

Surface Science

Room 120 - Session SS+CA+LS-TuA

Electrochemistry and Photocatalysis

Moderators: Jared Bruce, University of Nevada Las Vegas, Taku Suzuki, NIMS (National Institute for Materials Science), Japan

2:15pm **SS+CA+LS-TuA-1 Surface Sensitive Studies of the Electrolyte-Electrode Interface**, *Edvin Lundgren*, Lund University, Sweden **INVITED**
The electrified electrode electrolyte interface is notoriously difficult to study during electrochemical (EC) reactions. Most traditional surface science techniques are disqualified due to the use of electrons, on the other hand, several new in-situ experimental methods have been developed recently. Examples are Electro Chemical X-ray Photoelectron Spectroscopy (ECXPS), Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM), High Energy Surface X-Ray Diffraction (HESXRD) [4] and EC-IRAS [5].

In the first part of the talk, the corrosion of an industrial Ni base Ni-Cr-Mo alloy will be addressed. A comprehensive investigation combining several synchrotron-based techniques are used to study the surface region of a Ni-Cr-Mo alloy in NaCl solutions in situ during electrochemical polarization. X-Ray Reflectivity (XRR) and ECXPS were used to investigate the thickness and chemistry of the passive film. Grazing Incidence X-ray Diffraction (GIXRD) was used to determine the change in the metal lattice underneath the passive film. X-Ray Fluorescence (XRF) was used to quantify the dissolution of alloying elements. X-ray Absorption Near Edge Structure (XANES) was used to determine the chemical state of the dissolved species in the electrolyte. Combining these techniques allowed us to study the corrosion process, detect the passivity breakdown in situ, and correlate it to the onset of the Oxygen Evolution Reaction (OER) [6].

In the second part, an alternative approach to study the development of a model electro catalyst surface is presented. By using a combination of Grazing Incidence X-ray Absorption Spectroscopy (GIXAS) [7], 2D Surface Optical Reflectance (2D-SOR) [8] and Cyclic Voltammetry (CV) and a Au(111) electrode model surface, direct surface information during real-time CV can be obtained.

- [1] S. Axnanda et al, *Sci. Rep.* **5** (2016) 9788.
- [2] A. A. Gewirth, B. K. Niece, *Chem. Rev.* **97** (1997) 1129.
- [3] K. Itaya, *Prog. Surf. Sci.* **58** (1998) 121.
- [4] M. Ruge et al, *J. Electrochem. Soc.* **164** (2017) 608.
- [5] T. Iwasita, F. C. Nart, *Prog. Surf. Sci.* **55** (1997) 271.
- [6] A. Larsson et al, *Adv. Mat.* (2023) 230462.
- [7] H. Abe, Y. Niwa, M. A. Kimura, *Phys. Chem. Chem. Phys.* **22** (2020) 24974.
- [8] S. Pfaff et al, *ACS Appl. Mater. Interfaces* **13** (2021) 19530.

2:45pm **SS+CA+LS-TuA-3 Operando Studies of CO₂, CO and N₂ Catalytic Hydrogenation Reactions investigated with Ambient Pressure XPS**, *Peter Amann*, Scienta Omicron, Germany

Some of the most essential catalytic reactions for our energy society is to reduce CO₂ to hydrocarbons and alcohols to be used as fuels and base chemical for the chemical industry. Furthermore, the catalytic reduction of N₂ to ammonia has been considered as one of the most important discoveries during the 20th century to produce fertilizers for a growing population. Despite an enormous effort in studying these catalytic reactions we are still lacking experimental information about the chemical state of the catalytic surface and the adsorbates existing as the reaction is turning over. X-ray photoelectron spectroscopy (XPS) is a powerful surface sensitive technique that can provide almost all essential chemical information and it has been developed to operate also in a few mbar of pressure with great success for probing oxidation catalytic reactions. Unfortunately, this pressure regime is too low for the hydrogenation reactions to turn over. Here we will present how Fischer-Tropsch, methanol and ammonia synthesis reactions on single crystal metal surfaces have been probed during operando conditions in the pressure range 100 mbar-1 bar using a specially engineered XPS system built at Stockholm University (1) and permanently located at the PETRA III synchrotron in Hamburg. The instrument is commercially available at Scienta Omicron (BAR XPS) and can vary the incidence angle of the X-rays allowing it to be either surface or bulk sensitive. Examples will be presented about the chemical state of Zn in Cu-Zn methanol (2) and of Fe in Fischer-Tropsch (3,4) and ammonia

Tuesday Afternoon, November 5, 2024

synthesis reactions (5) as well as the various adsorbates at different pressures and temperatures.

- (1) P. Amann et al. *Rev. Sci. Instrum.* **90**, 103102 (2019)
- (2) P. Amann et al. *Science* **376**, 603-608 (2022)
- (3) D. Degerman et al. *J. Phys. Chem. C* **128**, 13, 5542-5552 (2024)
- (4) M. Shipilin et al. *ACS Catalysis* **12**, 7609-7621 (2022)
- (5) C.M. Goodwin et al. *Nature*, **625**, 282-286 (2024)

3:00pm **SS+CA+LS-TuA-4 Understanding the Intrinsic Activity and Selectivity of Cu for Ammonia Electrosynthesis from Nitrate**, *Zhuanghe Ren, K. Shi, Z. Meng, X. Feng*, University of Central Florida

Electrocatalysis play a central role in the development of renewable energy technologies towards a sustainable future, such as the recycling of nitrate from wastewater sources. The concentration of nitrate (NO₃⁻) in ground water, rivers, and lakes has been increasing due to the excessive use of agricultural fertilizers and the discharge of industrial wastewater, which has caused severe environmental problems such as eutrophication. Electrochemical reduction of nitrate to ammonia has emerged as a promising route for the recycling of nitrate from wastewater and sustainable ammonia production when powered by renewable electricity. Here I present our recent study of Cu catalyst for nitrate electroreduction, with a focus on its intrinsic activity and selectivity. Using polycrystalline Cu foils for benchmarking, we elucidated the impact of often overlooked factors on nitrate reduction, including Cu facet exposure, nitrate concentration, and electrode surface area. We find that an electropolished Cu foil exhibits a higher activity and selectivity for nitrate reduction to ammonia than a wet-etched Cu foil, benefiting from a greater exposure of Cu(100) facets that are more favorable for the reaction. While the NH₃ selectivity shows no apparent dependence on the nitrate concentration, it increases with Cu electrode area, which is attributed to a promoted conversion of intermediately produced NO₂⁻ to NH₃ on a larger electrode. Based on the understandings, we developed a modified Cu foil electrode with increased Cu(100) facets and surface area, which enhanced the NO₃RR activity by ~50% with a NH₃ Faradaic efficiency of 91% at -0.2 V vs RHE.

This work is supported by the National Science Foundation (NSF) Chemical Catalysis Program under Grant No. 1943732.

References:

- (1) Ren, Z.; Shi, K.; Feng, X. Elucidating the intrinsic activity and selectivity of Cu for nitrate electroreduction. *ACS Energy Lett.* **2023**, *8*, 3658-3665.

3:15pm **SS+CA+LS-TuA-5 Insights Into Photocatalytic Reduction Activities of Different Well-Defined Single Bulk Crystal TiO₂ Surfaces in Liquid**, *Olwale Ayode, W. Lu, H. Zhu, Z. Zhang*, Baylor University

Understanding the activity of TiO₂ photocatalysts is crucial for designing and optimizing efficient photocatalysts, requiring a fundamental understanding of the photooxidation and photoreduction activities of different TiO₂ crystal facets. Although photoreduction activities on several TiO₂ crystal facets have been extensively studied in reactor or ultra-high vacuum environments, studies of well-defined TiO₂ crystal facets in a liquid environment are still lacking. In this study, the photocatalytic reduction activities of resazurin (RZ) were investigated using well-defined bulk single-crystal anatase (001), anatase (101), rutile (001), and rutile (110) facets. The experiment used a liquid cell containing RZ solution and TiO₂ crystal. A lab-built Raman microscope monitored the photoluminescence (PL) spectra of RZ under UV irradiation. We observed an increase in peak intensity at 583 nm and a decrease at 630 nm in the PL spectra of the solution on the TiO₂ crystal facets upon UV illumination, suggesting a conversion from RZ to its product, resorufin (RS). Given that both RZ and RS have distinctive peaks, we used their ratios to estimate their concentrations. This enabled us to assess the conversion rate and reaction rate of the crystals. Our results show that rutile had significantly higher conversion rates and faster reaction rates than anatase for RZ reduction. Rutile (110) had conversion rates about four times greater, and rutile (001) about three times greater than anatase. Rutile (110) reaction rates were about 1.5 times faster than rutile (001) and significantly faster than anatase (101) & (001). Further evaluation of the photoreactivity was conducted using pseudo-order kinetics to determine the rate constant. The significant difference observed in rates between the rutile and anatase phases highlights the successful migration of electrons to the surface of the rutile crystal compared to the anatase surface, emphasizing the importance of crystal structure. The difference observed between rutile (001) and rutile (110) (as well as anatase facets 001 and 101) shows the effect of surface structure on photocatalytic activity. To advance the development of effective TiO₂-based photoreduction

Tuesday Afternoon, November 5, 2024

materials, we explored plasmon-assisted photoreactions. We have studied the impact of Au nanoparticles on the reactivity of the aforementioned TiO₂ facets. This study will involve modulating hot electron generation and increasing electric fields to better understand their effects on photoreactivity.

4:00pm **SS+CA+LS-TuA-8 Selectivity Control by Ionic Liquid Layers: From Surface Science to the Electrified Interface**, *Joerg Libuda*, Friedrich-Alexander-Universitaet Erlangen-Nuernberg, Germany **INVITED**

Recently, the concept of "Supported Catalysts with Ionic Liquid Layer" (SCILL) has attracted much attention in heterogeneous catalysis and electrocatalysis. In the SCILL concept, a heterogeneous catalyst is impregnated with a thin layer of ionic liquid (IL) that serves as a catalytic modifier. In this presentation, we will give an overview of selected surface science and electrochemical surface studies on the origin of this selectivity control.

In the surface science studies, we investigated the growth, wetting behavior, structure formation and thermal behavior of various ILs on a wide range of model catalysts (Pt, Pd and Au single crystal surfaces and supported nanoparticles) using scanning tunneling microscopy (STM), atomic force microscopy (AFM) and infrared reflection absorption spectroscopy (IRAS). We were able to show that most ILs form a strongly interacting wetting layer with a high degree of intrinsic structural flexibility. Depending on the conditions, 2D glassy or different crystalline wetting layers are formed, in which the molecular orientation is dynamic and allows the embedding of reactants and thus the modification of the reaction environment.

In our electrochemical surface science studies, we investigated the interaction of selected imidazolium-based ILs with reactive and non-reactive single-crystal electrodes (Au, Pt). Using electrochemical IRAS (EC-IRRAS), we monitored the potential-dependent adsorption of IL ions on the electrode and used electrochemical STM (EC-STM) to investigate the effects of the ILs on the electrode structure. We used the selective oxidation and reduction of hydrocarbon oxygenates as test reactions. For the selective electrooxidation of 2,3-butanediol (a very structure-sensitive reaction at Pt electrodes), we were able to show that small additions of specific ILs (e.g. [C₁C₂Im][OTf]) have a large effect on selectivity (e.g. on C-C bond cleavage and selectivity towards the two partial oxidation products acetoin and diacetyl). We attribute these effects to the possible adsorption of the IL anions on the Pt surfaces.

Our results rationalize the origin of selectivity control by IL coatings in heterogeneous catalysis and demonstrate the potential of ILs for selectivity control in electrocatalysis.

- [1] R. Eschenbacher et al., *J. Chem. Phys. Lett.* **12**, 10079 (2021)
- [2] T. Yang et al., *Angew. Chem. Int. Ed.* **61**, e202202957 (2022)
- [3] M. Kastenmeier et al., *J. Phys. Chem. C* **127**, 22975 (2023)
- [4] H. Bühlmeier et al., *Chem. Eur. J.*, in press (2024), DOI10.1002/chem.202301328
- [5] Y. Yang et al., *J. Phys. Chem. C*, accepted for publication (2024)

4:30pm **SS+CA+LS-TuA-10 Area Selective Atomic Layer Deposition for Spatial Control of Reaction Selectivity on Model Photocatalysts**, *Wilson McNeary*, National Renewable Energy Laboratory; *W. Stinson*, Columbia University; *W. Zang, M. Waqar, X. Pan*, University of California Irvine; *D. Esposito*, Columbia University; *K. Hurst*, National Renewable Energy Laboratory

Photocatalytic water splitting holds great potential in the pursuit of the U.S. Department of Energy's Hydrogen Shot initiative to bring the cost of H₂ to \$1/kg by 2031. A key challenge in the development of photocatalysts is increasing their overall solar-to-hydrogen efficiency by enhancing charge separation yields and redox selectivity. In this work, we use area selective ALD of oxide films (e.g., TiO₂ and SiO₂) to develop tunable interphase layers for selective oxidation and reduction reactions on a single substrate. This presentation details initial synthesis and characterization of monometallic Pt- and Au-based planar thin film electrodes in which Au regions were deactivated towards ALD growth through self-assembled thiol monolayers. The efficacy of thiols in suppressing ALD growth was assessed through ellipsometry, X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry. A patterned planar sample comprised of interdigitated arrays of Au and Pt, used as a surrogate for a photocatalyst particle containing two different co-catalysts, was exposed to ALD growth and removal of the inhibitor species. Area selectivity of the ALD coatings on the patterned substrates was evaluated through cross-sectional scanning transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM-EDS). Scanning electrochemical microscopy (SECM) was then used to probe the

Tuesday Afternoon, November 5, 2024

local activity of different regions of the patterned surface towards the hydrogen evolution reaction (HER) and iron oxidation and correlated with the ionic and e⁻ blocking effects of the area selective ALD coating. We will also detail the application of these findings to the ongoing development of 3D, particle-based photocatalysts

4:45pm **SS+CA+LS-TuA-11 Titanium-Based Catalysts for CO₂ Activation: Experimental Modelling of Hybride (Photo-)Catalysts**, *N. Kruse, J. Klimek, C. Groothuis, Lars Mohrhusen*, University of Oldenburg, Germany

Conversion of greenhouse gases and especially CO₂ into useful hydrocarbons via a low-cost route is among the major challenges of the current energy transition. For this purpose, photocatalysis may be a relevant technology, as sunlight is a free and unlimited energy source, and photoreactions usually do not require high temperatures. Oxide-based photocatalysts usually consist of a semiconducting oxide support with nanostructured (noble) metal particles.¹ Unfortunately, these metals are often expensive and have limited lifetimes due to for example sintering, coking or poisoning with carbon monoxide. Thus, for several reasons, it is attractive to develop strategies to replace noble metal in such systems.²

Titanium is one of the few elements, that are attractive in terms of its natural availability and considering various economic and ecological aspects. Titanium dioxide (TiO₂) for example offers a broad platform, as e.g. defects such as Ti³⁺ interstitials can boost the photocatalytic activity towards oxygen containing molecules.^{3,4} TiO₂ also readily forms hybrid systems with other oxides (e.g. WO₃ clusters)⁴ or sulfides such as MoS₂.⁵ Thus, we investigate titanium-based hybrid photocatalytic systems using well-defined model catalysts under ultrahigh-vacuum conditions.

Herein, we present selected results from well-defined model catalysts en route to the desired Ti-based hybrid materials, for example, nanostructured combinations of TiS₂ and TiO₂. TiS₂ has a broad light absorbance throughout the visible range, is easily reduceable and widely inert to CO poisoning, rendering it an attractive material. Our multi-method approach involves combinations of spectroscopy (esp. photoelectron spectroscopy (XPS)), microscopy (scanning tunneling microscopy (STM)) and reactivity studies (temperature-programmed desorption (TPD)). As one example, nanoparticles of TiS₂ as a classic 2D TMDC can be fabricated and studied on various substrates to derive an atomic-level understanding of structure-reactivity relationships.

References

- [1] Linsebigler, Lu, Yates: *Chem. Rev.* **95**, 735-758 (1995).
- [2] Shen et al. *Solar RRL* **4**, 1900546 (2020).
- [3] Mohrhusen, Al-Shamery *Catal. Lett.* **153**, 321-337 (2023).
- [4] Mohrhusen, Kräuter, Al-Shamery *PCCP* **21**, 12148-12157 (2021).
- [5] Kibsgaard et al., *J. Catal.* **263** 98-103 (2009).

5:00pm **SS+CA+LS-TuA-12 Tracking the Ultrafast Dynamics of a Photoinduced Reaction at the Surface of a Reactive Semiconductor: CH₃I Photoinduced Reaction on TiO₂ (110) Surface**, *A. Gupta*, University of Central Florida; *T. Wang*, University of Washington; *K. Blackman, C. Smith*, University of Central Florida; *X. Li*, University of Washington; *Mihai E. Vaida*, University of Central Florida

The detection of intermediate species during surface photoinduced reactions and the correlation of their dynamics with the properties of the surface is crucial to fully understand and control heterogeneous reactions. In this study, a technique that combines time-of-flight mass spectrometry with laser spectroscopy and fast surface preparation with molecules is employed to investigate the mechanism of photoinduced CH₃I reactions on a TiO₂(110) surface through the direct detection of intermediate species and final products. On a freshly prepared TiO₂(110) surface, the photoinduced reaction dynamics of CH₃I follows similar trends observed on other metal oxide surfaces.^{1,2} Specifically, the pump laser pulse at 266 nm excites the CH₃I molecule into the dissociative A-band, which leads to the formation of CH₃ and I intermediates that can further react to form I₂ and reform the CH₃I molecule. Subsequently, the probe laser pulse ionizes the intermediate and final products, which are detected by a mass spectrometer as a function of the pump-probe time delay. The minimum dissociation time of CH₃ obtained by monitoring the CH₃⁺ fragment, which is 110 fs, and the fast rise of the CH₃⁺ signal, indicates that CH₃I is adsorbed on pristine TiO₂(110) with I atom facing the surface. A fraction of the I atoms produced on a freshly prepared TiO₂(110) are trapped on the surface. On this TiO₂(110) surface decorated with I atoms, the CH₃ fragment can react with CH₃I to form CH₃ICH₃, which leads to a completely different dynamics at the surface due to a change into the pump-probe schema. The

Tuesday Afternoon, November 5, 2024

evolution dynamics of CH_3^+ and CH_3I^+ after the $\text{CH}_3\text{I}/\text{CH}_3$ photoexcitation will be discussed and compared with results obtained for CH_3I dosed on a freshly prepared $\text{TiO}_2(110)$ surface.

1. M. A. K. Pathan, A. Gupta and M. E. Vaida, *J. Phys. Chem. Lett.*, 2022, **13**, 9759-9765.
2. M. E. Vaida and T. M. Bernhardt, in *Ultrafast Phenomena in Molecular Sciences: Femtosecond Physics and Chemistry*, eds. R. de Nalda and L. Bañares, Springer International Publishing, Cham 2014, pp. 231-261.

5:15pm **SS+CA+LS-TuA-13 Kinetic Theory of Mixed-Potential-Driven Catalysis and the Experimental Proof**, M. Yan, N. Namari, R. Arsyad, H. Suzuki, University of Tsukuba, Japan; J. Nakamura, Kyushu University, Japan; **Kotaro Takeyasu**, Hokkaido University, Japan

It has recently been suggested that thermal heterogeneous catalysis can also involve electrochemical processes, resulting in selectivity that is markedly different from that of conventional thermal catalysis. If the catalyst is conductive and a suitable electrolyte is present nearby, anodic and cathodic half-reactions may occur simultaneously on a single catalyst surface, forming a mixed potential. This reaction is characterized by the anode and cathode being exposed to the same reactant, unlike conventional fuel cells where different reactants are supplied to each electrode. Interestingly, mixed potentials have been reported to be involved in reactions with gas molecules, such as the formation of H_2O_2 and the oxidation of alcohol. These reports suggest that electrochemical processes play a role in controlling catalytic activity and selectivity without external energy. Catalysts based on mixed potentials are a promising new category of catalysts for both basic research and industrial applications, but the principles that determine their activity and selectivity are not yet fully understood.

We first report the theoretical framework of mixed-potential-driven catalysis, including exchange currents, as a parameter of catalytic activity. The mixed potential and partitioning of the overpotential were determined from the exchange current by applying the Butler–Volmer equation at a steady state far from equilibrium [1].

To prove the theoretical framework, we measured the short-circuit current in a model reaction system without applying an external potential to demonstrate electron transfer for enzyme-like glucose oxidation. Specifically, glucose oxidation includes paired electrochemical anodic glucose oxidation and cathodic oxygen reduction, as evidenced by the consistency between the predicted and measured mixed potentials in identical reaction environments. Therefore, it can be categorized as a mixed-potential-driven catalysis. We further demonstrated that the Gibbs free energy drop, as the total driving force, was partitioned into overpotentials to promote each half-reaction in the mixed-potential-driven catalysis. This driving force partitioning, which is controlled by catalytic activity, is a powerful tool for guiding the design of mixed-potential-driven catalytic systems [2].

[1] M. Yan, N. A. P. Namari, J. Nakamura, K. Takeyasu, *Commun. Chem.* 7, 69 (2024).

[2] M. Yan, R. Arsyad, N. A. P. Namari, H. Suzuki, K. Takeyasu, *ChemCatChem*, accepted (2024).

Author Index

Bold page numbers indicate presenter

— A —

Amann, P.: SS+CA+LS-TuA-3, **1**
Arsyad, R.: SS+CA+LS-TuA-13, **3**
Ayoade, O.: SS+CA+LS-TuA-5, **1**

— B —

Blackman, K.: SS+CA+LS-TuA-12, **2**

— E —

Esposito, D.: SS+CA+LS-TuA-10, **2**

— F —

Feng, X.: SS+CA+LS-TuA-4, **1**

— G —

Groothuis, C.: SS+CA+LS-TuA-11, **2**

Gupta, A.: SS+CA+LS-TuA-12, **2**

— H —

Hurst, K.: SS+CA+LS-TuA-10, **2**

— K —

Klimek, J.: SS+CA+LS-TuA-11, **2**

Kruse, N.: SS+CA+LS-TuA-11, **2**

— L —

Li, X.: SS+CA+LS-TuA-12, **2**

Libuda, J.: SS+CA+LS-TuA-8, **2**

Lu, W.: SS+CA+LS-TuA-5, **1**

Lundgren, E.: SS+CA+LS-TuA-1, **1**

— M —

McNeary, W.: SS+CA+LS-TuA-10, **2**

Meng, Z.: SS+CA+LS-TuA-4, **1**

Mohrhusen, L.: SS+CA+LS-TuA-11, **2**

— N —

Nakamura, J.: SS+CA+LS-TuA-13, **3**

Namari, N.: SS+CA+LS-TuA-13, **3**

— P —

Pan, X.: SS+CA+LS-TuA-10, **2**

— R —

Ren, Z.: SS+CA+LS-TuA-4, **1**

— S —

Shi, K.: SS+CA+LS-TuA-4, **1**

Smith, C.: SS+CA+LS-TuA-12, **2**

Stinson, W.: SS+CA+LS-TuA-10, **2**

Suzuki, H.: SS+CA+LS-TuA-13, **3**

— T —

Takeyasu, K.: SS+CA+LS-TuA-13, **3**

— V —

Vaida, M.: SS+CA+LS-TuA-12, **2**

— W —

Wang, T.: SS+CA+LS-TuA-12, **2**

Waqar, M.: SS+CA+LS-TuA-10, **2**

— Y —

Yan, M.: SS+CA+LS-TuA-13, **3**

— Z —

Zang, W.: SS+CA+LS-TuA-10, **2**

Zhang, Z.: SS+CA+LS-TuA-5, **1**

Zhu, H.: SS+CA+LS-TuA-5, **1**