

Surface Science Division

Room 203C - Session SS+HC+MI-MoM

Dynamical Processes at Surfaces

Moderator: Gareth Parkinson, TU Wien

8:20am **SS+HC+MI-MoM1 Light Induced Single-Molecule Dynamics at Surfaces**, *Wilson Ho*, University of California, Irvine **INVITED**

Inhomogeneity of different length scales is one of the fundamental characters of matter that has its origin in the spatial variations of the charge and mass distributions. While many changes in nature and in the laboratory can be observed with the naked eyes, ultimately the interactions that lead to these changes occur at the atomic scale. In addition, heterogeneity influences the time scale that transformations occur at different locations, and the average time may differ significantly from the local times. The desire to understand and control changes in the charge and mass distributions would require experimental tools that possess simultaneous spatial and temporal resolutions to reveal the heterogeneity. This joint Å-fs resolution can be achieved by the combination of a femtosecond laser with a low temperature scanning tunneling microscope (fs-STM) that probes chemical transformations of single molecules. These experiments demonstrate the fs-STM approach in probing the effects of heterogeneity in space and time on the chemical dynamics in single molecules.

9:00am **SS+HC+MI-MoM3 Probing the Effects of Surface Structure on the Dissociative Chemisorption of Methane**, *Eric High¹, D.G. Tinney, A.L. Utz*, Tufts University

Vibrational state-resolved reactivity measurements reveal details of fundamental processes that impact reactivity in the field of heterogeneous catalysis. Insights into energy flow during reaction obtained from observations of non-statistical mode-specific and bond-selective enhancements observed for methane and its isotopologues on transition metal surfaces are one example. By providing reactive gas-molecules with precisely defined energy in well-defined energetic coordinates, state-selective experiments have also proven to be valuable probes of how surface atom motion affects overall reactivity. In this work, we will present vibrational state-resolved data collected via IR laser excitation of the antisymmetric stretch of supersonically expanded CH₄ gas molecules incident on a Ni(997) surface. We will focus on measurements investigating both the low and high incident energy regimes on this lightly stepped single crystal at a wide range of surface temperatures (T_s = 120 K to 1000 K). We will explore the possibility of benchmarking site-specific reaction barriers for dissociative chemisorption with molecules near the energy threshold for reaction. For higher energy molecular beams incident on higher surface temperatures, we will report on how the presence of steps on the Ni(997) surface modifies the kinetics of surface-bound C diffusion into the Ni subsurface and bulk and how this process impacts subsequent methane reactivity on this surface.

9:20am **SS+HC+MI-MoM4 Adsorption and Diffusion of NH₃ on Anatase-TiO₂ (101)**, *Kræn Christoffer Adamsen, S. Koust, E.L. Kolsbjerg, B. Hammer, S. Wendt, J.V. Lauritsen*, Aarhus University, Denmark

Fundamental understanding of catalytic processes for NO_x removal (Selective Catalytic reaction, SCR) is vital for improving existing catalysts and developing new. In the SCR cycle, NO_x is known to react from gas-phase on adsorbed ammonia on VO_x/TiO₂ based catalysts, and adsorption of ammonia on such oxides is therefore of great importance for fundamental understanding of NO_x-removal and SCR catalysis. Here we present a fundamental study of the static and dynamic behaviour of ammonia on anatase-TiO₂ (101), the predominant facet on anatase-TiO₂ nanoparticles. High resolution Scanning Tunneling Microscopy (STM) of static adsorbed ammonia molecules at room temperature, indicates a strong binding to the surface. Through synchrotron radiation XPS ammonia was found to adsorb molecularly. The strong binding of ammonia was further quantified by Temperature Programmed Desorption (TPD) which also shows a highly coverage dependent binding energy, indicating molecular repulsion. All experimental obtained results are in accordance with a proposed theoretically calculated DFT-model of ammonia adsorption.

Next, single ammonia molecule diffusion measured utilizing the high-speed Aarhus STM, show diffusibility to all neighbouring sites. Molecular repulsion also show a clear effect on static structures, where nearest

neighbouring site occupation is rarely observed. Statistical analysis of intermolecular coordination supplied repulsion energies, which agree with observed values in TPD spectra and theory. For diffusion, we conclude that molecular repulsion increases the diffusibility for higher coordinated ammonia molecules. However when two ammonia occupy two nearest neighbour sites, they have the possibility of diffusing through a rolling effect, where ammonia can move more easily in one direction, this phenomena has also been seen for water on other oxide surfaces. Our analysis thus shows a surprisingly complex diffusion behaviour of NH₃ on anatase TiO₂(101), which however resembles water dimer diffusion of water dimers on Rutile-TiO₂ (110).

9:40am **SS+HC+MI-MoM5 Non-equilibrium Growth of Metastable Clusters as a Means of Controlling Supramolecular Structure.**, *Ryan Brown*, Clarkson University; *A.S.A. Kandel*, University of Notre Dame

This poster will review the use of non-equilibrium growth conditions to produce supramolecular structures not easily accessible using traditional self-assembly approaches. Specifically, the formation of cyclic, hydrogen-bonded clusters at the vacuum-solid interface following the direct injection of a solution into a high vacuum chamber gives insight into the utility of employing non-equilibrium growth conditions for producing supramolecular structures with metastable configurations. When deposited in a rapidly evaporating droplet, hydrogen bonding small molecules can form clusters with 5-fold symmetry if the correct combination of hydrogen bonding groups are present. These features persist at room temperature, but evolve into more complex structures upon mild annealing. Initial studies of this phenomenon in ferrocenecarboxylic acid, 1,1'-ferrocenedicarboxylic acid, indole carboxylic acid, and isatin will be discussed. Finally, future systems and directions of study will be discussed.

10:00am **SS+HC+MI-MoM6 Ultrafast Dynamics of Reaction Pathways on Metal Surfaces**, *Jerry LaRue*, Chapman University

Important chemical processes often occur on the femtosecond timescale, requiring the use of femtosecond excitation and probing techniques to study them. Optical femtosecond laser pulses are a convenient method of initiating catalytically important reactions on metal surfaces, such as CO hydrogenation and CO oxidation, on the femtosecond timescale. Using femtosecond x-ray pulses from free electron lasers (FEL), we have selectively probed the bond making and breaking processes of these reactions using O and C k-edge x-ray absorption and emission spectroscopies to obtain time-resolved electronic structure maps. These electronic structure maps reveal the time evolution of different surface species along the reaction pathway, providing new insights into the reaction dynamics on metal catalysis. This talk will highlight past and recent results in reaction dynamics on metal surfaces as investigated using femtosecond x-ray pulses and supported through density functional theory (DFT) calculations and *ab initio* molecular dynamics (AIMD) simulations. Specific systems include CO desorption CO oxidation, and CO hydrogenation on ruthenium.

10:40am **SS+HC+MI-MoM8 Designer Solids via Multi-Heteroepitaxy: Layer-by-Layer Deposition of Molecular Frameworks on Solid Substrates**, *Christof Wöll*, Karlsruhe Institute of Technology, Germany **INVITED**

Realizing molecular "Designer Solids" by programmed assembly of building units taken from libraries is a very appealing objective. Recently metal-organic frameworks (MOFs) have attracted a huge interest in this context. Here, we will focus on MOF-based electrochemical [1,2], photoelectro-chemical [3] and photovoltaic devices [4,5]. Internal interfaces in MOF heterostructures are also of interest with regard to photon-upconversion [6] and can be used for the crosslinking of sandwiched, reactive monomers [7]. Since the fabrication of reliable and reproducible contacts to MOF-materials represent a major challenge, we have developed a layer-by-layer (lbl) deposition method to produce well-defined, highly oriented and monolithic MOF thin films on a number of different substrates. The resulting films are referred to as SURMOFs [8]. The fabrication of hetero-multilayers (see Fig. 1) is rather straightforward with this lbl method. In this talk, we will describe the principles of SURMOF fabrication as well as the results of systematic investigations of electrical [9] and photophysical properties exhibited by empty MOFs and after loading their pores with functional guests. Furthermore, we will discuss further applications realized by loading MOFs with nanoparticles or quantum dots.

References:

¹ Morton S. Traum Award Finalist

Monday Morning, October 22, 2018

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11:20am **SS+HC+MI-MoM10 Isotope Enrichment via Non-Equilibrium Differential Condensation and Reflection using Supersonic Beam Gas-Surface Scattering**, *Jacob Graham, A. McMillan, K. Nihill, S.J. Sibener*, University of Chicago

Isotopically enriched materials have a variety of uses including chemical labeling, energy, medicine, and quantum computing. To stimulate the further development of these applications, modern, efficient isotope enrichment methods are needed. Non-equilibrium supersonic beam gas-surface scattering and differential condensation is shown to be a new and broadly applicable route to isotope enrichment. This enrichment is demonstrated with ^{36}Ar and ^{40}Ar isotopes reflecting from low temperature condensates of argon, with differences arising in the condensation coefficient, which depend on the degree of collisional energy exchange for each isotope at the interface. The enrichment factors were found to be tunable as a function of incident beam kinetic energy. For example, ^{36}Ar was found to be *enriched* relative to ^{40}Ar in the scattered fraction by greater than a factor of two, for a seeded beam of argon in helium having incident velocity 1650 m/s. In a separate and complementary experiment under the same conditions, the amorphous argon condensate was found to be *depleted* in its ^{36}Ar content, confirming this effect. This observed isotope selectivity during deposition introduces a new method for isotopic enrichment and purification as well as *in-situ* isotopic materials engineering.

11:40am **SS+HC+MI-MoM11 Structural Reorganization of Sequentially Adsorbed Two-component Self-assembled Monolayers after Soft Ultraviolet Irradiation**, *C. Gerber, Rebecca Quardokus*, University of Connecticut

Sequentially adsorbed anthracene dicarboxylic acid and octanethiol on Au(111) form ordered regions of octanethiol, gold vacancy islands, and areas of disorder near domain boundaries and vacancy islands. Vapor deposition of octanethiol after drop-cast deposition of anthracene dicarboxylic acid on Au(111) results in small ($\sqrt{3} \times \sqrt{3}$)R30° and c(4x2) octanethiol domains. Initial exposure to soft ultraviolet irradiation increases disorder with only a few small close-packed octanethiol domains remaining. Repeated exposure to soft ultraviolet irradiation shows some removal of octanethiol molecules and sequential imaging by scanning tunneling microscopy gives snapshots of the stepwise reordering of the domains that ultimately leads to a structurally reordered monolayer consisting of larger domains of low-coverage octanethiol in a $p \times \sqrt{3}$ structure.

Author Index

Bold page numbers indicate presenter

— A —

Adamsen, K.C.: SS+HC+MI-MoM4, **1**

— B —

Brown, R.D.: SS+HC+MI-MoM5, **1**

— G —

Gerber, C.: SS+HC+MI-MoM11, **2**

Graham, J.: SS+HC+MI-MoM10, **2**

— H —

Hammer, B.: SS+HC+MI-MoM4, **1**

High, E.A.: SS+HC+MI-MoM3, **1**

Ho, W.: SS+HC+MI-MoM1, **1**

— K —

Kandel, A.S.A.: SS+HC+MI-MoM5, **1**

Kolsbjerg, E.L.: SS+HC+MI-MoM4, **1**

Koust, S.: SS+HC+MI-MoM4, **1**

— L —

LaRue, J.L.: SS+HC+MI-MoM6, **1**

Lauritsen, J.V.: SS+HC+MI-MoM4, **1**

— M —

McMillan, A.: SS+HC+MI-MoM10, **2**

— N —

Nihill, K.: SS+HC+MI-MoM10, **2**

— Q —

Quardokus, R.: SS+HC+MI-MoM11, **2**

— S —

Sibener, S.J.: SS+HC+MI-MoM10, **2**

— T —

Tinney, D.G.: SS+HC+MI-MoM3, **1**

— U —

Utz, A.L.: SS+HC+MI-MoM3, **1**

— W —

Wendt, S.: SS+HC+MI-MoM4, **1**

Wöll, C.: SS+HC+MI-MoM8, **1**