

## Symposium Chemical Reactions on Nanomaterials: Progress from in-situ Experimental Studies and Theoretical Investigations (SYCR)

jointly organized by  
Metall- und Materialphysik (MM),  
Oberflächenphysik (O),  
Dünne Schichten (DS),  
Chemische Physik und Polymerphysik (CPP), and  
Vakuumphysik (VA)

Prof. Dr. Reinhard Denecke  
Physikalische Chemie II  
Universität Leipzig  
Linnestr. 2  
D-04103 Leipzig  
denecke@uni-leipzig.de

PD Dr. Karsten Reuter  
Fritz-Haber-Institut der  
Max-Planck-Gesellschaft  
Faradayweg 4-6  
D-14195 Berlin  
reuter@fhi-berlin.mpg.de

Dr. Andreas Stierle  
Max-Planck-Institut für  
Metallforschung  
Heisenbergstr. 3  
D-70569 Stuttgart  
stierle@mf.mpg.de

### Overview of Invited Talks and Sessions (BAR SCHÖ)

#### Invited Talks

SYCR 1.1	Thu	14:00–14:30	BAR SCHÖ	<b>Reactivity trends in CO oxidation from ultrahigh vacuum to elevated pressures</b> — ●WAYNE GOODMAN
SYCR 1.2	Thu	14:30–15:00	BAR SCHÖ	<b>Ruthenium oxide as oxidation catalyst</b> — ●ROBERT SCHLÖGL, DIRK ROSENTHAL, FRANK GIRSDIES, RAOUL BLUME, OLAF TIMPE
SYCR 1.3	Thu	15:00–15:30	BAR SCHÖ	<b>Low dimensional surface oxides in the oxidation of Rh particles</b> — ●FLORIAN MITTENDORFER
SYCR 1.4	Thu	16:00–16:30	BAR SCHÖ	<b>In-situ microscopy of chemical reactions on transition metal surfaces</b> — ●PETER SUTTER
SYCR 1.5	Thu	16:30–17:00	BAR SCHÖ	<b>Live STM and X-ray observations of catalytic processes</b> — ●JOOST W.M. FRENKEN
SYCR 1.6	Thu	17:00–17:30	BAR SCHÖ	<b>Computational materials design: Alloys for selective hydrogenation catalysis</b> — ●THOMAS BLIGAARD

#### Sessions

SYCR 1.1–1.6	Thu	14:00–17:30	BAR SCHÖ	<b>Chemical Reactions on Nanomaterials</b>
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## SYCR 1: Chemical Reactions on Nanomaterials

Time: Thursday 14:00–17:30

Location: BAR SCHÖ

**Invited Talk** SYCR 1.1 Thu 14:00 BAR SCHÖ  
**Reactivity trends in CO oxidation from ultrahigh vacuum to elevated pressures** — ●WAYNE GOODMAN — Texas A&M University, College Station, TX, USA

CO oxidation on Ru, Pd, Rh, and Pt surfaces has been investigated between 10<sup>-8</sup> - 10 Torr and for a variety of temperatures and O<sub>2</sub>/CO ratios. Polarization modulation reflectance absorption infrared spectroscopy (PM-RAIRS) was used to identify the CO coverage as a function of the reaction rate for a variety of conditions up to 10 Torr. For reaction pressures less than 10<sup>-6</sup> Torr, X-ray photoelectron spectroscopy (XPS) was used to measure the surface coverages of CO and Oads. A clear continuum with respect to reaction rates, surface composition, and overall mechanism is apparent over the entire pressure range investigated, i.e. there is no evidence of a pressure gap.

**Invited Talk** SYCR 1.2 Thu 14:30 BAR SCHÖ  
**Ruthenium oxide as oxidation catalyst** — ●ROBERT SCHLÖGL, DIRK ROSENTHAL, FRANK GIRSDIES, RAOUL BLUME, and OLAF TIMPE — Fritz-Haber-Institut der Max-Planck-Gesellschaft

The role of ruthenium oxide as potent catalyst for the oxidation of CO and methanol is controversially discussed using arguments from low-pressure experiments and from theory. We use bulk RuO<sub>2</sub> and in-situ XPS plus in-situ XRD to elucidate the multiple nature of catalytic states in both reactions. Under pressures above 1 mbar a transient surface oxide is the most active state performing solely selective oxidation of methanol. Co-existing other states are less potent catalysts with different selectivity in ethanol oxidation. Surprising structural transformations and kinetic oscillations in CO oxidation underline the chemical dynamics of this metallic oxide with high anion mobility.

**Invited Talk** SYCR 1.3 Thu 15:00 BAR SCHÖ  
**Low dimensional surface oxides in the oxidation of Rh particles** — ●FLORIAN MITTENDORFER — Faculty of Physics, Univ. Vienna, Austria

Transition metal particles are commonly used catalysts for a wide range of oxidation reactions. Accordingly, a wealth of surface science studies has been dedicated to the investigation of the adsorption of oxygen on the low-indexed metal surfaces. Nevertheless, most of the studies have been performed in ultrahigh vacuum, and only in the recent years the research performed under higher pressures has led to the discovery of ultra-thin surface oxide films present under realistic conditions.

We have studied the surface oxides formed on various facets of Rh with the help of density functional (DFT) calculations using the Vienna Ab-initio Simulations Package (VASP). We find the formation of 2-dimensional surface oxides with a common structure on all three low-indexed surfaces, while the presence of step edges leads to the formation of 1-dimensional oxide stripes on the higher indexed surfaces.

The surface oxides play an important role for two different aspects of the oxidation process: On the one hand the thermodynamic stability of the 2D oxides results in an increased presence of low-indexed facets of Rh nanoparticles at high oxygen partial pressures. On the other hand the 1D oxides are a nucleation center for the formation of 2D oxides. The different structures of the 1D oxides present at the step edges lead to a preferred growth direction of the 2D oxides, in agreement with experimental data.

**30 min break**

**Invited Talk** SYCR 1.4 Thu 16:00 BAR SCHÖ  
**In-situ microscopy of chemical reactions on transition metal surfaces** — ●PETER SUTTER — Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973 (USA)

In catalytic chemistry on metals, distinct surface and thin-film phases

generated under reaction conditions can strongly influence the activity and selectivity of the catalyst. Investigating the formation mechanisms, structure, and reactivity of nanoscale domains of these phases is challenging, since it requires experimental techniques that can acquire spectroscopic information with high spatial and temporal resolution during a chemical reaction.

In-situ low-energy electron microscopy allows observing the structure, electronic properties, and catalytic activity of evolving nanoscale surface phases in real time at elevated temperatures and gas pressures. We review the recent progress in this approach by discussing oxidation reactions on 4d late transition metals, such as ruthenium (Ru) and rhodium (Rh). The initial oxidation of Ru(0001), for instance, was predicted to involve the formation of a surface oxide as a precursor to the bulk oxide, which in turn is believed to be the primary active phase in oxidation catalysis in this system. By mapping multiple sets of spectroscopic data, in-situ microscopy not only identifies a more intricate competition between surface and bulk oxides, but also shows unexpected effects in oxidation catalysis due to the nanometer-scale heterogeneity of the surface, thus providing unique insight into the evolution and functionality of a catalytic surface system.

**Invited Talk** SYCR 1.5 Thu 16:30 BAR SCHÖ  
**Live STM and X-ray observations of catalytic processes** — ●JOOST W.M. FRENKEN — Kamerlingh Onnes Laboratory, Leiden University, The Netherlands

Catalytic processes are followed in situ with two dedicated instruments: the ReactorSTM and the ReactorSXR. Both instruments allow us to investigate the surface structure of a model catalyst with atomic precision under realistic reaction conditions, i.e. at high temperatures in a flow of a reactive gas mixture at pressures up to several atmospheres. The two techniques, Scanning Tunneling Microscopy and Surface X-Ray Diffraction, provide complementary information on the structure and the morphology of the catalyst surface. Simultaneously with this, both instruments use mass spectrometry to record the partial pressures of the reactants and the reaction products. This combination of techniques enables us to directly correlate the measured reaction rates and reaction kinetics with the catalyst structure and composition. Examples will be shown for the oxidation of carbon monoxide on several metal surfaces. We find that under reaction conditions, surface oxides are formed that we identify as the most active phase. We observe spontaneous, self-sustained reaction oscillations that will be explained in terms of periodic metal-oxide transitions.

**Invited Talk** SYCR 1.6 Thu 17:00 BAR SCHÖ  
**Computational materials design: Alloys for selective hydrogenation catalysis** — ●THOMAS BLIGAARD — Center for Atomic-scale Materials Design, Dept. of Physics, Build. 307, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

Scaling relations are presented which have the capability to estimate adsorbate-surface bond energies for hydrogen-containing molecules on transition metal surfaces with reasonable accuracy. The relations provide a method for estimating hydrogenation reaction energies, leading to new possibilities in using electronic structure simulations in the search for new catalysts. Using the selective hydrogenation of acetylene to ethylene as an example, it is shown how the adsorption energy of one single species can be used as a descriptor for the catalytic activity and selectivity. A number of alloys are investigated and new catalysts are singled out and experimentally tested, leading to the suggestion of new potential catalysts not containing precious metals. That scaling relations hold for adsorption energies of molecules larger than one carbon atom, suggests they can provide a method for treating the surface chemistry of more complex hydrocarbons. It is finally shown that the scaling model surprisingly can be generalized to the surfaces of more complex materials such as oxides and nitrides.