

## Surface Science

Room: Picuris - Session SS1-MoA

### Nanocluster Reactivity

Moderator: G.B. Fisher, University of Michigan

2:00pm **SS1-MoA1 Size and Shape of the Au/TiO<sub>2</sub>(110) Nanoparticles That Catalyze the Oxidation of CO**, *J. Jupille*, Inst. des Nanosciences de Paris, France, *M.-C. Saint-Lager*, *A. Bailly*, Inst. Néel, France, *G. Cabailh*, Inst. des Nanosciences de Paris, France, *S. Garaudée*, Inst. Néel, France, *R. Lazzari*, Inst. des Nanosciences de Paris, France, *P. Dolle*, Inst. Néel, France, *O. Robach*, CEA, France, *I. Laoufi*, Inst. Néel, France, *H. Cruguel*, Inst. des Nanosciences de Paris, France

The catalytic activity of supported gold nanoparticles [1] has generated great excitement over the two last decades. In contrast with the inertness of the bulk gold, the catalytic activity of gold nanoparticles increases dramatically as their size decreases. Most studies have focused on the catalytic oxidation of CO in particular because gold catalyzes that reaction at temperature as low as 200 K with an even better activity than platinum [2]. The origin of the property is still debated. Following the earlier suggestion that reactive sites are at the edge of the Au/oxide interface [2], it was alternatively proposed from density functional approaches, in the frame of a pure gold pathway, that the activity of gold nanoparticles mostly comes from low coordinated atoms [3]. In a very different manner, the activity of gold nanoparticles was attributed to a quantum size effect with a maximum in activity for two-atom-thick clusters [4].

To date, a direct characterization of the morphology of gold nanoclusters during catalytic reactions is lacking. The present works reports on observations by Grazing Incidence Small Angle X-Ray Scattering (GISAXS) of Au/TiO<sub>2</sub>(110) supported particles during the catalytic oxidation of CO, by using a dedicated set up. The analysis chamber, operated from ultra-high vacuum to normal pressure, is acting as a reactor [5]. The reactivity is determined by mass spectrometry. In the present case (20 mbar O<sub>2</sub> + 0.1 mbar CO on Au/TiO<sub>2</sub>(110) at 200 K), it rapidly increases for particles < 5 nm. GISAXS demonstrates that reacting gold particles are always three-dimensional with an aspect ratio H/D ≈ 0.6 (H and D are the height and diameter of the particles, respectively) which, for the smallest particles under study (D = 2 nm) still corresponds to 4 atomic layers of gold. The reaction mechanism is discussed via the relationship between the reactivity and the particle geometry.

- [1] M. Haruta et al., Chem. Lett. 2 (1987) 405.
- [2] G. R. Bamwenda et al., Catal. Lett. 44 (1997) 8.
- [3] I. N. Remediakis et al., Angew. Chem. Int. Ed. 44 (2005) 1824.
- [4] M. Valden et al., Science 281 (1998) 1647.
- [5] M.-C. Saint-Lager et al., Rev. Sci. Instrum. 78 (2007) 083902.

2:20pm **SS1-MoA2 Formation and Thermal Stability of Platinum Oxides on Size-Selected Platinum Nanoparticles: Support Effects**, *L.K. Ono*, *J.R. Croy*, *H. Heinrich*, *B. Roldan Cuenya*, University of Central Florida

Metal-loaded diblock-copolymer micelles have been used to synthesize size-selected self-assembled Pt nanoparticles (NPs). Ex-situ atomic force microscopy (AFM) and transmission electron microscopy (TEM) as well as in-situ X-ray photoelectron spectroscopy (XPS) measurements were performed to investigate the formation and thermal stability of PtO<sub>x</sub> species on Pt NPs supported on SiO<sub>2</sub>, ZrO<sub>2</sub>, and TiO<sub>2</sub> thin films. For a given particle size distribution, the role played by the NP support on the stability of Pt oxides was studied. Our findings are: (i) the formation of PtO<sub>2</sub> species upon atomic oxygen exposure and a two-step thermal decomposition process (PtO<sub>2</sub> → PtO → Pt) from 300 K to 600 K upon annealing in vacuum; (ii) the enhanced stability of PtO<sub>x</sub> species on ZrO<sub>2</sub> as compared to SiO<sub>2</sub> and TiO<sub>2</sub> upon annealing in O<sub>2</sub>, and in vacuum, possibly due to its stabilization at the NP/support interface; (iii) the onset of strong NP/support interactions above 600 K and the formation of Pt-Ti and/or Pt-Ti-O alloys for the Pt-NP/TiO<sub>2</sub> system associated with the creation of O-vacancies on TiO<sub>2</sub> upon annealing in vacuum, leading to the encapsulation of Pt by TiO<sub>x</sub> above 700 K.

The size-dependent stability of PtO<sub>x</sub> species in Pt NPs supported on SiO<sub>2</sub> as compared to bulk Pt(111) will be demonstrated based on temperature programmed desorption measurements.

2:40pm **SS1-MoA3 Catalytic Reactivity of Mass Selected Nanoparticles**, *I. Chorkendorff*, Technical University of Denmark  
**INVITED**

It has recently been shown that for both the technologically important steam reforming process [1] and the methanation reaction [2] the rates are strongly dependent on the particles' size. This is ascribed to the nature of the nanoparticles and in particular the presence of step and kink sites on the nanoparticles. The abundance of such sites is expected to be very dependent on the size and the synthesis procedure. In this work we have investigated the nature of mass selected Ruthenium nanoparticles and specifically their reactivity with respect to gasses relevant for the above mentioned processes. Ruthenium is known to be a very good catalyst for both processes, and in some situations it may be superior to the commonly used Nickel catalyst despite its much higher price. Nanoparticles of sizes relevant for the above mentioned processes (2-10 nm) are manufactured by a sputter magnetron and subsequently mass selected by a quadropole mass spectrometer. The nanoparticles are soft landed on various substrates (HOPG or SiO<sub>2</sub>) and the influence and the advantages of the substrates will be discussed. The nanoparticles have been characterized in situ by SEM, AES, ISS, TPD and STM while ex-situ TEM has been used. The surface area and the stability of the nanoparticles were initially determined by temperature programmed desorption, and their ability to dissociate CO was evaluated using isotopically labeled gasses. The nature of the CO bonding and dissociation will be correlated with similar investigations on purpose stepped single crystals of Ruthenium (Ru(0 1 54)) demonstrating how the activity can be evaluated as a function of size. The reactivity of such mass selected nanoparticles has also been measured in a newly developed micro reactor on a chip with a volume of only 235 nl. This small volume combined with the fact that all the reactants and products can be led directly into a quadropole mass spectrometer for analysis allows for a close correlation of size and overall reactivity at high pressure and temperature conditions.

#### References:

- [1] G. Jones, J. G. Jakobsen, S. S. Shim, J. Kleis, M. P. Andersson, J. Rossmel, F. Abild-Pedersen, T. Bligaard, S. Helveg, B. Hinnemann, J. R. Rostrup-Nielsen, I. Chorkendorff, J. Sehested, and J. K. Nørskov, "First Principles Calculations and Experimental Insight into Methane Steam Reforming over Transition Metal Catalysts", J. Catal. 259 (2008) 147-160.
- [2] M. P. Andersson, F. Abild-Pedersen, I. Remediakis, J. Engbaek, O. Lytken, S. Horch, J. H. Nielsen, J. Sehested, J. R. Rostrup-Nielsen, J. K. Nørskov, and I. Chorkendorff, "H<sub>2</sub> Induced CO dissociation on nickel surfaces", J. Catal. 255 (2008) 6-19.

3:40pm **SS1-MoA6 Optical Nanocalorimetric Measurements of Pd Catalytic Light-Off Temperature and Catalytic Activity of Pd Nanoparticles-Size Dependent Effects**, *C. Langhammer*, *M.K. Larsson*, *B.H. Kasemo*, *I.L. Zorić*, Chalmers University of Technology, Sweden

Nanocalorimetric studies of reaction rates for the H<sub>2</sub> + O<sub>2</sub> → H<sub>2</sub>O reaction on supported Pd nanoparticles were performed, under realistic (T, p) conditions, by measuring *local* temperature of catalytic nanoparticles using the indirect nanoplasmonic sensing method<sup>1, 2</sup>. This method utilizes a sensing platform consisting of a 2D array of nanoplasmonic Au sensor nanodisks, coated with a few nm thick SiO<sub>2</sub> spacer layer onto which Pd nanoparticles, with an average size of 2.2, 3.9, 6.5 and 18 nm, were prepared. The chemical power generated by the above exothermic reaction causes a temperature rise of the nanocatalyst and the sensing Au nanodisks, which in turns leads to a spectral shift of the localized surface plasmon resonance (LSPR) of the latter. During the experiments the surrounding temperature was scanned from RT to 300°C for each reactant concentration. By subtracting the calibrated temperature dependence of the Au LSPR from the observed spectral shifts during the reaction we obtain local temperature changes on the Pd nanocatalysts, which is directly proportional to the reaction rate, as a function of surrounding temperature for different reactant concentration  $a = \text{H}_2/[\text{H}_2 + \text{O}_2]$  in the feed gas and for Pd nanocatalysts of different sizes. A clear transition in the measured reaction rate, from the kinetically limited, low temperature regime, via a light-off, into the mass transport limited regime was observed. In the low temperature kinetically limited regime an Arrhenius analysis yields apparent activation energies, for a given catalyst size, that vary as a function of reactant concentrations in agreement with the data in the literature. A shift of the light-off temperature towards higher values, observed at higher a values, is accounted for by an increased catalyst self poisoning by hydrogen. By following a nonmonotonic change of the light-off temperature, at a given a value, for four different sizes of the Pd nanocatalyst, we were able to extract information about the size dependence of the catalytic activity for our systems. This was achieved by subtracting away the size dependence of the surface area as obtained from the TEM pictures of the nanocatalysts. The

catalytic activity of the smallest nanoparticles (2.2 nm) shows an almost three fold increase compared to the activity of 18nm nanoparticles.

1. Larsson, E.M., Langhammer, C., Zorić, I. & Kasemo, B. Nanoplasmonic Probes of Catalytic Reactions. *Science* **326**, 1091-1094 (2009).

2. Langhammer, C., Zhdanov, V.P., Zorić, I. & Kasemo, B. Size-Dependent Kinetics of Hydriding and Dehydriding of Pd Nanoparticles. *Physical Review Letters* **104**, 135502 (2010).

4:00pm **SS1-MoA7 Photochemistry on Metal Nanoparticles: Comparison of Nanosecond and Femtosecond Laser Induced NO Photodesorption from NO Dimer Layers on Supported Ag Nanoparticles**, K.H. Kim, D. Mulugeta, Fritz-Haber-Inst. der Max-Planck-Gesellschaft, Germany, K. Watanabe, Tokyo Univ. of Science, Japan, D. Menzel, Fritz-Haber-Inst. der Max-Planck-Gesellschaft and TU München, Germany, H.-J. Freund, Fritz-Haber-Inst. der Max-Planck-Gesellschaft, Germany

Metal nanoparticles (MNP) have special electronic and optical properties due to their dimensions being smaller than many length parameters of electrons and photons with solids; this leads to drastic changes of surface photochemistry [1]. For oxide-supported Ag nanoparticles (AgNPs), we have reported before on strong influences of the initial excitation (2.3 – 4.7 eV, in particular of Mie plasmons at 3.5 eV), and of the mean particle size (2 to 12 nm), on the photodesorption cross sections (PCSs) of NO from NO dimer layers [2,3], using nanosecond laser pulses. However, the mechanism of desorption remains the same as on Ag(111) [2-4], as indicated by detailed measurements of final state energy distributions (translational, rotational, and vibrational) of the desorbing molecules [5], except for the smallest particles at the highest excitation energy [2] where much higher final state energies are found. These results are compatible with desorption via a transient ion, negative (TNI) in most cases [4], and positive (TPI) in the latter case [2]. In the entire range of nanosecond laser excitation, strictly linear behavior is found.

We have now done similar measurements using femtosecond laser excitation (3.1 eV photons only), increasing the excitation density by more than  $10^4$  for the same photon fluences. No change is seen on Ag(111), while for AgNPs femtosecond plasmon excitation drastically increases the PCSs as well as changes the dynamics, as indicated by different final state energies of the desorbed NO. We interpret this behavior as due to the confinement of excitation in the NPs which then leads to multiple pump-up of hot electrons during the laser pulse.

After a general survey of the basics of photochemistry on nanoparticles as compared to surfaces of bulk crystals, and of the indicated previous results, the recent measurements will be described and discussed, aiming at conclusions about their relevance for the understanding of excitations and photochemistry on nanoparticles.

[1] K. Watanabe, D. Menzel, N. Nilius, and H.-J. Freund, *Chem. Rev.* **106**, 4301 (2006)

[2] D. Mulugeta, K. H. Kim, K. Watanabe, D. Menzel, and H.-J. Freund, *Phys. Rev. Lett.* **101**, 14613 (2008)..

[3] K. H. Kim, K. Watanabe, D. Menzel, and H.-J. Freund, *J. Am. Chem. Soc.*, **131**, 1660 (2009).

[4] F.M. Zimmermann and W. Ho, *Surf. Sci. Rep.* **22**, 127 (1995), and references therein.

[5] D. Mulugeta, Ph.D. Thesis, TU Berlin 2010; and D. Mulugeta, K. Watanabe, D. Menzel, and H.-J. Freund, to be published.

4:20pm **SS1-MoA8 H/D Exchange on Pd Nanoparticles: Effects of *cis*-2-butene Co-adsorption, and Implications for Isomerization and Hydrogenation of Alkenes over Pd**, A. Savara, W. Ludwig, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, R.J. Madix, Harvard University, S. Schauer mann, H.-J. Freund, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

On Pd(111), HD production from H<sub>2</sub> and D<sub>2</sub> is believed to occur by a Langmuir-Hinshelwood mechanism: H + D → HD. However, there has been discussion about the possibility that subsurface hydrogen plays a role in the associative desorption of hydrogen, and consequently the H/D exchange reaction.

The ability of Pd nanoparticles to accommodate weakly bound subsurface hydrogen differs from that of Pd(111) single crystals. As such, we have studied H/D exchange over well-defined Pd nanoparticles and Pd(111) for comparison, in the temperature range between 200 K and 350 K.

Over the Pd nanoparticles, the HD production occurs at a slightly higher rate than over Pd(111), but with a similar temperature dependence. From both the pressure and temperature dependence of the steady state reaction rate, it is not possible to tell if there is an influence from subsurface hydrogen on the HD production, over either the single crystals or the nanoparticles.

Unexpectedly, co-adsorbed *cis*-2-butene nearly deactivates the H/D exchange reaction, while the catalyzed isomerization of and hydrogenation of *cis*-2-butene occur with persistent activity under these reaction conditions – indicating that hydrogen/deuterium is still available on the catalyst *despite* deactivation of the H/D exchange reaction.

We interpret these results to be indicative of a “portal” model for dissociative hydrogen adsorption in the presence of butene. In a “portal” model, adsorption occurs at dispersed sites on the surface, and from there the adsorbates diffuse to the rest of the surface prior to reaction. Under this interpretation, hydrocarbons block most of the surface sites for hydrogen, thus inhibiting *both* dissociative adsorption of hydrogen molecules and recombination of adsorbed hydrogen atoms. Consequently, hydrogen molecules dissociate on the minority of open spaces remaining, and the formed hydrogen atoms diffuse between the organic adsorbates. These hydrogen atoms then react with organic adsorbates, while only a small percentage of hydrogen atoms find an open space at the same time as a second hydrogen/deuterium atom to desorb with: thereby preventing HD formation under these conditions, while persistent isomerization and hydrogenation occurs. These findings may have important kinetic and mechanistic implications for alkene hydrogenation and isomerization over Pd catalysts, and potentially other transition metal catalysts.

4:40pm **SS1-MoA9 Cu/CuOx Nanoclusters on ZnO(1010): Electronic, Catalytic, Morphological Structure**, Z. Zhang, M. Patterson, M. Ren, Y. Losovyi, J. Flake, R.L. Kurtz, P.T. Sprunger, Louisiana State University

ARUPS, STM, and EELS has been used to study the electronic, atomic and chemical structure of Cu and CuO nanoclusters on non-polar ZnO(1010) surface. Within the backdrop of developing high performance CO<sub>2</sub> reduction catalyst (methanol production), our studies show that higher yield rate are found for Cu(I) surface species. ARPUS results from nanocluster CuOx/ZnO reveals that the oxidation process is highly dependent on the cluster size (smaller size). Moreover, CO adsorption (BE and vibrational) are distinctly different between Cu and CuOx nanoclusters supported on ZnO. Reaction studies confirm that methanol production is 4 times higher on partially oxidized Cu nanoclusters. Photoemission shows a small amount of Cu(II) even upon repeated oxidation/annealing processes, indicating a preferential stability of Cu(I) in the supported nanoclusters, due to interfacial effects with the substrate. This talk will include results from EELS/TPD and STM/AFM studies to better elucidate the chemical adsorption and intermediates as a function of CuOx size and structure.

5:00pm **SS1-MoA10 Femtosecond-laser Photoemission of Deposited MoxSy Clusters on Al2O3/NiAl(110)**, J. Zhou, State University of New York at Stony Brook, N. Camillone III, Brookhaven National Laboratory, M.G. White, State University of New York at Stony Brook

The electronic structures of supported size-selected Mo<sub>x</sub>S<sub>y</sub> clusters on an ultrathin aluminum oxide film on NiAl(110) are studied by two-photon photoemission spectroscopy. The Mo<sub>x</sub>S<sub>y</sub> clusters are produced by magnetron sputtering in gas phase and selected by a quadrupole mass filter. The mass-selected clusters are deposited on the ultrathin aluminum oxide film which has wide band gap to minimize the electronic interaction between clusters and NiAl(110) substrate. The formation of the aluminum oxide film on NiAl(110) results in a 0.3 eV decrease in work function and disappearance of the surface state of NiAl(110). With 0.1 ML Mo<sub>6</sub>S<sub>6</sub> deposited on the surface, the photoemission spectrum is similar with that of bare alumina oxide film because of the absence of interaction between isolated clusters on the film. When the cluster coverage increases to 0.2 ML, some features origin from the cluster are observed and reveal that the clusters are semiconductor with a band gap of about 0.6 eV. A variety of other molybdenum sulfide clusters, Mo<sub>x</sub>S<sub>y</sub> (x/y: 2/6, 3/7, 5/7, 6/8, 7/10), are also investigated and they exhibit different electronic properties with specific molybdenum to sulfide ratio.

5:20pm **SS1-MoA11 Formation of Homogeneous Rh Clusters on Al<sub>2</sub>O<sub>3</sub> from [Rh<sup>II</sup>(OAc)<sub>2</sub>]<sub>2</sub> Precursor Elucidated by STM and XAFS Analyses**, Z.W. Chen, Osaka University, Japan, W.-J. Chun, International Christian University, Japan, K. Fukui, Osaka University, Japan

Choice of a catalyst precursor sometimes affects the activity and selectivity of the catalyst due to local structures of precursors apart from the thermodynamically favored one. We have studied on precursor dependent structure of Rh/Al<sub>2</sub>O<sub>3</sub> catalysts by using STM and X-ray absorption fine structure (XAFS). Our STM results showed that homogeneous Rh clusters can be randomly dispersed on the Al<sub>2</sub>O<sub>3</sub> thin film (5 Å) on NiAl(110) by thermal decomposition of [Rh<sup>II</sup>(OAc)<sub>2</sub>]<sub>2</sub> precursors in vacuum. By statistical analyses of density, height, and diameter of the particles as a function of heat treatment temperature, we concluded that the particle typically included two Rh atoms, hence reflected the precursor composition. In situ STM measurements during heating process also showed that the precursors decomposed around 420 K. The Rh clusters were stable against

aggregation up to 800 K. These features were quite different from the typical Rh/Al<sub>2</sub>O<sub>3</sub> catalyst prepared from RhCl<sub>3</sub> precursor, where particle size was larger and aggregation easily occurred at such high temperature.

In order to determine the local structure of the clusters and elucidate the precursor dependency on the final structures, we performed XAFS measurements for Rh K-edge at NW-10A station in KEK-IMSS-PF. The Rh/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared from three Rh precursors, [Rh<sup>II</sup>(OAc)<sub>2</sub>]<sub>2</sub>, Rh<sup>III</sup>(OAc)<sub>3</sub>, RhCl<sub>3</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The precursor Rh<sup>III</sup>(OAc)<sub>3</sub> was selected because of its similar local structure to RhCl<sub>3</sub>. The as-deposited samples were heated to 500 K, 650 K, 800 K, respectively in vacuum and XAFS were measured after each heat treatment.

In the case of RhCl<sub>3</sub>, only one peak assignable to Rh-Rh bond appeared after heat treatment above 500 K and its coordination number was increased at higher temperature. It indicated that metallic Rh particles formed just after decomposition of RhCl<sub>3</sub>, and they aggregated at high temperature. In contrast, in the case of Rh acetate precursors, both of [Rh<sup>II</sup>(OAc)<sub>2</sub>]<sub>2</sub> and Rh<sup>III</sup>(OAc)<sub>3</sub>, the peak assignable to Rh-O bond was predominant. A weak peak of Rh-Rh bond was also observed in the case of [Rh<sup>II</sup>(OAc)<sub>2</sub>]<sub>2</sub>. Curve-fitting results suggested that the particle roughly included two Rh atoms each, which was qualitatively consistent with the STM results. In the case of Rh<sup>III</sup>(OAc)<sub>3</sub> precursors, Rh species were dispersed as single atoms after decomposition and they agglomerated at above 650 K. We supposed that Rh-O bond was formed in the process of the acetate-containing precursors decomposition stabilized the small Rh particles on the Al<sub>2</sub>O<sub>3</sub> surface.

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