

## O 87: Surface chemical reactions

Time: Friday 10:30–12:45

Location: MA 042

O 87.1 Fri 10:30 MA 042

**Detection of carbon monoxide in a hydrogen-rich atmosphere with Kelvin Probe measurements.** — ●STEFAN SIMON<sup>1</sup>, CHRISTOPH SENFT<sup>1</sup>, RONIYUS MARJUNUS<sup>1,2</sup> und WALTER HANSCH<sup>1</sup> — <sup>1</sup>Universität der Bundeswehr, München, Germany — <sup>2</sup>University of Lampung, Bandar Lampung, Indonesia

For fuel cell applications, it is necessary to have a CO free hydrogen gas, because CO containments lead to a lower efficiency of fuel cells. It is possible to remove this carbon monoxide from the hydrogen gas by mechanisms called water gas shift reaction (WGS) or preferential oxidation catalyst (PROX). For these methods it is important, that the amount of CO has to be known. Therefore, a sensor which can detect CO in hydrogen and regulate these CO adsorption mechanisms would be a great advantage. A problem is that CO and H<sub>2</sub> are both reducing gases. So the reaction for the two gases on top of the surface is in principle the same. In this talk a sensitive layer based on modified platinum is presented, which can detect carbon monoxide in a hydrogen-rich atmosphere. The detection mechanism is based on changing the work function by the gases, which is then measured with a kelvin probe system.

O 87.2 Fri 10:45 MA 042

**Click-type on-surface formal [2+2] cycloaddition visualized by Scanning Tunneling Microscopy** — ●SYLWIA NOWAKOWSKA<sup>1</sup>, PETRA FESSER<sup>2</sup>, CRISTIAN IACOVITA<sup>1</sup>, ANELIA SHCHYRBA<sup>1</sup>, CHRISTIAN WÄCKERLIN<sup>3</sup>, SARANYAN VIJAYARAGHAVAN<sup>1</sup>, NIRMALYA BALLAV<sup>3</sup>, KARA HOWES<sup>2</sup>, JEAN-PAUL GISSELBRECHT<sup>4</sup>, MAURA CROBU<sup>2</sup>, CORINNE BOUDON<sup>4</sup>, MEIKE STÖHR<sup>5</sup>, THOMAS A. JUNG<sup>3</sup>, and FRANÇOIS DIEDERICH<sup>2</sup> — <sup>1</sup>University of Basel, Switzerland — <sup>2</sup>ETH Zürich, Switzerland, — <sup>3</sup>Paul Scherrer Institute, Switzerland — <sup>4</sup>C.N.R.S. Université de Strasbourg, France — <sup>5</sup>University of Groningen, The Netherlands

A porphyrin module has been functionalized with one electron-rich alkyne substituent and three di(tert-butyl)phenyl moieties as imaging groups. STM measurements in combination with X-ray photoelectron spectroscopy studies demonstrated the occurrence of a formal [2+2] cycloaddition/cycloreversion between the donor-activated alkyne and the electron-deficient exocyclic double bond of TCNQ on Au(111). At low coverage, monomeric and self-assembled dimeric species of the initial compounds as well as of the reaction product, a TCNQ-conjugated porphyrin, could be visualized and manipulated with the STM tip. [1] These results motivated us to explore the self-assembly and the reactive assembly of difunctionalized porphyrins equipped with two electron-rich alkyne substituents and their reaction with electron-deficient linkers.

[1] P. Fesser et al., Chem. Eur. J., 17 (2011) 5246-5250

O 87.3 Fri 11:00 MA 042

**H-atom relay reactions in real space** — ●TAKASHI KUMAGAI<sup>1</sup>, HIROSHI OKUYAMA<sup>2</sup>, TETSUYA ARUGA<sup>2</sup>, IKUTARO HAMADA<sup>3</sup>, THOMAS FREDERIKSEN<sup>4</sup>, and HIROMU UEBA<sup>5</sup> — <sup>1</sup>Fritz-Haber Institute of the Max-Planck Society — <sup>2</sup>Kyoto University — <sup>3</sup>Tohoku University — <sup>4</sup>Donostia International Physics Center — <sup>5</sup>Toyama University

The relay mechanism, in which H-atom transfer occurs in a sequential fashion along hydrogen bonds, plays an essential role in many functional compounds. The scanning tunneling microscope (STM) is used to assemble and control a test-bed for real-space observation of H-atom relay reactions at a single-molecule level. We demonstrate that the transfer of H-atoms along hydrogen-bonded chains assembled on a Cu(110) surface is controllable and reversible, and is triggered by excitation of molecular vibrations induced by inelastic tunneling electrons. The one-dimensional chain complexes consisted of water and hydroxyl groups are constructed in a step-by-step manner using a combination of STM manipulation and controlled dissociation of water molecules. Time-resolved measurement of the H-atom relay enables us to determine the rate as a function of tunneling current and bias voltage. The experimental findings are rationalized by ab initio calculations for adsorption geometry, active vibrational modes and reaction pathway, to reach a detailed microscopic picture of the elementary processes.

O 87.4 Fri 11:15 MA 042

**Reaction of Monolayer and Multilayer 2H-Phthalocyanine**

**with a Cu(111) Surface** — ●MIN CHEN<sup>1</sup>, JIE XIAO<sup>1</sup>, HANS-PETER STEINRÜCK<sup>1</sup>, and J. MICHAEL GOTTFRIED<sup>2</sup> — <sup>1</sup>Friedrich-Alexander-Universität Erlangen-Nürnberg — <sup>2</sup>Philipps-Universität Marburg

The in-situ metalation of adsorbed tetrapyrrole molecules (e.g., porphyrins and phthalocyanines) continues to be a subject of interest. To clarify the mechanism of the initial interaction and subsequent reaction of 2H-phthalocyanine (2HPc) with a Cu(111) surface, various coverages of 2HPc vapor-deposited onto Cu(111) were studied by X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). It was found that adsorbed 2HPc is partially or completely metalated by reaction with Cu atoms from the substrate at 300 K, while for other tetrapyrroles such as 2H-tetraphenylporphyrin and 2H-tetrakis(3,5-di-tert-butylphenyl)porphyrin no metalation was observed under these conditions. The differences in reactivity may be related to the specific molecular geometries, which lead to the different distances between the reactive molecular center and the substrate. Furthermore, the metalation mechanism of 2HPc multilayers on Cu(111) will be discussed; in particular the question whether Cu atoms detach from the substrate and diffuse into the 2HPc multilayer or whether the 2HPc molecules in the multilayer migrate to the Cu/organic interface. Our XPS and TPD results suggest that the surface-confined metalation reactions depend critically on the molecular geometry.

O 87.5 Fri 11:30 MA 042

**Front dynamics in the O<sub>2</sub> + NH<sub>3</sub> reaction on Rh(110) surfaces investigated with LEEM** — ●BENJAMIN BÖRKENHAGEN<sup>1</sup>, MATHÍAS RAFTI<sup>2,3</sup>, GERHARD LILIENKAMP<sup>1</sup>, WINFRIED DAUM<sup>1</sup>, and RONALD IMBIHL<sup>3</sup> — <sup>1</sup>Institut für Energieforschung und physikalische Technologien, TU-Clausthal, Leibnizstraße 4, D-38678 Clausthal-Zellerfeld — <sup>2</sup>Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Fac. Cs. Exactas, Universidad Nacional de La Plata. 64 y Diag. 113 (1900) La Plata, Argentina — <sup>3</sup>Institut für Physikalische Chemie und Elektrochemie, Leibniz-Universität Hannover, Callinstr. 3-3a, D-30167 Hannover

Recent research on the O<sub>2</sub> + NH<sub>3</sub> reactions on Rh(110) focused on interface instabilities in this bistable reaction system. Since the surface structures and changes in the surface anisotropy presumably play a central role in the mechanism of the front instabilities we studied this reaction system in the 10<sup>-6</sup> and 10<sup>-5</sup> mbar range with LEEM (low energy electron microscopy) and  $\mu$ LEED. We identified the mixed coadsorbate phase c(2 × 4)-O,N and the c(2 × 6)-O phase in the bistable range. At higher temperatures we discovered the formation of  $\mu$ m-sized islands and studied phase transitions on these islands in detail. The phase transition front breaks up into separate fronts on each island. The small fronts are mainly influenced by the microscopic surface structure such as surface steps.

O 87.6 Fri 11:45 MA 042

**Surface chemical reactions constrained in one dimension** — ●DINGYONG ZHONG<sup>1,2</sup>, GERHARD ERKER<sup>3</sup>, HARALD FUCHS<sup>1,2</sup>, and LIFENG CHI<sup>1,2</sup> — <sup>1</sup>Physikalisches Institut, Universität Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany — <sup>2</sup>Center for Nanotechnology (CeNTech), Universität Münster, Heisenbergstr. 11, 48149 Münster, Germany — <sup>3</sup>Organisch-Chemisches Institut, Universität Münster, Corrensstr. 40, 48149 Münster, Germany

Although bulk gold has long been considered minimally reactive, exhibiting poor catalytic activity, the Au(110) surface which exhibits a one-dimensional (1D) geometrical constraint, can act as the platform for carbon-hydrogen bond activation of inert alkanes. The 1.22 nm wide atomic grooves resulting from the missing-row reconstruction of Au(110) surface efficiently confine the diffusion of adsorbed molecules and constrain the molecules into a 1D pathway, their interactions restricted to neighboring molecules in the easy-diffusion direction within the atomic channels. The hydrogen atoms on terminal methyl or penultimate methylene groups can dissociate and desorb from the surface at 420 to 470 K, leading to carbon-carbon bond formation between the residual alkyl chains. The studies imply that the physical and chemical behaviors of molecule-on-surface systems can be dramatically altered by 1D spatial constraint.

O 87.7 Fri 12:00 MA 042

**Electrochemically triggered phosphating of Si-Al-coated steel**

— •PAUL SCHNEIDER, ANDREAS ERBE, and FRANK UWE RENNER —  
Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany

Tri-cation phosphating has been investigated on Si-Al-coated steels. Phosphate crystal growth on these surfaces can be initiated by cathodic polarisation, leading to hydrogen evolution and subsequent generation of a pH gradient. The electrochemically generated pH gradient replaces the pH gradient which is obtained by pickling on Fe and Zn-rich surfaces whose oxides are not stable under the technologically relevant pH. The dependence of the crystal morphology and composition on the applied potential has been investigated by scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX), X-ray diffraction and X-ray photoelectron spectroscopy (XPS). The obtained phosphate layers mainly consist of hopeite with varying Mn content. In a second step, the time dependence of the crystal nucleation and growth has been studied by switching the passive surface to a potential where crystal growth was observed. First crystals were observed after 2 s of polarisation. Subsequently, both number of crystals as well as crystal size increases. A complete surface coverage is obtained after 2 min of active phosphating.

O 87.8 Fri 12:15 MA 042

**Sensor Material for Small Concentration Measurement of Carbon Monoxide in Air at Room Temperature Based on Work Function Properties** — •RONIYUS MARJUNUS<sup>1,2</sup>, STEFAN SIMON<sup>1</sup>, JOSEF BIBA<sup>1</sup>, MICHAEL GÖRLICH<sup>1</sup>, CHRISTOPH SENFT<sup>1</sup>, and WALTER HANSCH<sup>1</sup> — <sup>1</sup>Universität der Bundeswehr München, Neubiberg, Germany — <sup>2</sup>University of Lampung, Bandar Lampung, Indonesia

Carbon monoxide (CO) is a toxic gas and its measurement is very important for safety and fire protection. Until now, many CO sensors can be found in markets but most of them are based on resistance behaviour and the prices are expensive. A different approach in making

sensor is using the work function properties of incorporated sensitive layer. We have concerned many materials and their stoichiometry to find a good sensitive layer. Data of work function change/Contact Potential Different (CPD) measurement with Pt-based shows a promising sensitivity. The results exhibit the work function change/CPD is around 10 mV for 30 ppm (MAK-value) of CO in dry/wet air.

O 87.9 Fri 12:30 MA 042

**Aggregation and Metal/Surface Reactivity of DPDI on Cu(111)** — •TONI IVAS<sup>1</sup>, SUSANNE MARTENS<sup>1</sup>, MANFRED MATENA<sup>6</sup>, JONAS BJÖRK<sup>2</sup>, JORGE LOBO-CHECA<sup>3</sup>, LUTZ H. GADE<sup>4</sup>, THOMAS A. JUNG<sup>1</sup>, and MEIKE STÖHR<sup>5</sup> — <sup>1</sup>University of Basel — <sup>2</sup>Linköping University — <sup>3</sup>CIN2, Barcelona — <sup>4</sup>Universität Heidelberg — <sup>5</sup>University of Groningen — <sup>6</sup>DIPC, San Sebastian

The perylene derivative DPDI (4,9-diaminoperylene-quinone-3,10-diimine) forms a very stable nanoporous network on Cu(111) crystals upon thermal dehydrogenation. This hexagonal network has been intensively investigated and has proven to serve as an ideal structure for the studying of host-guest assemblies, due to the considerably large pore size and the remarkable stability in particular. The pores of the dehydro-DPDI network act as quantum wells confining surface states of copper electrons and thereby producing 2D arrays of quantum dots. The DPDI network was predicted to consist of dehydrogenated DPDI forming hydrogen bonds but the recently obtained data hints at the possibility that DPDI is bound through a complex coordination network which includes copper adatoms after thermal activation/dehydrogenation. A new model has now been developed, where the DPDI is expected to undergo three dehydrogenation steps in total as well as an additional cyclization step. The hereby obtained "dehydro-DPDI" is then thought to form the coordination network. Theoretical studies as well as recent experimental results obtained by Normal Incidence X-ray Standing Wave (NIXSW) technique strongly support this new model.