEIJER¹, EWALD JANSSENS², VU THI NGAN², MINH THO NGUYEN², and PETER LIEVENS² — ¹Fritz-Haber-Institut der MPG, Berlin — ²University of Leuven, Belgium

Changing the composition of a metal cluster naturally will alter its physical and chemical properties; however, often these changes are not gradual but lead to very different and unexpected behavior. In the last years several of such mixed cluster systems have been predicted by theory and also identified in experiments to exhibit unusual stabilities. In many cases this stabilization is supposed to be related to the formation of structures that are stabilized by both, electronic and geometrical effects. We focus on the determination of the geometrical structure of such isolated clusters in the gas-phase via vibrational spectroscopy. Cluster complexed with weakly bound ligands, i.e. rare gas atoms, are irradiated with intense and tunable far-IR radiation from the Free Electron Laser for Infrared eXperiments FELIX. Absorption leads to a heating of the cluster and subsequent evaporation of the ligand. This process is observed via mass spectrometry that allows determining the clusters far-IR spectra size and composition selectively. The influence of doping on the structural properties will be exemplified for silicon and gold clusters doped with transition metal atoms.

Invited Talk

O 73.2 Thu 14:30 MA 005

Molecular adsorption on bimetallic particles supported on well defined oxide surfaces — ●THOMAS RISSE — Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin, Germany

The admixture of a second metal has proven to be a suitable method to tune the desired properties of solid-supported metal particles. This presentation will focus on the adsorption properties of molecules on nanometer-sized bimetallic particles deposited on single crystalline oxide films. Such systems can serve as model systems for heterogeneous catalysts, which allow investigations with the rigor of modern surface science while grasping essential aspects of the complexity of real catalytic systems. The adsorption properties of molecules on bimetallic particles depend on a variety of parameters such as elemental and surface composition, particle size, or metal substrate interaction. Co/Pd and Fe/Pd particles grown by physical vapor deposition on a well defined alumina film will be used as model systems to explore the dependence of the adsorption properties on the abovementioned parameters. The experiments take advantage of the nucleation properties of the different metals which allow -by appropriate deposition conditions- to tune the particle's surface composition, shape, or degree of crystallinity. To allow for a microscopic analysis of the observed effects, investigations of the adsorption properties will be amended by structural characterization of the systems. Furthermore experiments on simple reactions such as reaction of the systems with oxygen or methanol decomposition will be discussed with respect to their susceptibility to the admixture of a second metal component.

Invited Talk

O 73.3 Thu 15:00 MA 005

Bimetallic Catalysis - Fundamental effects studied on well defined model systems — ●R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

Bimetallic catalysts are well known to often exhibit a significantly better performance, in activity and/or selectivity, than the respective components [1]. Based on catalytic measurements using catalysts with varying composition, different electronic and geometric effects were introduced to explain these observations [2]. Direct proof, however, was hardly possible because of the mostly unknown surface composition of the catalyst particles. Adsorption and reaction studies on bimetallic surfaces with well-defined, varied distribution of surface atoms, as identified, e.g., by high resolution scanning tunneling microscopy with chemical contrast, allow for the first time to directly identify and separate these effects [3]. Furthermore, they provide a solid basis for comparison with theory [3]. The potential of combined experimental and theoretical studies is demonstrated using different adsorption/reaction systems as example.

1. J.H. Sinfelt, Surf. Sci. 500 (2002) 923.

2. W.M.H. Sachtler, in Handbook of Heterogeneous Catalysis, G.

Ertl, H. Knözinger, and J. Weitkamp, Eds. (VCH-Wiley, Weinheim, 1997), Vol. 3.

3. M. Ruff, N. Takehiro, P. Liu, J.K. Norskov, R.J. Behm, Chem. Phys. Chem. 8 (2007) 2068.

O 73.4 Thu 15:30 MA 005

Specific Synthesis of Pt Nanowires for Catalytic Applications — ●DANIELA FENSKE^{1,4}, HOLGER BORCHERT^{2,4}, JAN KEHRES^{1,4}, JOANNA KOLNY-OLESIAK^{2,4}, MARCUS BÄUMER^{3,4}, and KATHARINA AL-SHAMERY^{1,4} — ¹IRAC, University of Oldenburg, Germany — ²EHF, University of Oldenburg, Germany — ³IAPC, University of Bremen, Germany — ⁴Center of Interface Science (CIS), Germany

Metallic nanomaterials are of great interest in the last years due to their interesting properties as new materials for optical, electronic, magnetic or catalytic applications. Particularly size and morphology of such nanoparticulate systems offer also high potential for material improvement. A promising issue is the preparation of platinum nanowires by means of colloidal chemistry which allows obtaining particles with well-defined size and shape by use of stabilizing ligands.

Recent efforts have been focused on the development of synthesis based on Jana and Peng et.al. [1] to obtain these nanowires. Therefore we were able to prepare dodecylamine-capped Pt nanowires with 2 nm in diameter and several multiple in length in varying the synthesis conditions. The influence of temperature, stabilisers and reducing agents on the morphology has been investigated. The catalytic activity of such nanowires immobilized at different oxidic supports could also be demonstrated on the example of CO oxidation and will be compared to spherical Pt and bimetallic colloidal nanoparticles [2]. [1]: N. R. Jana, X. Peng, J. Am. Chem. Soc. 2003, 125, p.14280-14281 [2]: H. Borchert, D. Fenske, J. Kolny-Olesiak, J. Parisi, K. Al-Shamery, M. Bäumer, Angew. Chem. Int. Ed. 2007, 46, p.2923-2926

O 73.5 Thu 15:45 MA 005

Structural fluxionality in the CO adsorption on pure and binary silver-gold clusters Ag_nAu_m^+ — ●DENISIA M. POPOLAN and THORSTEN M. BERNHARDT — Institut für Oberflächenchemie und Katalyse, Albert-Einstein-Allee 47, Universität Ulm, 89069 Ulm, Germany

Temperature dependent reactivity measurements performed in a low energy ion beam apparatus, consisting of a sputter cluster ion source and a temperature variable octopole ion trap combined with a tandem mass spectrometers arrangement, shed new light on the reactive behaviour of pure and binary silver-gold cluster cations with CO. Several trends in the size and composition dependent reactivity were observed. While all investigated clusters form carbonyl products, the formation kinetics and maximum number of adsorbed CO strongly vary for the different cluster ions. In the case of the trimers, the largest saturation coverage is observed for Au_3^+ . In contrast, for the pentamer clusters the maximum number of adsorbed CO molecules, at low temperatures, increases with increasing number of silver atoms n in Ag_nAu_m^+ , correlated with a decrease in the CO binding energy. The results are discussed in terms of enhanced structural fluxionality due to the larger silver content in combination with a gradual change in the bonding type of CO to the metal clusters.

15 min. break

O 73.6 Thu 16:15 MA 005

Ligand versus ensemble effects in the adsorption on nanostructured bimetallic surfaces — SUNG SAKONG¹, YOSHIHIRO GOHDA², and ●AXEL GROSS³ — ¹Fachbereich Physik, Universität Duisburg-Essen, Duisburg, Germany — ²Department of Applied Physics, The University of Tokyo, Japan — ³Institut für Theoretische Chemie, Universität Ulm, Germany

We have performed total energy calculations based on density functional theory addressing the reactivity of nanostructured bimetallic surface alloys. The catalytic activity of alloys is determined by electronic, geometric and structural factors which are often summarized employing the terms *ligand* and *ensemble* effects. Using the systems PdCu [1] and PtAu [2] as examples, we show that bimetallic systems

can exhibit properties that do not correspond to an intermediate behavior in between those of the pure components but that are rather beyond those of both components [3]. Furthermore, whereas single atoms of the surface alloys can show a decreasing interaction strength with adsorbates (ligand effect), the binding at the most favorable adsorption sites can still become stronger when the concentration of the more reactive metal is increased (ensemble effect). The electronic and geometric effects underlying these phenomena will be addressed.

- [1] S. Sakong, C. Mosch, and A. Groß, *PCCP* **9**, 2216 (2007).
 [2] Y. Gohda and A. Groß, *Surf. Sci.* **601**, 3702 (2007).
 [3] A. Groß, *Topics Catal.* **37**, 29 (2006).

O 73.7 Thu 16:30 MA 005

From adlayer to surface alloy - Change in chemical properties of bimetallic PtRu/Ru(0001) surfaces — •THOMAS DIEMANT, ANDREAS BERGBREITER, JOACHIM BANSMANN, HARRY HOSTER, and ROLF JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

The chemical and catalytic properties of bimetallic surfaces are of high interest as model systems for bimetallic catalysts. We studied the influence of the structural properties of PtRu/Ru(0001) model systems on their chemical properties. STM measurements show a change of the surface morphology in dependence of the deposition/annealing temperature. Deposition of Pt at room temperature (300 K) leads to dendritic Pt islands, while heating to 700 K results in rounded Pt islands. Annealing to even higher temperatures leads to the gradual formation of a surface alloy, which is completed at 1300 K. This surface alloy is characterised by a statistical distribution of the constituents in the surface layer. The change of the structural properties induces changes in the chemical surface properties, which were tested by the interaction of CO and D₂ with the model surfaces. The CO and D₂ TPD spectra show a redistribution of the intensity in the desorption peaks due to the modification of the surface structure. The influence of the surface structure is also evidenced in IR spectra of CO adsorbed on the model surfaces. We will correlate the change of the chemical properties of the bimetallic PtRu/Ru(0001) model systems to the modification of the structural properties and explain the variation of the chemical properties in terms of ligand, ensemble, and strain effect.

O 73.8 Thu 16:45 MA 005

Adsorption of CO on PdRu surfaces alloys studied by infrared reflection absorption spectroscopy — •HEINRICH HARTMANN, THOMAS DIEMANT, JOACHIM BANSMANN, and ROLF JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

The adsorption of CO on PdRu surface alloys on Ru(0001) has been studied by IRAS. The surface alloys were created by evaporating Pd on a Ru(0001) substrate and subsequent annealing to 1100 K. STM imaging shows a tendency toward island formation (phase separation) of the two constituents. IRAS experiments were performed to determine the CO adsorption sites on these bimetallic alloys. CO shows the same tendency for occupation of adsorption sites on the mixed PdRu surface as on the pure Ru(0001) and Pd(111) surfaces. On the Ru parts of the alloys CO adsorbs in a linear on-top configuration, on the Pd parts the adsorption of CO takes place on threefold-hollow sites (at small CO coverages) and on linear and bridge sites at (higher CO coverages). For all absorption bands the C-O vibration shifts to lower frequencies compared to the pure Ru(0001) and Pd(111) sur-

faces. These shifts are attributed to a modification of the electronic properties of the system.

O 73.9 Thu 17:00 MA 005

Decomposition of methanol by Pd, Co and bimetallic Co-Pd catalysts: model studies bridging the pressure gap — TOBIAS NOWITZKI¹, HOLGER BORCHERT¹, BIRTE JÜRGENS¹, PETER BEHREND², YULIA BORCHERT¹, THOMAS RISSE³, •VOLKMAR ZIELASEK¹, SUZANNE GIORGIO⁴, CLAUDE R. HENRY⁴, and MARCUS BÄUMER¹ — ¹Institut für Angewandte und Physikalische Chemie, Universität Bremen — ²UFT, Universität Bremen — ³Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — ⁴CRM-CNRS, Campus de Luminy, Marseille

Bimetallic particles may exhibit catalytic activities which reach far beyond those of the monometallic components. For the Co/Pd combination which is, e.g., of technological relevance for the hydrogenation of CO on the route from natural gas to liquid fuel, we have studied the interaction of model catalysts with methanol in order to obtain mechanistic information on decomposition reactions. In UHV studies, STM, TPD and XPS were performed at mono- and bimetallic nanoparticles prepared by PVD on thin epitaxial alumina films on NiAl(110). In comparison, the performance of Co/Pd nanoparticles, wet-chemically prepared on MgO, was studied in continuous flow reactors using DRIFTS and gas phase analysis at ambient pressure. This dual approach provides a consistent picture: The decomposition of methanol proceeds in two reaction pathways, the relative importance of which varies with the particle compositions. CO desorption is the limiting factor for activity at lower temperatures. Although electronic effects in the bimetallic system facilitate CO desorption, they do not compensate the lower intrinsic activity of Co sites compared to Pd sites.

O 73.10 Thu 17:15 MA 005

UPS investigations of ultrathin Au films deposited on Pd(110) — •MARCO MOORS¹, TOMASZ KOBIELA¹, MARKO KRALJ², TOBIAS PERTRAM¹, CONRAD BECKER¹, and KLAUS WANDEL¹ — ¹Institute of Physical and Theoretical Chemistry, University of Bonn, Germany — ²Institute of Physics, University of Zagreb, Croatia

The surface morphology and the local electronic properties of ultrathin Au films deposited on Pd(110) under UHV conditions have been studied by ultraviolet photoelectron spectroscopy and related methods. Investigations of bimetallic systems concerning morphology and adsorption properties are of great interest for the development of new catalysts with higher efficiency and durability. Our UPS and PAX experiments verified former STM studies [1] which showed a strong temperature dependence of the surface morphology. The Au-Pt surface prepared at 150 K is already quite flat and undergoes only a weak smoothening by annealing to 250 K. At a surface temperature of * 600 K gold starts to diffuse into the bulk forming a well ordered Au-Pd surface alloy with a maximal alloy concentration on the surface reached at 850 K. At an annealing temperature of 1050 K the surface gold depletion is completed. Besides the characterization of the Au-Pt system several adsorption experiments with various catalytic relevant molecules like CO and methanol have been performed.

- [1] M. Kralj, A. Bailly, M.-C. Saint-Lager, S. Degen, A. Krupski, C. Becker, P. Dolle, M. De Santis, K. Wandelt; *Surf. Sci.* **600** (2006) 2614.