Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-TuM

Energetic Processes and Tailored Surfaces in Heterogeneous Catalysis

Moderators: Tim Schäfer, Georg-August Universität, Göttingen, Germany, **Arthur Utz**, Tufts University

8:40am **HC+AS+SS-TuM-3 Adsorption and Reaction of Acetic Acid on Single-Crystal and Faceted Nanoparticle Anatase $TiO_2(101)$ Surfaces**, *C. O'Connor, R. Ma, Y. Wu, W. DeBenedetti, F. Gao, Y. Wang, G. Kimmel,* ***Zdenek Dohnálek,*** Pacific Northwest National Laboratory

Understanding the adsorption and reactivity of carboxylic acids on anatase TiO_2 is of great interest in catalysis for the potential synthesis of selective carbon-coupling reaction products. A comparative investigation of the adsorption and reaction of acetic acid on single-crystal planar and faceted nanoparticle anatase $TiO_2(101)$ surfaces was performed using a combination of infrared spectroscopy, temperature-programmed reaction spectroscopy and scanning tunneling microscopy. Acetic acid adsorbs as bidentate acetate and monodentate acetic acid dependent on the adsorption temperature as determined by infrared spectroscopy and scanning tunnelling microscopy measurements on single-crystal TiO_2 under ultra-high vacuum conditions. The adsorption of bidentate acetate has a saturation coverage of 0.5 ML. However, high-density phases containing a mixture of bidentate acetate and monodentate acetic acid and solely monodentate acetic acid occur at low temperature conditions. The sole presence of bidentate acetate is observed at elevated temperature due to the facile conversion of monodentate acetic acid to bidentate acetate and desorption of monodentate acetic acid which precludes investigating the reactivity of high-density phases under vacuum conditions. The presence of monodentate acetic acid persists to notably higher temperatures on the faceted nanoparticles than single-crystal TiO_2. The reaction of bidentate acetate produces ketene and water as determined by temperature-programmed reaction spectroscopy on single-crystal TiO_2. Notably, there is an absence of carbon-carbon coupled products, such as acetone, from the sole reaction of bidentate acetate. The selectivity of bidentate acetate is independent of coverage up to the saturation coverage. Similarly, the reaction of acetic acid on faceted nanoparticle TiO_2 produces predominantly ketene and water as determined by temperature-programmed reaction spectroscopy under low vacuum conditions. This study provides mechanistic insight into the reactivity and stability of surface-bound intermediates that are present for the reaction of acetic acid on anatase TiO_2 catalysts.

9:00am **HC+AS+SS-TuM-4 Phase Transformation of Single Micro-Sized TiO_2 Crystals**, *W. Lu, H. Zhu, N. Craft, K. Park,* ***Zhenrong Zhang,*** Baylor University

Understanding the reactivity of various crystal faces in different polymorphs of TiO_2 in photoreaction is important for many photocatalytic applications. Here, we monitored and studied the anatase-rutile phase transition (ART) processes of individual micro-sized TiO_2 crystals from the pure anatase phase to the mixed-phase, then to the rutile phase. High-quality micro-sized anatase TiO_2 crystals with a large percentage of (001) facets were hydrothermally synthesized. Micro-Raman spectroscopy mapping and scanning electron microscope (SEM) images were obtained at different annealing stages to correlate the crystal structure transformation with the morphology change. The ART processes of individual anatase particles are distinctive and depend on the various defects which serve as rutile nucleation sites. Two types of transition pathways are observed. In one type of growth pathway, rutile nucleation was formed at a corner of an anatase crystal. The rutile phase then gradually propagated over the rest part of the microparticle. The phase concentration calculated from Raman spectra revealed that the ART transition follows the first-order reaction mechanism. In the other type of growth pathway, multiple rutile nucleation sites formed simultaneously on different edges and corners of the microcrystal. The rutile phase then spreads over the whole crystal from these nucleation sites forming multi-grain crystals.

9:20am **HC+AS+SS-TuM-5 Reactivity of Formic Acid on Single Atom Rh Supported on $Fe_3O_4(001)$**, ***Christopher Lee,*** *M. Sharp, S. Smith, B. Kay, Z. Dohnálek,* Pacific Northwest National Laboratory

Single-atom catalysis is a growing area of research due to the potential to qualitatively transform the activity and selectivity of supported metal catalysts. However, the fundamental surface science studies of their unique properties have not been widely studied. Here we investigate the reactivity of formic acid on several model Rh catalysts, including single Rh adatoms, Rh incorporated into the support oxide lattice, and metallic Rh clusters on $Fe_3O_4(001)$ under ultrahigh vacuum conditions. The single Rh adatoms are found to be the most active towards CO_2 production, followed by incorporated Rh and then by Rh nanoclusters. While the reaction of formic acid with $Fe_3O_4(001)$ primarily results in CO desorption at ~570 K, the addition of small amounts of single adatom Rh (~0.01 Rh per $Fe_3O_4(001)$ unit cell (u.c.)) results in a dramatic shift towards CO_2 production at lower temperatures starting at 540 K and dropping to ~470 K at larger HCOOH coverages. The incorporated Rh system also yields CO_2 product, but it takes ~15-20 times as much Rh to achieve the same activity as the Rh adatoms. Rh nanoclusters exhibit reactivity similar to metallic Rh with low-temperature CO_2 and H_2 desorption at ~310 K while still producing substantial amounts of CO_2 at 450-500 K, not observed on pure $Fe_3O_4(001)$. These differences demonstrate that different forms of Rh supported on $Fe_3O_4(001)$ affect the reactivity of the catalytic surface beyond the local stabilized transition metal site. The stabilized adatoms turn over multiple adsorbates to products demonstrating the importance of spillover from the support oxide. Furthermore, the single Rh adatoms and incorporated Rh exhibit an intermediate activity distinct from metallic Rh nanoparticles or the $Fe_3O_4(001)$ substrate, demonstrating the additional degree of reactive tuning provided by single-atom catalysts. The similarity in reactive behavior between the Rh adatom and mixed Rh oxide systems hints toward a common mechanism between the systems. The much larger reactivity of the Rh adatom system suggests that under reaction conditions, a small amount of the mixed Rh oxide may be dynamically converted to Rh adatom and that the Rh adatom is responsible for the lower temperature CO_2 activity.

9:40am **HC+AS+SS-TuM-6 WO_3/Ag_2S type-II Hierarchical Heterojunction for Improved Charge Carrier Separation and Photoelectrochemical Water Splitting Performance**, ***Jyoti Yadav,*** *J. Singh,* IIT DELHI, India

In the present work, WO_3/Ag_2S heterojunction was fabricated to achieve an improved photoelectrochemical (PEC) water splitting performance. To prepare the working electrodes,a two step method was adopted which includes, a thin film of WO_3 deposited using DC sputtering and a well-separated Ag_2S nanorods fabricated by glancing angle deposition,. The PEC response was studied for bare WO_3, Ag_2S, and WO_3/Ag_2S heterojunction. The as-prepared WO_3/Ag_2S heterojunction samples revealed higher absorption as well as higher photocurrent density of 2.40 mA/cm^2 (at 1V Ag/AgCl) as compared to bare WO_3 thin film (0.34 mA/cm^2). The enhancement in the photocurrent density of WO_3/Ag_2S electrodes could be ascribed to the formation of the type-II heterojunction between WO_3 and Ag_2S which effectively separates and transfers the charge carriers at the interface. In addition, increased trapping of light due to vertically tilted Ag_2S nanorods structures results in an effective absorption of light. Furthermore, electrochemical impedance spectra measurements showed that WO_3/Ag_2S samples have lower charge transfer resistance at the semiconductor electrolyte interface with high flat band potential. The present work provides a deeper insight on the role of the interface formed between WO_3 and Ag_2S for the photoelectrochemical water splitting response.

11:00am **HC+AS+SS-TuM-10 Using Photon-Stimulated Desorption to Probe the Structure and Reaction Dynamics of Molecules Adsorbed on $TiO_2(110)$**, ***Greg Kimmel,*** Pacific Northwest National Laboratory **INVITED**

TiO_2 is a widely used photocatalyst. Its ability to oxidize organic contaminants makes it useful, for example, in air and water purification systems and as a thin-film coating for self-cleaning surfaces. As a result of titanium dioxide's practical applications and its potential use in photocatalytic water spitting, it has been the subject of a tremendous amount of research. We have investigated the photon-stimulated reactions of small molecules, such as O_2, CO, and acetone, on rutile $TiO_2(110)$. Experiments on clean, well-characterized single crystal surfaces, including azimuth- and angle-resolved measurements of photo-desorption products, provide key insights into the photochemical reactions of interest. This talk will highlight examples of this approach, including the photochemistry of chemisorbed O_2, the photo-oxidation of CO, and the photon-stimulated reactions of acetone. For the photo-oxidation of CO, the results show that a bridging O-O-C-O intermediate ejects CO_2 perpendicular to the bridging oxygen rows, which is consistent with density functional theory calculations. However, in contrast to earlier suggestions, the reaction kinetics show that the oxidation is a multi-step process. For acetone, the azimuth-resolved measurements of the methyl fragments revealed a second reaction channel that probably involves an enolate intermediate on the surface.

11:40am **HC+AS+SS-TuM-12 Comparison of Pt, Rh and Ir Single Atoms on a Fe_2O_3 Model Support***, **Gareth Parkinson**, A. Rafsanjani Abbasi, L. Puntscher, F. Kraushofer, P. Sombut, C. Wang,* TU Wien, Austria*; M. Meier,* University of Vienna, Austria*; M. Eder, J. Pavelec, G. Franceschi, M. Riva, M. Schmid, U. Diebold,* TU Wien, Austria*; C. Franchini,* University of Vienna, Austria

Understanding how the local environment of a “single-atom” catalyst affects stability and reactivity remains a significant challenge. Fe_2O_3 is the most common iron-oxide support material utilized for SAC, but little is known about how metal adatoms bind at its surfaces. In this talk, I will compare and contrast the behavior of Pt, Rh,[1,2] and Ir atoms on the flat, well-ordered (1×1) termination of Fe_2O_3(1-102).[3,4] Using a combination of scanning probe microscopy and spectroscopic data, as well as theoretical calculations, I will demonstrate significant differences between the adsorption site and thermal stability of the metals, as well as differences in their interaction with water and carbon monoxide.

[1] F. Kraushofer *et al.*, Single Atom Catalysts: Surface Reduction State Determines Stabilization and Incorporation of Rh on α-Fe_2O_3(1-102) (Adv. Mater. Interfaces 8/2021). *Advanced Materials Interfaces***8**, 2170045 (2021).

[2] F. Kraushofer *et al.*, Single Rh Adatoms Stabilized on α-Fe_2O_3($1\bar{1}02$) by Coadsorbed Water. *ACS Energy Letters***7**, 375-380 (2022).

[3] F. Kraushofer *et al.*, Atomic-Scale Structure of the Hematite α-Fe_2O_3(1-102) “R-Cut” Surface. *J. Phys. Chem. C***122**, 1657-1669 (2018).

[4] G. Franceschi *et al.*, A Model System for Photocatalysis: Ti-Doped α-Fe_2O_3(1-102) Single-Crystalline Films. *Chem. Mater.***32**, 3753-3764 (2020).

12:00pm **HC+AS+SS-TuM-13 HC Graduate Student Finalist Talk: Preparation and Characterization of Model Homotopic Catalysts: Rh Adatoms, Nanoparticles, and Mixed Oxide Surfaces on Fe_3O_4(001)***, **Marcus Sharp**,* PNNL/WSU*; C. Lee, M. Mahapatra, S. Smith, B. Kay, Z. Dohnálek,* PNNL

Single atom catalysts have emerged as a new catalyst frontier due to the need for improved catalyst activity and selectivity. Yet key fundamental challenges exist regarding understanding of how their activity and stability depend on their coordination environment. Surface science studies have the tools necessary to investigate such monodispersed single atom catalysts and their chemistry under well-controlled reaction conditions. Here, we have studied the behavior of Rh on the Fe_3O_4(001) single crystal surface using X-ray photoelectron spectroscopy (XPS), temperature programed desorption (TPD), and scanning tunneling microscopy (STM). We employ the Fe_3O_4(001) reconstructed surface that has been shown to stabilize single 2-fold coordinated metal adatoms to elevated temperatures. By varying the Rh deposition and annealing temperature, we have identified a series of model catalysts possessing unique Rh sites. These catalysts include Rh adatoms, mixed surface layers with octahedrally-coordinated Rh, small Rh clusters, and large Rh nanoparticles on both mixed and pure Fe_3O_4 surfaces. STM and XPS are used to characterize the Rh coverage, species, binding, and particle size distribution. Subsequently, CO and CO_2 adsorption is employed to characterize the chemical and redox properties of these sites. CO binds strongly with Rh adatoms, clusters, and nanoparticles desorbing at higher temperatures but interacts weakly with the Rh-octahedral species. In contrast, CO_2 interacts most weakly with Rh adatoms and nanoparticles, while interactions between Rh-octahedral and Fe-octahedral are indistinguishable. Further, CO_2 is used to distinguish between metallic Rh sites and Fe_3O_4(001) sites, which shows good agreement with our STM results. These model systems allow us to directly investigate reaction mechanisms on different types of catalytic sites furthering our understanding of how to selectively tune catalyst sites for desired reaction pathways. Future studies are directed toward understanding the energetics and reaction pathways of the hydrogenation of unsaturated hydrocarbons and carbonyl functional groups.

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