

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 24 - Session HC+SS-ThA

Combined Experimental and Theoretical Explorations of the Dynamics of Heterogeneously Catalyzed Reactions

Moderator: L. Gabriela Avila-Bront, College of the Holy Cross

2:20pm **HC+SS-ThA-1 Building the World's Greatest Microscope: Revealing the Atomic Scale Dynamics of Surface Chemistry**, *A Wodtke*, Max Planck Institute for Biophysical Chemistry, Germany; *O Buenermann*, *H Jiang*, *Y Dorenkamp*, Institute for Physical Chemistry University of Goettingen, Germany; *A Kandratsenka*, *S Janke*, **Daniel Auerbach**, Max Planck Institute for Biophysical Chemistry, Germany **INVITED**

In 1929, Nobel Laureate Paul Dirac made comments to the effect that Chemistry had been solved. With the advent of quantum mechanics "The underlying physical laws necessary for the mathematical theory of... ..the whole of chemistry are... ..completely known.... However, on a practical level computational chemistry is still in an early stage of development. Dirac went on: "the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble." Despite electrifying advances in computational power since that time, Dirac is still right. The theory of chemistry requires approximations before theoretical descriptions and predictions of chemical reactions can be made.

The advent of the Born-Oppenheimer Approximation led to the development of the standard model of chemical reactivity where the electronically adiabatic potential energy surface for nuclear motion is derived and quantum motion of the nuclei on that surface can be calculated. For simple gas phase reactions, this approach has become an extraordinarily useful and reliable tool. For surface chemistry, additional approximations are commonly made: 1) classical mechanics for describing nuclear motion, 2) density functional theory (usually at the generalized gradient level) for calculating electronic states, 3) reduced dimensionality approximations and as before 4) the Born-Oppenheimer approximation to separate electronic and nuclear degrees of freedom. I call this collection of approximations the provisional model for surface chemistry as we in the field are still testing and improving it.

In this talk, I will describe how a fruitful interplay between experiment and theory can lead to accurate atomic-scale simulations of simple reactions at metal surfaces. I will describe the very significant challenges surface chemistry presents including the problems of high dimensionality and the common failure of the Born Oppenheimer approximation. I will present two concrete examples. In the first, results of a full dimensional experimentally validated theoretical approach to hydrogen atom adsorption at a metal surface that includes the effects of Born-Oppenheimer failure leads to an atomic scale view of H-atom adsorption at a noble metal as well as an explanation for chemicurrents. In the second, energy loss dynamics occurring on a 25-fs time scale can be inferred from the scattering of hydrogen atoms from a graphene surface where a transient C-H chemical bond is formed. The H interaction on graphene is strongly influenced by the choice of metal substrate upon which the graphene is grown.

3:00pm **HC+SS-ThA-3 Calibrating Electronic Structure Calculations – A Joint Experimental-Theoretical Approach**, *Arthur Utz*, *E Dombrowski*, *E High*, Tufts University

Computational chemistry holds great promise for guiding the design of new catalytic materials, but current density functional theory (DFT) methods typically do not provide the level of absolute chemical accuracy ($\Delta E \leq 1$ kcal \approx 4 kJ/mol) required to distinguish between potential catalysts with similar activation energies, nor can they accurately predict product selectivity when the rate-limiting barriers to different reaction products are similar. Two factors are primary contributors to this shortcoming. First, the most widely used DFT functionals for reactions on metals (PBE and RPBE) are not quantitatively accurate, and are prone to systematic errors that either over- or underestimate barrier heights. Second, few experimental measurements provide accurate and unambiguous benchmarks for testing DFT predictions.

In this contribution, we will describe recent results from a joint experimental-computational study to address these limitations. We performed conventional and internal state-resolved beam-surface reactivity measurements for tri-deutero methane (CHD₃) molecules

incident on a clean Ni(111) surface to obtain robust benchmark data for comparison with theory. Our collaborators in the Kroes group at Leiden University then used these data to "calibrate" a hybrid functional based on a linear combination of PBE and RPBE functionals via the specific reaction parameter density functional theory (SRP-DFT) approach. *Ab initio* molecular dynamics (MD) calculations using the SRP-DFT functional yielded predictions of initial reaction probability, S_0 as a function of incident translational energy, E_{trans} , for comparison with experiment.

We used measurements of S_0 for CHD₃ molecules predominantly in their vibrational ground state ($v=0$) and incident at the lowest incident translational energy (E_{trans}) studied to constrain the define the SRP-DFT functional. We then used that functional, without further modification, to predict the reactivity of a thermal ensemble of CHD₃ molecules whose reactivity was dominated by C-D stretching and bending vibrations, as well as of the laser excited C-H stretching states, over a wide range of E_{trans} . We found that despite the significant difference in energy distribution within these three ensembles of molecules, the single SRP-DFT functional yielded chemically accurate predictions of reactivity. The presentation will outline our approach and results on this system, as well as more recent work exploring the generality of this approach to other chemical systems and surface structures.

3:20pm **HC+SS-ThA-4 CO₂, CO and H₂O on Copper Surfaces: A HPXPS Study Supported by DFT Calculations**, *A Regoutz*, *G Kerherve*, *J Kahk*, *J Lischner*, *David Payne*, Imperial College London, UK

CO₂ is a source for the production of carbon based fuels, including methanol, and presents an attractive alternative to fossil fuels. Copper is an ideal catalyst for the reduction of CO₂, as it is able to direct reactions through stable intermediates, e.g. CO. For example important questions concern the influence of oxygen on the catalytic activity and whether oxides are formed on the surface, and the role of H₂O and CO (as co-adsorbents) during exposure to CO₂. As copper-based systems are an excellent material for the reduction of CO₂ a detailed understanding of the basis of its catalytic activity is essential and absolutely necessary for any further development.

X-ray photoelectron spectroscopy (XPS) is used widely in solid-state science but due to its nature as an ultra high vacuum technique (pressure 10⁻¹⁰ mbar) it is not possible to study more realistic gas-solid interfaces. High-pressure XPS (HPXPS) is an advanced method which allows the measurement of solid samples at elevated pressures of between 1 and 30 mbar [1]. Over the last few years, this technique has been applied to understanding the chemistry of CO₂ (and mixtures of gases) on copper surfaces [2-4] leading to a number of surface mechanisms being postulated.

This work presents results on the interaction of CO₂ with a variety of Cu surfaces (polycrystalline and single-crystals) by HPXPS. In contrast to previously published work, these experiments are supported by state-of-the-art density functional theory calculations, in an effort to enable accurate determinations of the binding energies of the various surface-bound species present during reaction.

It is hoped that the presented results provide a starting point for the detailed understanding of these copper surfaces, using HPXPS in conjunction with theory, and lead to the identification unknown phenomena.

[1] G. Kerherve, D.J. Payne et al., Rev. Sci. Instrum., **88** 033102 (2017)

[2] T. Koitaya et al. Topics in Catalysis, **59** 526 (2016)

[3] B. Eren et al. J. Am. Chem. Soc., **138**, 8207 (2016)

[4] X. Deng et al., Langmuir, **24**, 9474 (2008)

4:00pm **HC+SS-ThA-6 Dissociative Adsorption of Methane on Transition Metal Surfaces and Supported Atoms from First Principles Calculations**, *Heriberto Fabio Busnengo*, CONICET and Universidad Nacional de Rosario, Argentina **INVITED**

The study of dissociative adsorption of methane on transition-metal surfaces and transition-metal atoms deposited on oxide surfaces is of great importance to understand the reaction mechanisms governing the catalytic steam reforming process used to produce molecular hydrogen. In particular, the understanding of the origin of the role of surface temperature, surface defects involving reduced coordination metal atoms, and possible effects of the oxide support have significantly increased during the last years thanks to both, experiments and first principles calculations.

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In this talk we will describe and discuss some of these recent advances by focusing on theoretical developments allowing us today, to model with unprecedented accuracy the interaction of methane with transition metal atoms under ultra high vacuum conditions and in particular, molecular beam experiments. This has been possible in part, thanks to the increase of processing power of modern computers, to methodological developments allowing to describe quantum mechanically the molecule-surface interaction dynamics, and new methods to accurately represent full dimensional interaction potentials from first principles calculations.

4:40pm **HC+SS-ThA-8 Methane Steam Reforming: Using External Electric Fields to Enhance the Catalytic Performance of Ni-based Catalysts, Fanglin Che**, University of Toronto, Canada; *J Gray, S Ha, J McEwen*, Washington State University

According to the Annual Energy Outlook, natural gas production in the U.S. is projected to continue rising through 2040. To make the most of this abundant natural resource and at the same time reduce emissions of harmful greenhouse gases it is imperative that we fully understand the catalytic reactions which are used in methane processing – particularly methane steam reforming (MSR). MSR is our reaction of interest also because the conversion of methane to syngas greatly affects the charge-transfer chemistry and consequently influences the SOFCs' performance. There are two significant issues facing MSR: (i) Coke formation; (ii) High temperatures of above 900 K. To address these issues, we are interested in the effect of an electric field on this process. [1,2]

Based on a field-dependent microkinetic model of the MSR reaction and corresponding experimental evidence, we find that a positive electric field can significantly enhance the methane conversion and reduce the formation of coke over a pure Ni surface. [3-8] The reason for such an improvement can be correlated with the fact that a positive field polarizes the Ni surface with a partial positive charge, which assists the first C-H bond cleavage of a methane molecule. [9] Changing the oxygen vacancy concentration and increasing the applied electric field value affects the charge of the Ni cluster in a Ni/YSZ cermet as well. Interestingly, we find that the C-H bond cleavage of methane becomes more favorable as the Ni cluster becomes more positively charged. We also find that the carbon complex resulting from the dissociation of a CH molecule at the triple phase boundary region of a Ni/YSZ cermet results in a more positively charged Ni cluster, which facilitates the cleavage of the first C-H bond in methane as compared to when the carbon complex is absent. This indicates that the initial carbon species resulting from the decomposition of methane assists in the first C-H bond cleavage of a methane molecule rather than the formation of coke that poisons the Ni-based catalyst. Overall, this work provides valuable information for a new design of electrochemical systems to enhance methane activation.

[1] Stüve, E. M. *Chem. Phys. Lett.* **2012**, *519*, 1.

[2] Kreuzer, H. J. *Surf. Sci. Anal.* **2004**, *36*, 372.

[3] Che, F. et al., *Catal. Sci. Technol.* **2014**, *4020*.

[4] Che, F. et al., *Phys. Chem. Chem. Phys.* **2014**, *16*, 2399.

[5] Che, F. et al., *J. Catal.* **2015**, *332*, 187.

[6] Che, F. et al., *Appl. Catal. B* **2016**, *195*, 77.

[7] Che, F. et al., *ACS Catal.* **2017**, *7*, 551.

[8] Che, F. et al., *ACS Catal.* **2017**, *under review*.

[9] Che, F. et al., *Angew. Chem. Int. Ed.* **2017**, *129*, 3611.

5:00pm **HC+SS-ThA-9 Mullite Support Boosts Active Oxygen Atoms for Enhanced Platinum Sub-nanometer Clusters Catalysis, Xiao Liu, J Cai, B Shan, R Chen**, Huazhong University of Science and Technology, China

Platinum (Pt) catalysts have been widely utilized in catalysis due to their excellent catalytic activity, such as CO oxidation, water-shift gas reaction and preferential CO oxidation in hydrogen. As the high cost and large demand of Pt, the improvement of its catalytic efficiency has attracted great attention to reduce its loading. Since catalytic reactions usually happen on surface, the decreasing of Pt catalyst's size to increase the fraction of exposed atoms is a widely accepted strategy to try to utilize each Pt atom. However, the low temperature activities of the Pt sub-nanometer clusters and single atoms have been greatly limited due to the seriously CO poison effect, which prevents the supplying of active oxygen. Therefore, searching new approaches to supply active oxygen atoms at low temperature is important to enhance the activity and efficiency of Pt catalysts. In this work, the density functional theory (DFT) calculations shows that the designed Pt cluster supported on SmMn₂O₅ mullite structure exhibits high activity for O₂ dissociation than pure SmMn₂O₅

surface. Inspired by the theoretical results, we have prepared uniform and high dispersed sub-nanometer Pt clusters on SmMn₂O₅ supports (Pt_n/SmMn₂O₅) via atomic layer deposition method. The interfacial structure of Pt_n/SmMn₂O₅ characterized by high-resolution transmission electron microscopy agrees well with our designed model. The as-prepared Pt_n/SmMn₂O₅ catalyst has shown outstanding room temperature CO oxidation activity and low apparent activation energy, which could result from the strong interfacial interactions as indicated by the X-ray photoelectron spectra and X-ray absorption fine structure results. The *in-situ* diffuse reflectance infrared Fourier transform spectroscopy, ¹⁸O isotope-labelling experiments and DFT calculations shows that the active oxygen supplied by the SmMn₂O₅ surface is critical to the room temperature CO oxidation activity.

5:20pm **HC+SS-ThA-10 Calorimetric Energies of Small Adsorbates on Ni(111) and NiO(111) Surfaces, with Comparison to Pt(111) to Explain Differences in Catalytic Activity between Ni vs Pt, Wei Zhao, S Carey, Z Mao, S Morgan, C Campbell**, University of Washington

Catalysts based on nickel and nickel oxides are of great importance in chemical industry, such as methane steam reforming and biomass conversions. We present here calorimetric measurements of the energies of several catalytically relevant adsorbed intermediates on Ni(111), including methyl, bidentate formate, H₂O, benzene and phenol, and also the enthalpies of H₂O and HCOOH dissociative adsorption on NiO(111). We will also give an extensive comparison of these energies on Ni(111) to previous calorimetric measurements on Pt(111), providing the insight into the catalytic properties and reaction efficiency for these two metals. Besides the crucial importance of these measured energies for understanding related catalytic relations, they also provide important experimental benchmarks that can be used to improve the accuracy of the related quantum mechanical calculations.

5:40pm **HC+SS-ThA-11 Defect Formation on MoS₂ via Methanol to Methoxy Conversion, Prescott Evans, H Jeong, S Beniwal, P Dowben**, University of Nebraska - Lincoln; *D Le, T Rahman*, University of Central Florida

Coverage dependent defect formation, via methanol adsorption on MoS₂ and conversion into methoxy, was investigated utilizing scanning tunneling microscopy, photoemission and modeled by density functional theory (DFT). The adsorption of methanol on MoS₂ at 110 K followed by annealing of the sample near 350 K or the adsorption of methanol on MoS₂ at 350 K results in the formation of numerous point defects at the surface of the MoS₂ substrate. Larger multi-point defects, nominally ~1 nm in size as well as line defects on the MoS₂ sample surface become increasingly apparent with multiple cycles of methanol exposure and annealing. X-ray spectroscopy studies of the exposure of MoS₂ to methanol are consistent with a conversion to methoxy, and the production of defects, based on the reaction kinematics, and the significant shifts in oxygen binding energies. The experimental results indicate a small but persistent activation energy for the reaction. The energy favorability of the combination of defect creation and methoxy formation is also suggested by density functional theory. A strongly bound methanol surface species is not favored on the defect free MoS₂ surface.

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