Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 201A - Session HC+SS-ThM
In-situ Analysis of Heterogeneously Catalyzed Reactions

Moderator: Sharani Roy, University of Tennessee Knoxville

8:00am **HC+SS-ThM-1 Structural Characterization of ZnO on Cu(111) by using STM and XPS: Role of Cu-ZnO Interface in Methanol Synthesis***, **Mausumi Mahapatra**, J Rodriguez,* Brookhaven National Laboratory

The ZnO–copper interface plays an important role in the synthesis of methanol from the hydrogenation of (CO_2+ $4H_2$--> CH_3OH + $2H_2O$). The deposition of nanoparticles of ZnO on Cu(111), θ_{oxi} < 0.3 monolayer, create a stable and highly active interface between ZnO and Cu. The ZnO-copper catalysts may be prepared by two different methods: 1) Zn vapor deposited on Cu(111) at ~600 K in an oxygen ambient (reactive vapor deposition), 2) Zn vapor deposited on Cu(111) at 300 K following by heating the surface with oxygen to 600 K (oxidation of surface alloy). The reactivity and stability of the catalysts prepared by the above two methods were tested under CO_2 hydrogenation reaction conditions in a reactor and by using AP-XPS: 1) The ZnO-copper catalyst prepared by method 1 was stable whereas that prepared by method 2 was not stable at the elevated temperatures (500–600 K) used for the CO_2 hydrogenation. The temperature dependent growth and the structural characterization of the ZnO/Cu(111) catalyst, θ_{oxi} < 0.3 monolayer was explored by using STM. Our results show that the size and shape of the ZnO nanoparticles are dependent on the growth temperature. The ZnO/Cu(111) surface prepared by reactive vapor deposition at 450-600 K results in large ZnO triangular islands. However the surface oxidation of a Zn/Cu(111) alloy resulted in very small ZnO clusters.

8:20am **HC+SS-ThM-2 Dissociative Adsorption of CO_2 on Cu-surfaces***, **Benjamin Hagman**,* Lund University, Sweden*; A Posada-Borbón, A Schaefer,* Chalmers University of Technology, Gothenburg, Sweden*; C Zhang,* Lund University, Sweden*; M Shipilin,* Stockholm University, Sweden*; N Martin,* Chalmers University of Technology, Gothenburg, Sweden*; E Lundgren,* Lund University, Sweden*; H Grönbeck,* Chalmers University of Technology, Gothenburg, Sweden*; J Gustafson,* Lund University, Sweden

Due to the urgent problem of global warming, there is a need to reduce the release of the greenhouse gas CO_2 into the atmosphere. A potential approach to limit the CO_2 release is to convert it into useful chemical products, such as methanol [1]. However, the recycling of CO_2 is a challenging task as the molecule is rather inert, which makes it difficult to activate for reduction and subsequent hydrogeneration. The most used metal for this activation is Cu, and a fundamental understanding of how CO_2 interacts with Cu surfaces would promote the development of new catalysts for the reduction of CO_2 [2].

We have studied the CO_2 interaction with both Cu(100) and stepped Cu(911) surfaces at elevated CO_2 pressures using Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS). APXPS gives us the ability to probe the changes of the surface during the chemical reaction. In our case, we see that CO_2 chemisorbs on the surface and dissociates to O and CO, of which CO desorb, while the atomic oxygen remains on the surface.

For the Cu(100) surface, we observe that the rate of oxygen uptake from CO_2 dissociation is constant until the atomic oxygen coverage approaches 0.25 ML, where the rate decreases. After 0.25 ML the rate remains constant until a saturation appears as the oxygen coverage approaches 0.5 ML. Density Functional Theory (DFT) calculations indicate that CO_2 can adsorb and dissociate on both the terraces and steps on Cu(100), however, the dissociation is expected to take place mainly on the step as the barrier for the dissociation is lower at such sites. The atomic oxygen, from the dissociation at the step, is expected to diffuse away from the step to the terrace, leaving the number of active sites constant, and explaining the constant oxygen uptake rate. Both the experiment and DFT calculations indicate that the atomic oxygen from the dissociation of CO_2 poisons the adsorption and dissociation of CO_2 at an oxygen coverage above 0.25 ML, however, we believe that the step can remain active after 0.25 ML.

To confirm the role of the steps on Cu(100), we have also studied the interaction of CO_2 and Cu(911). We observe the CO_2 adsorption is significantly facilitated by the presence of the steps on the Cu(911) surface as compared to the flat Cu(100). The effect of the facilitated CO_2 adsorption on the subsequent dissociation will be discussed.

References:

[1] W. Wang, et al., Chem. Soc. Rev., **40** (2011), pp. 3703-3727

[2] M. D. Porosoff, et al., Energy Environ. Sci., **9** (2016), pp. 62-73.

8:40am **HC+SS-ThM-3 Infrared Spectroscopy of Carbon Dioxide Hydrogenation over the Cu(111) Surface Under Ambient Pressure Conditions***, C Kruppe, **Michael Trenary**,* University of Illinois at Chicago

Copper catalysts are used in the water gas shift reaction to convert mixtures of carbon monoxide and water to hydrogen and carbon dioxide. Conversely, the reverse water gas shift reaction utilizes carbon dioxide as a resource. Related to the reverse water gas shift reaction is the synthesis of methanol from carbon dioxide and hydrogen. The mechanisms of these reactions involve several possible surface intermediates, each of which should be identifiable by their vibrational spectra. We have used reflection absorption infrared spectroscopy (RAIRS) to study these reactions under ambient pressures in the range of 0.1 to 150 Torr. In the presence of 150 Torr of carbon dioxide, a peak is observed at 1294 cm^{-1}, which is assigned to the symmetric stretch of an adsorbed CO_2 molecule that is bent through its interaction with the surface. Upon addition of 150 Torr of $H_2(g)$ at 300 K, the 1294 cm^{-1} peak of CO_2 is greatly diminished, while new peaks appear due to gas phase water. By performing the experiment with polarized infrared radiation, the gas phase and surface species are easily distinguished. When the Cu(111) surface is annealed to higher temperatures, numerous changes occur in the spectra revealing the formation of a series of surface intermediates containing C–H bonds, including methoxy, OCH_3. The results demonstrate that CO_2 hydrogenation is readily achieved over a Cu(111) model catalyst and that surface intermediates can be easily detected with RAIRS.

9:00am **HC+SS-ThM-4 Oxide Formation on Ir(100) Studied by in-Situ Surface X-ray-Diffraction***, **Stefano Albertin**, U Hejral,* Lund University, Sweden*; R Felici,* SPIN-CNR, Italy*; R Martin,* University of Florida*; M Jankowski,* ESRF, France*; J Weaver,* University of Florida*; E Lundgren,* Lund University, Sweden

Methane (CH_4) conversion into higher added value hydrocarbons is done through a number of complex catalytic steps, and has been studied for many years [1]. The initial and often rate limiting step in the reaction is the dissociation of the molecule on the metal catalyst surface. Because alkane C–H bonds are among the least reactive known, no process for direct conversion of CH_4 into methanol (CH_3OH) has so far been developed.

IrO_2(1 10) surface grown on Ir(100) has shown facile dissociation of CH_4 at liquid nitrogen temperatures [2], as well as oxidizing H_2 to -OH [3]: two steps that could have importance for the development of a new direct methane-to-methanol catalysts.

In this contribution we will present recent results from in-situ Surface X-ray Diffraction (SXRD) recorded at beamline ID03 at the ESRF from the oxidation of a Ir(100) surface. We find that the Ir(100) surface oxidizes into a bulk oxide at a temperature of 775 K and a pressure of 5 mbar of O_2 similar to what observed in [2], forming a predominantly rutile IrO_2(110) oriented surface. Our study also demonstrates that lowering the partial O_2 pressure or the temperature results in the formation of a number of different Ir sub-oxides similar to the ones found for Ir(111) [4], and the structures formed will be discussed in this contribution.

[1] D. M. Bibby, C.D. Chang, R.F. Howe and S. Yurchak, Eds. *Methane Conversion, Vol. 36 of Studies in Surface*

Science and Catalysis (Elsevier, Amsterdam, 1988).

[2] Z. Liang, T. Li, M. Kim, A. Asthagiri, and J. F. Weaver, Science **356** (2017) 299.

[3] Li, T., Kim, M., Liang, Z. et al. Top Catal (2018) 61: 397

[4] Y. B. He, A. Stierle, W. X. Li, A. Farkas,N. Kasper, and H. Over, J. Phys. Chem. C **112** (2008) 11946.

9:20am **HC+SS-ThM-5 Dynamic Nanocatalysts: Environmental Effects***, **Beatriz Roldan Cuenya**,* Fritz-Haber Institute of the Max Planck Society, Germany **INVITED**

In order to comprehend the catalytic performance of metal nanostructures, their dynamic nature and response to the environment must be taken into consideration. The working state of a nanocatalyst might not be the state in which the catalyst was prepared, but a structural and/or chemical isomer that adapted to the particular reaction conditions. Furthermore, deactivation phenomena taking place under reaction conditions can only be understood, and ultimately prevented, if sufficient information is available on the catalyst morphology, structure, chemical state, and surface composition while at work.

I will first describe novel approaches for the synthesis of size- and shape-controlled nanoparticles and nanostructured metallic films (e.g. Au, Cu, Ag, Zn, CuZn, CuCo, CuNi, AgSn, NiGa) and their functionalization/activation based on plasma treatments. Subsequently, I will illustrate how to follow the evolution of their morphology and surface composition under different gaseous and liquid chemical environments in the course of a catalytic reaction. This will be implemented using a synergistic combination of *in situ* and *operando* microscopy (EC-AFM, STM, TEM) and spectroscopy (XAFS, AP-XPS) methods. It will be highlighted that for structure-sensitive reactions, catalytic activity, selectivity, and stability can be tuned through controlled synthesis. Examples of catalytic processes which will be discussed include the gas- and liquid-phase oxidation of 2-propanol and the gas-phase hydrogenation and electrochemical reduction of CO_2. Emphasis will be given to elucidating the role of the size, shape, composition, chemical state, surface defects and roughness of the catalysts in the activity and selectivity of the former reactions.

11:00am **HC+SS-ThM-10 Atomic Layer Deposition (ALD) Synthesis of Au/TiO₂/SBA-15 Catalysts***, W Ke, X Qin,* ***Francisco Zaera,*** University of California, Riverside

Au/Titania catalysts have received much attention in recent years because of their ability to promote photocatalytic water splitting as well as selective low-temperature oxidation reactions. The uniqueness of these catalysts is ascribed to both the nanometer-size of the gold nanoparticles and the reducibility of the titania support. Here we report results from studies on the use of ALD to control the titania film thickness, to tune its degree of reducibility and explore the role of that reducibility in catalysis. SBA-15, a mesoporous solid with well-defined pore structure, was used as the base material in order to be better able to characterize the deposited titania films. Surface reducibility was tested as a function of film thickness by CO infrared-absorption spectroscopy titrations and by EPR, and the catalytic performance via kinetic measurements for CO oxidation. Unique trends were observed at intermediate (2-4 ALD cycles) film thicknesses.

11:20am **HC+SS-ThM-11 Enhanced Stability of Pt/Cu Single-Atom Alloy Catalysts: In Situ Characterization of the Pt/Cu(111) Surface in an Ambient Pressure of CO***,* ***Juan Pablo Simonovis Santamaria,*** Brookhaven National Laboratory

Research in catalysis has steered towards the design and synthesis of more efficient catalysts that can yield better quality products at lower costs. In this regard, bimetallic alloys where the active metal is mono-atomically dispersed have shown unique activity, selectivity and stability compared to their monometallic counterparts. These so called single atom alloys (SAA) are of interest since small amounts of active metals can be used reducing catalysts cost. However, the chemical interactions between active site and reacting molecules are still poorly understood, thus careful characterization of these moieties under reaction conditions is needed to elucidate fundamental reaction steps that can clarify the role of the active site during the catalytic process.

In this study, we used ambient pressure X-ray photoelectron spectroscopy (AP-XPS) performed at the 23-ID-2 (IOS) beamline at the National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory to compare the stability of Pt/Cu(111) SAA in ultrahigh vacuum (UHV) and ambient pressure conditions, particularly how its surface structure and composition can be influenced by the presence of a reactant gas such as CO. Because of the surface and chemical sensitivities of AP-XPS, we can directly probe the Pt atoms to clearly identify surface/subsurface layers of the metal and monitor its evolution under different experimental conditions.

Our study showed that the Pt (0.05 ML)/ Cu(111) SAA is thermally unstable above 400 K under UHV conditions, since higher temperatures cause Pt on the surface to migrate to the subsurface and, eventually, to the bulk. This metal diffusion into the subsurface could lead to the deactivation of a potential catalyst. However, under ambient pressures of CO, the surface and subsurface Pt are thermally stable up to 500 K, resisting diffusion into the bulk. In fact, thermal treatment in CO of a sample that was previously heated under UHV conditions lead to the recovery of Pt that had diffused to the subsurface, suggesting that, within 300-500 K the diffusion process is reversible to some extent. However, this thermal stability as well as surface recovery in CO comes at the expense of slightly enhanced CO−Pt interactions likely caused by the presence of neighboring subsurface Pt resulting from the thermal-induced restructuring of the subsurface layer. Whether the post-heated surface still resists the poisoning effects of CO remains to be seen, but these results demonstrate the importance of studying not only the changes in the surface of a catalyst under reaction conditions but also the near-surface region, which may also influence the reactivity of the catalyst.

11:40am **HC+SS-ThM-12 Multiscale Modelling of Metal Oxide Interfaces and Nanoparticles***,* ***Kersti Hermansson****, P Mitev, J Kullgren, P Broqvist,* Dept of Chemistry-Ångström, Uppsala University, Sweden **INVITED**

Redox-active metal oxide surfaces and interfaces – such as electrodes, catalysts, and sensors – play crucial roles in our society and in the development of new materials and greener technologies. In the scientific literature, a full arsenal of experimental methods are being used to help characterize such interfaces. At the same time, the number of theoretical studies in the literature steadily increases, providing mechanistic information at a detail that is hard to beat by experiment. *Are such theoretical results accurate enough*?

I will describe some of our efforts to develop multiscale modelling protocols for metal oxide surfaces and nanoparticles (e.g. of CeO_2, ZnO and MgO). We combine a range of theoretical methods including ***DFT, tight-binding-DFT*** [1]***, and reactive force-field models*** A key question is whether it is really possible to model redox-active metal oxides *without including the electrons*?

The O_2 chemistry of reducible oxides is rich and famous and I will therefore also discuss various aspects of how adsorbed oxygen on nanoparticles and clusters can stabilize in the form ***superoxide ions*** (O_2^-) and the implications that this may have on their reactivities. Microkinetic modelling results to mimic experimental TPD spectra will be presented as well as mechanistic detail that is currently only possible to obtain from modelling.

The H_2O molecule deserves special attention as ***hydroxylation/hydration*** changes the properties and reactivities of metal oxides, often with far-reaching consequences. We recently studied a thick water film on a ZnO(10-10) surface using MD simulations from a neural-network-generated potential landscape of DFT quality combined with anharmonic vibrational frequency calculations.[2] and were able to relate H-bond structure and frequencies in a meaningful way. In an attempt to reach a step further in terms of understanding found that a ***parabola-like*** **'*****OH frequency vs. in-situ electric field*****'** ***relation*** holds for both intact and dissociated water molecules on ionic surfaces [3], and for both thin and thick films (unpublished).

I will also inform about the European Materials Modelling Council (https://emmc.info/), which aims to promote the use of materials modelling in –not least– industry.

References:

[1] J. Kullgren et al., *J. Phys. Chem. C* 121, 4593−4607 (**2017**).

[2] V.Quaranta et al., *J. Chem. Phys*. 148, 241720 (**2018**).

[3] G. G. Kebede et al., *Phys.Chem.Chem.Phys.* 20, 12678 (**2018**)

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