

creating local micro-reactors with different catalytic activity, will be discussed on the bases of recent results with bimetallic systems.[2] The effect of electron confinement will be shown for oxidation of ultrathin metallic films, where varying the film thickness the sensible differences in the local oxidation rate are observed and correlated to periodic changes in the density of electronic states induced by quantum-well states crossing the Fermi level.[3] 1. P. Dudin et al, J. Chem. Phys. B 109, 2005, 13649. 2. A. Locatelli et al, J. Am. Chem. Soc. 127, 2005, 2351. 3. L. Aballe et al, Phys. Rev. Lett. 93, 2004, 196103.

9:30 Invited oral

Surface reaction kinetics studied with atomic-scale lateral resolution

Norbert Kruse, Matthieu Moors, Thierry Visart de Bocarmé

Université Libre de Bruxelles, Chemical Physics of Materials, Campus Plaine, CP 243, Brussels B-1050, Belgium

E-mail: nkruse@ulb.ac.be

This presentation reviews the recent progress made in imaging catalytic and non-catalytic surface reactions and in providing information on the local chemical composition of reactive layers. The methodical approach is based on video-Field Ion Microscopy (FIM) and atom-probe Pulsed Field Desorption Mass Spectrometry (PFDMS). The usefulness of the approach will be demonstrated in several case studies.

First, the carbonylation of Nickel to $\text{Ni}(\text{CO})_4$ will be presented. This reaction involves subcarbonyls, $\text{Ni}(\text{CO})_{2,3}$ as intermediates. Time-resolved PFDMS studies - in this method short field pulses of variable repetition frequency are used to field-desorb reactive species during the ongoing reaction - reveal $\text{Ni}(\text{CO})_2$ formation to be the slowest step in the overall reaction. In FIM this process is seen to coincide with Ni kink sites detaching in a repetitive manner so that an originally hemispherical Ni crystal ("field emitter") is transformed into a polyhedral one. Second, we show that strong morphological changes do also occur during the reaction of CO and mixtures of CO/H_2 with Co crystals. In this latter case video-FIM allows mapping of the catalytic activity and revealing the competition between morphological reshaping and chemical restructuring due to carbon deposition. C_xH_y species are detected by PFDMS during the ongoing CO/hydrogen reaction. The ion intensities of these species depend on the reaction time (ms time scale at 450 K and 10^{-3} mbar, $\text{H}_2/\text{CO}=2$) and methane is the first product of this hydrogenation. The data will be directly compared to transient kinetic build-up measurements using Co supported model catalysts.

Finally, video-FIM data on the interaction of ethylene with Ni and Co crystals will be shown. In both cases step sites cause a strong promotion of ethylene decomposition. In the Ni case, graphitic overlayers seem to form at intermediate temperatures (~600 K). These layers undergo an explosive clean-off reaction (with hydrogen) in which chemical fronts ignite in (001) planes before travelling in a self-accelerating manner toward the central (001) plane of the crystal. In a similar study, a Ni crystal is heated to ~1000 K in the presence of 10^{-2} Pa ethylene. Subsequent in-situ quenching and FIM imaging at 500 K reveals string-like structures arranged in a concentric manner in the outskirts of the crystal. These structures point away from the crystal centre. A tentative explanation of this obser-

vation is based on the formation of carbon nanofibers and their repulsive interaction with the positive electric field present during imaging.

10:00 Invited oral

Catalytic reactions on platinum metals nanofacets: Spectroscopy on an atomic scale

Yuri Suchorski

Otto-von-Guericke-Universitaet Magdeburg, Chemisches Institut, Universitaetsplatz 2, Magdeburg D-39106, Germany

E-mail: yuri.suchorski@vst.uni-magdeburg.de

The technical importance of heterogeneous catalysts has motivated an intensive development of model systems emulating the behaviour of dispersed metals on oxidic supports. One of the successful approaches is the creation of arrays of the small metal particles, grown on a planar oxidic support. Most surface-sensitive spectroscopies, however, average the collected data (in the best case over few catalytic pellets of the sample), thus the individual characteristic of the single particles are often "smoothed out". This creates difficulties in addressing the details of the reaction mechanisms on the single metal nanoparticles.

Field Ion Microscopy (FIM), Field Emission Microscopy (FEM) and Lithium Field Desorption (Li-FDM) Microscopy can in principle allow investigation of local reaction kinetics on the structurally heterogeneous surface of a single apex of a Pt or Rh tip. The surface of such a tip can be characterized with atomic resolution by FIM and catalytic reactions on well-defined nanosized facets can be monitored in situ with a resolution ≤ 2 nm using the mentioned above microscopies [1].

By using the probe-hole techniques the field ions of reacting entities emitted from few selected surface sites can be collected and analyzed in a retarding potential experiment (field ion appearance energy spectroscopy, FIAES [2]). FIAES provides the binding energy of the neutral molecules adsorbed on these selected sites. The probe-hole approach can be also combined with the mass analysis by magnetic separation (mass-to-charge resolved potential analyses) or with the time of flight (ToF) measurements.

[1] V.V. Gorodetskii, V.I. Elochin, J.W. Bakker, B.E. Nieuwenhuys, *Cat.Today* 105 (2005)

183; Y. Suchorski and J. Beben, *Prog. Surf. Sci.* 74 (2003) 3, and references therein

[2] Y. Suchorski, W.A. Schmidt, N. Ernst, J.H. Block, H.J. Kreuzer, *Prog. Surf. Sci.* 48 (1995) 121

Coffee break

Tuesday morning, 5 September, 10:30

Parallel Session

Tuesday morning, 5 September, 11:00

Chair: Jacques Vedral