

## Surface Science Division

### Room 319 - Session SS1+AS+HC-FrM

#### Oxide Surface Structure and Reactivity

**Moderators:** Andrew Gellman, Carnegie Mellon University, Zhenrong Zhang, Baylor University

8:20am **SS1+AS+HC-FrM-1 Operando Photoluminescence Microscopy Study of Photoreduction of Resazurin on TiO<sub>2</sub> Microcrystals**, Hao Zhu, Z. Zhang, W. Lu, B. Birmingham, Baylor University

Titanium dioxide (TiO<sub>2</sub>) has been extensively studied for its photo-reactivity-related applications in solar cells, clean hydrogen energy, and environmental remediation. It is commonly accepted that the anatase (A) phase is more photoreactive than the rutile (R) phase. However, the reversed relative photo activities were often reported. In addition, mixed-phase TiO<sub>2</sub> has shown the highest photoactivity but the synergetic effect is not clear. Understanding the syngenetic effect at the two-phase interface will lead to a new era of catalyst design.

In this work, operando photoluminescence microscopy was used to investigate the photoreduction of resazurin on anatase microcrystals, rutile microcrystals, rutile (110) single crystals, and anatase (001) single crystals. Our results show that the rate of resazurin photoreduction on the rutile (110) surface was higher than that on the anatase (001) surface. The reaction rates on anatase microcrystals with a large percentage (001) facet are faster than that on anatase (001) single crystals and close to the reaction rate on rutile (110) single crystals. The reaction rate of the anatase microcrystals depends on the morphology and structure of each individual particle. The mechanism of the syngenetic effects at the rutile/anatase interface was also studied on the synthesized A-R two-phase microcrystals.

8:40am **SS1+AS+HC-FrM-2 Unraveling Surface Structures of Ga-Promoted Transition Metal Catalysts in CO<sub>2</sub> Hydrogenation**, Si Woo Lee, M. Lopez Luna, S. Shaikhutdinov, B. Roldan Cuenya, Fritz Haber Institute of the Max Planck Society, Germany

Gallium-containing intermetallic compounds and alloys with transition metals have recently been reported to be active in the hydrogenation of CO<sub>2</sub> to methanol. However, the promotional role of Ga in these catalysts is still poorly understood, in particular due to the lack of information about the surface structures of the catalysts, especially under reaction conditions. In this respect, studies using surface-sensitive techniques applied to well-defined model systems can provide key information to elucidate the reaction mechanism and provide the basis for the rational design of Ga-promoted TM catalysts.

In this work, we employed *in situ* Near Ambient Pressure Scanning Tunneling Microscopy (NAP-STM) and X-ray Photoelectron Spectroscopy (NAP-XPS), which make possible the studies of surfaces in the reaction atmosphere, to monitor the structural and chemical evolution of the Ga/Cu surfaces in the CO<sub>2</sub> hydrogenation reaction. NAP-STM images recorded in the reaction mixture revealed temperature- and pressure-dependent de-alloying of the initially formed, well-ordered c(2x2)-Ga/Cu(111) surface alloy and the formation of Ga-oxide islands embedded into the Cu(111) surface. Thus, NAP-STM studies revealed that the surface undergoes de-alloying and phase separation into Ga-oxide and (1x1)-Cu exposing Ga-oxide/Cu(111) interfacial sites. Notably, in our atomically-resolved STM image on Ga-oxide/Cu(111), it is clearly observed that Ga-oxide grows into an ultrathin oxide layer with (4√3x4√3)R30° superstructure when grown on Cu(111). From NAP-XPS studies on Ga/Cu(111) in the presence of CO<sub>2</sub> and H<sub>2</sub>, the formation of formate was observed, and this intermediate was finally transformed into methoxy at elevated reaction temperatures, the final surface-bound intermediate of methanol synthesis. In contrast to Ga-containing Cu catalyst, on the other hand, there was no reaction intermediate at high temperature on the Ga-free Cu(111) surface, demonstrating that the further reaction does not occur any more from chemisorbed CO<sub>2</sub><sup>δ-</sup> on Cu alone. Therefore, the GaO<sub>x</sub>/Cu interface formed under reaction conditions may expose catalytically active sites, that should be taken into account for elucidating the reaction mechanism on the Ga-promoted systems. For the first time, our *operando* surface characterizations reveal strong evidence that Cu-Ga catalysts are activated in CO<sub>2</sub> hydrogenation with the formation of embedded oxide-metal interfacial sites by de-alloying transition, which allow us to prove the promotional role of Ga in Cu-Ga catalysts.

9:00am **SS1+AS+HC-FrM-3 Stabilization of Active Cu Sites on Oxide Surfaces**, Dario Stacchiola, Brookhaven National Laboratory INVITED

Cu-based catalysts are active for partial and full oxidation reactions. Copper can be oxidized under moderate oxidant pressures and temperature to Cu<sub>2</sub>O, and further to CuO under typical catalytic reaction conditions. We present here model systems using both copper oxide thin films and single crystals used to interrogate the effect of alkali, metal, and oxide modifiers on the stability of exposed active Cu sites. *In situ* experiments allow the observation of dynamic processes and phases under reaction conditions.

9:40am **SS1+AS+HC-FrM-5 An optimized IRAS Setup to Investigate Adsorbates on Metal-Oxide Single Crystals**, David Rath, J. Pavelec, U. Diebold, M. Schmid, G. Parkinson, TU Wien, Austria

The IRAS system GRISU (GRazing incident Infrared absorption Spectroscopy Unit) was developed to investigate adsorbates on metal oxide single crystals with maximum sensitivity. GRISU combines the commercially available FTIR spectrometer Bruker Vertex 80v with a UHV chamber [1].

The compact design utilizes only one CF150 flange (6") on the UHV chamber, ensuring the precise positioning of all the optical components and the high-performance requirements.

The system features five mirrors for beam guidance placed in HV and UHV environments and optimizes the system's performance, flexibility, and usability. The result is a small controllable focal-spot diameter (max. 3 mm) on the sample, motorized optical components, and apertures that control the shape of the illumination area on the sample to reduce the background signal. A second aperture limits the incidence angle range of the infrared radiation illuminating the sample. Incidence angles between 49° and 85° are possible.

The simulated system (done with a ray-tracing program and a simplified spectrometer model) shows an efficiency of 13 %, i.e., 13 % of the radiation passing through the first aperture (∅ 6 mm) after the IR source in the FTIR spectrometer reaches the detector after being reflected from the molecular beam spot (∅ 3.5 mm) on the sample. Compared to a commercially available system with two parabolic mirrors with a focal length of 250 mm, the efficiency is about 20x higher.

The performance of the system is demonstrated by first measurements.

[1] J. Pavelec, et al., J. Chem. Phys. 146, 014701 (2017).

10:00am **SS1+AS+HC-FrM-6 Photochemical Fluorination of TiO<sub>2</sub>(110)**, Melissa Hines, W. DeBenedetti, Q. Zhu, M. Hasany, D. Somaratne, Cornell University

Fluorine has been widely reported to improve the photoreactivity of TiO<sub>2</sub> nanocrystals, but surface science studies of this enhancement have been stymied by the lack of well controlled fluorination chemistries. Fluorine-terminated rutile (110) surfaces were produced by the photochemical degradation of solution-prepared carboxylate monolayers in the presence of XeF<sub>2</sub> (g) at room temperature. The reaction initially produces a multi-nanometer-thick surface layer with a nominal composition of TiOF<sub>2</sub>. The TiOF<sub>2</sub> layer largely dissolves with immersion in room temperature H<sub>2</sub>O, leaving behind a fluorinated surface terminated by 0.8 monolayers of F bound to initially undersaturated Ti atoms. Scanning tunneling microscopy images showed that the fluorinated surface was rough on an atomic scale, displaying short, atomically straight rows parallel to the [001] direction. The fluorinated surface remained notably contamination free, even after immersion in solution and exposure to air for tens of minutes. The relatively high reactivity of the TiOF<sub>2</sub> surface layer towards etching can be rationalized in terms of disrupted charge balance in the surface layer. Consistent with this, density functional theory simulations showed that the removal of bridging O atoms from the fully fluorinated surface to produce O<sub>2</sub> would be exoergic.

10:20am **SS1+AS+HC-FrM-7 Surface Structures of La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> (001) Thin Films**, Erik Rheinfrank, M. Brunthaler, G. Franceschi, M. Schmid, U. Diebold, M. Riva, Institute of Applied Physics, TU Wien, Austria

Lanthanum-strontium manganite (La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub>, LSMO) is a perovskite oxide used as a cathode material in solid oxide fuel cells, which convert chemical energy to electrical energy. To gain deeper insights into the reaction mechanisms, it is important to understand the structure of the surface at the atomic scale. To this end, we grow atomically flat single-crystalline LSMO thin films on Nb-doped SrTiO<sub>3</sub> (STO) substrates via pulsed laser deposition (PLD). Previously, this has been achieved already for the (110) orientation [1,2]. Here, we use a similar approach on the (001) surface that is commonly used for oxide-based electronics and spintronics. The as-grown films were transferred in UHV from the PLD chamber to a

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surface science system, and characterized with scanning tunneling microscopy, x-ray photoelectron spectroscopy, and low-energy electron diffraction. We show how the LSMO surface structures change due to variation of the oxygen chemical potential upon annealing. Moreover, Ar<sup>+</sup> sputtering and subsequent annealing removes preferentially Mn over La. This can be exploited to transform a B-site (Mn) terminated surface into an A-site (La/Sr) rich surface. The B-site terminated surface is recovered by depositing Mn from an MnO target.

[1] Franceschi et al., J. Mater. Chem. A, 2020, **8**, 22947-22961

[2] Franceschi et al., Phys. Rev. Materials, 2021, **5**, L092401

10:40am **SS1+AS+HC-FrM-8 Adsorption of Organophosphate Nerve Agent VX on the (101) Surface of Anatase Titanium Dioxide**, *Gloria Bazargan*, NRC Research Associate, U.S. Naval Research Laboratory; *I. Schweigert*, *D. Gunlycke*, Chemistry Division, U.S. Naval Research Laboratory

We quantify the adsorption of the organophosphate venomous agent X (VX) on the clean and hydroxylated (101) surfaces of anatase titanium dioxide (TiO<sub>2</sub>) with density functional theory (DFT) calculations. Our results show that adsorption on the clean anatase (101) surface occurs through the VX phosphoryl oxygen (O=P) site and involves the formation of a Ti···O=P dative bond. Steric effects inhibit adsorption through the VX nitrogen and sulfur sites by the formation of Ti···N and Ti···S dative bonds. On the hydroxylated (101) surface, adsorption similarly proceeds through the VX phosphoryl oxygen site but entails the formation of surface-adsorbate hydrogen bonds. Additionally, weak non-covalent interactions between the surface hydroxyl groups and the adsorbate's nitrogen and sulfur atoms stabilize VX/(101) complexes formed by adsorption through these secondary sites.

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