

## O 7: Heterogeneous Catalysis: Experiment

Time: Monday 10:30–13:00

Location: MA 141

## O 7.1 Mon 10:30 MA 141

**Mechanisms in the Photocatalytic Hydrogen Evolution**

— ●MARTIN TSCHURL<sup>1</sup>, CONSTANTIN WALENTA<sup>1</sup>, SEBASTIAN KOLLMANNBERGER<sup>1</sup>, CARLA COURTOIS<sup>1</sup>, RUI PEREIRA<sup>2</sup>, MARTIN STUTZMANN<sup>2</sup>, and UELI HEIZ<sup>1</sup> — <sup>1</sup>Chair of Physical Chemistry, Department of Chemistry & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany — <sup>2</sup>Walter Schottky Institute and Physics Department, Technische Universität München, Am Coulombwall 4, 85748 Garching, Germany

Sustainable energy production and storage is considered one of the major challenges of the future, as the burning of fossil fuels has a severe impact on our climate. One promising technology to meet this challenge is photocatalysis, which is inspired by the idea to use (sun)light for the generation of renewable fuels as e.g. hydrogen. State-of-the-art materials often comprise co-catalyst loaded semiconductors, but these systems are still limited in efficiency. The development of more powerful catalysts may have been hindered by lack of insights on a molecular scale, as the exact mechanistic details are so far surprisingly little understood. In this talk, detailed mechanisms of the hydrogen evolution on a titania model systems are presented and the consequences for the development of future catalyst materials are discussed.

## O 7.2 Mon 10:45 MA 141

**Temperature Effects in the Photocatalysis of Co-Catalyst Decorated Titania (110)**

— ●CARLA COURTOIS<sup>1</sup>, CONSTANTIN WALENTA<sup>1</sup>, SEBASTIAN KOLLMANNBERGER<sup>1</sup>, MARTIN TSCHURL<sup>1</sup>, RUI PEREIRA<sup>2</sup>, MARTIN STUTZMANN<sup>2</sup>, and UELI HEIZ<sup>1</sup> — <sup>1</sup>Chair of Physical Chemistry, Department of Chemistry & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany — <sup>2</sup>Walter Schottky Institute and Physics Department, Technische Universität München, Am Coulombwall 4, 85748 Garching, Germany

In this study, we show the influence of temperature for photocatalytic reactions on an n-type semiconductor surface. The reactions are investigated for different temperatures under very well defined conditions (UHV). The photooxidation mechanisms proceed via a direct hole transfer to the adsorbed molecules. It is found that the outcome of the photochemical reactions is strongly governed by the thermal adsorption/desorption properties of the involved molecules and can be controlled by the judicious choice of the reaction conditions.

## O 7.3 Mon 11:00 MA 141

**Evolution of the reactivity of gas-phase cationic tantalum-2 oxide clusters with methane**

— ●GEORGE GODDARD<sup>1,2</sup>, JAN ECKHARD<sup>1</sup>, TSUGUNOSUKE MASUBUCHI<sup>1</sup>, MARTIN TSCHURL<sup>1</sup>, and UELI HEIZ<sup>1</sup> — <sup>1</sup>Chair of Physical Chemistry, Department of Chemistry & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany — <sup>2</sup>Department of Chemistry, Durham University, Durham, U.K. DH1 3LE

Metal clusters have long been looked at as model catalysts, particularly in the activation of C-H bonds. It is also known that the presence of ligands can have large effects on reactivity. Here the reaction pathway and kinetics of Ta<sub>2</sub>O<sub>x</sub><sup>+</sup> with methane were investigated for  $x = 0-6$ . Ta<sub>2</sub>O<sub>3</sub><sup>+</sup> purely shows molecular adsorption, as does Ta<sub>2</sub>O<sub>4</sub><sup>+</sup> and Ta<sub>2</sub>O<sub>6</sub><sup>+</sup>. Conversely, Ta<sub>2</sub>O<sup>+</sup> is unreactive, whilst Ta<sup>+</sup> eliminates H<sub>2</sub> to give a carbene adsorbate, and Ta<sub>2</sub>O<sub>2</sub><sup>+</sup> shows both intact adsorption and dehydrogenated products of methane. Finally the stoichiometric Ta<sub>2</sub>O<sub>5</sub><sup>+</sup>, which occurs with the lowest abundance causes hydrogen atom abstraction. The reaction was repeated using deuterated methane to confirm mass assignments and to calculate the kinetic isotope effect for each reaction step. This has led to an elucidation of the mechanism and of the structure of the clusters in question.

## O 7.4 Mon 11:15 MA 141

**Methane activation mediated by free tantalum cluster cations: reactivity governed by cluster size**

— ●TSUGUNOSUKE MASUBUCHI<sup>1</sup>, JAN ECKHARD<sup>1</sup>, GEORGE GODDARD<sup>1,2</sup>, MARTIN TSCHURL<sup>1</sup>, ROBERT BARNETT<sup>3</sup>, UZI LANDMAN<sup>3</sup>, and UELI HEIZ<sup>1</sup> — <sup>1</sup>Chair of Physical Chemistry, Department of Chemistry & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany — <sup>2</sup>Department of Chemistry, Durham University, Durham, U.K. DH1 3LE — <sup>3</sup>School of Physics Georgia

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Methane activation, which involves C-H bond cleavage, is an important topic for versatile use of methane as a feedstock. Many efforts have been made to seek efficient C-H activation of methane in the non-scalable size regime. In this contribution, we report the reactivity of size-selected tantalum cluster cations toward methane molecules, which are investigated under multi-collision conditions. Under such conditions cluster ions are thermalized to desired temperatures, adjustable in a wide range, thus advantageous to explore reaction kinetics.

The mass spectrometric approach shows that tantalum clusters with a certain size exhibit hydrogen elimination from methane at room temperature. On the other hand, the number of the dehydrogenated molecules bound to the cluster changes with cluster size. This feature is associated with the formation of dehydrogenated products.

## O 7.5 Mon 11:30 MA 141

**Operando X-ray absorption study on the influence of Ce<sup>3+</sup> species on activity of Au/CeO<sub>2</sub> catalysts in the CO oxidation**

— ●JOACHIM BANSMANN, ALI ABEL-MAGEED, GABRIELA KUCEROVA, YUCHEN WANG, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

The catalytic activity and the deactivation behavior of Au/CeO<sub>2</sub> catalysts in the CO oxidation reaction depend strongly on the reductive or oxidative nature of the pretreatment [1]; oxidative pretreatments result in higher reaction rate. Detailed studies led to the following findings: Independent of the initial chemical state of the Au NPs directly after the pretreatments, the Au NPs always assumed a metallic state a few minutes after starting the reaction.

In this project, we investigated a possible influence of the chemical state of the ceria support (the ratio of Ce<sup>3+</sup> to Ce<sup>4+</sup> species) on the catalytic activity of Au/CeO<sub>2</sub> catalysts in the CO oxidation reaction by operando XAS measurements at the Ce L<sub>3</sub> edge. Directly after reductive pretreatments, the ceria support has a relatively high fraction of Ce<sup>3+</sup> species (6-10%), whereas only 1% was found in case of an oxidative pretreatment. Independent of the initial state of the support, the amount of Ce<sup>3+</sup> species decreased rapidly (within 10 min) during reaction (1%CO, 1%O<sub>2</sub>, rest N<sub>2</sub>) to values between about 1% or even less (oxidative pretreatment). Higher values are only observed in CO rich gas mixtures. These findings are discussed with respect to activity of the catalyst and the chemical state of the Au NPs.

[1] A. Abd-El Moemen et al., J. Catal. 341 (2016) 160

## O 7.6 Mon 11:45 MA 141

**Segregation Phenomena in Size-Selected Bimetallic CuNi Nanoparticle Catalysts**

— ●LUKAS PIELSTICKER<sup>1</sup>, IOANNIS ZEGKINOGLU<sup>1</sup>, NURIA J. DIVINS<sup>1</sup>, and BEATRIZ ROLDAN CUENYA<sup>1,2</sup> — <sup>1</sup>Department of Physics, Ruhr University Bochum — <sup>2</sup>Department of Interface Science, Fritz-Haber Institute of the Max Planck Society

Catalytic systems based on bimetallic alloy nanoparticles (NPs) often exhibit significantly superior catalytic properties compared to their monometallic counterparts. The spatial atomic distribution in such bimetallic nanocatalysts plays a pivotal role in their efficiency and stability. Employing near-ambient pressure (NAP-XPS) and ultrahigh vacuum X-ray photoelectron spectroscopy (XPS) together with atomic force microscopy (AFM), surface segregation, restructuring, and sintering phenomena in size-controlled CuNi NPs supported on SiO<sub>2</sub>/Si substrates were systematically investigated as a function of temperature, chemical state, and reactive gas environment [1]. The depth profile of the elemental composition of the particles was determined under operando CO<sub>2</sub> hydrogenation conditions by varying the X-ray photon energy. The morphological changes induced by adding CO to the reaction mixture were investigated. Our study showed that the initial chemical state of the NPs and the adsorbate-induced effects sensitively affect restructuring in CuNi nanocatalysts, suggesting that their surface atomic composition and thus their catalytic properties can be tuned by appropriate plasma and annealing treatments.

[1] Pielsticker et al., J. Phys. Chem. B, Just Accepted Manuscript (2017), DOI: 10.1021/acs.jpcc.7b06984.

## O 7.7 Mon 12:00 MA 141

**Preparation and catalytic properties of chitosan supporting**

**silver-based composite** — •YUHAN WU<sup>1</sup>, YANG XU<sup>1</sup>, CHENGLIN ZHANG<sup>1</sup>, ZHIYONG LIU<sup>2</sup>, and YONG LEI<sup>1</sup> — <sup>1</sup>Institut für Physik & IMN MacroNano (ZIK), Technische Universität Ilmenau, 98693, Ilmenau, Germany — <sup>2</sup>School of Chemistry & Chemical Engineering, Shihezi University, 832003 Shihezi, P. R. China

In this study, we reported two novel silver-based composite, Ag nanoparticles/N-doped carbon composite (Ag/NC) and Ag/AgCl loaded N-doped carbon composite photocatalyst (Ag/AgCl/NC). At first, Ag/NC was fabricated by a facile and green one-step hydrothermal treatment, during this progress the environmentally benign and renewable natural chitosan was used as not only reducer and stabilizer, but also as a nitrogen source and carbon source. Secondly, Ag/AgCl/NC composite photocatalyst was synthesized via in situ oxidation reaction by adding FeCl<sub>3</sub>. The Ag/NC and Ag/AgCl/NC were characterized using X-ray diffraction, transmission electronic microscopy, energy dispersive X-ray spectra, UV-visible diffused reflectance spectra, X-ray photoelectron spectroscopy and nitrogen adsorption-desorption measurements, respectively. The obtained two kinds of composite exhibited superior catalytic activity and stability for the degradation of organic contaminants.

O 7.8 Mon 12:15 MA 141

**Decreasing the Pressure Gap: High-Pressure Low-Energy Electron Microscopy** — •BENJAMIN BORKENHAGEN<sup>1</sup>, THORSTEN FRANZ<sup>2</sup>, BERNHARD VON BOEHN<sup>3</sup>, RONALD IMBIHL<sup>3</sup>, CZESLAW KOZIOL<sup>2</sup>, WINFRIED DAUM<sup>1</sup>, and GERHARD LILIENKAMP<sup>1</sup> — <sup>1</sup>IEPT, TU Clausthal, Leibnizstraße 4, 38678 Clausthal-Zellerfeld — <sup>2</sup>ELMITEC GmbH, Albrecht-von-Grodeck-Str. 3, 38678 Clausthal-Zellerfeld — <sup>3</sup>PCI, Leibniz Universität Hannover, Callinstraße 3A, 30167 Hannover

Low-energy electron microscopy (LEEM) is a powerful tool for real-time studies on single crystal and polycrystalline surfaces, providing high surface sensitivity, chemical and structural contrast at lateral resolution as good as 2 nm. However, it is limited to vacuum environments with pressures below 10<sup>-5</sup> mbar. High-pressure LEEM extends the accessible pressure range to 0.1 mbar and beyond, enabling microscopic in situ investigations of dynamic processes within a broad range of reaction conditions. We introduce high-pressure LEEM and present results from first high pressure experiments, including surface modification by oxidation and a catalytic surface reaction.

O 7.9 Mon 12:30 MA 141

**Scanning tunneling microscopy study of the structure and interaction between carbon monoxide and hydrogen on the Ru(0001) surface** — •BARBARA A J LECHNER<sup>1,2</sup>, XIAOFENG FENG<sup>1</sup>, PETER J FEIBELMAN<sup>3</sup>, JORGE I CERDÁ<sup>4</sup>, and MIQUEL

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As the earth's crude oil supply dwindles, the Fischer-Tropsch process to create hydrocarbon fuels from two abundant resources, carbon monoxide and hydrogen, gains in significance. Here, we use scanning tunneling microscopy (STM) to investigate the spatial arrangement of CO and H coadsorbed on a model catalyst surface, Ru(0001). We find that at cryogenic temperatures, CO forms small triangular islands of up to 21 molecules with hydrogen segregated outside of the islands. Furthermore, whereas for small island sizes (3-6 CO molecules) the molecules adsorb at hcp sites, a registry shift toward top sites occurs for larger islands (10-21 CO molecules). To characterize the CO structures better and to help interpret the data, we carried out density functional theory (DFT) calculations of the structure and simulations of the STM images, which reveal a delicate interplay between the repulsions of the different species.

O 7.10 Mon 12:45 MA 141

**High-pressure STM study of the low-temperature Fischer Tropsch synthesis on Co(0001)** — •BERNHARD BÖLLER, KATHARINA DURNER, and JOOST WINTERLIN — Ludwig-Maximilians-Universität, Munich

We report an operando high-pressure STM study of a Co(0001) single crystal model catalyst, performed under several 100 mbar of syngas (2 : 1 mixtures of H<sub>2</sub> and CO) at 493 K. Under these conditions, ethane and propane can be detected as products, in addition to methane, which is in contrast to previous experiments performed at 10 mbar and at higher H<sub>2</sub>-to-CO ratios that only gave methane. The experiments thus represent a critical step toward the actual Fischer Tropsch synthesis of higher hydrocarbons. Massive problems had to be solved with respect to gas cleanliness, in particular from sulfur compounds and Ni(CO)<sub>4</sub> that decomposed on the sample surface to give sulfur and nickel. These contaminants led to strong effects on the surface that can misleadingly indicate morphology changes induced by the reaction conditions. However, after extensive experimental measures the surface could be kept free from S and Ni on the timescale of hours. Also the amounts of surface carbon and oxygen, as measured by ex situ XPS, were low. Under these conditions, atomically resolved STM data showed no significant changes of the surface morphology, except for an enhanced mobility of steps, in contradiction to established models of the low-temperature Fischer Tropsch synthesis.