Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room B113 - Session HC+SS-ThM

Dynamics and Mechanisms in Heterogeneously Catalyzed Reactions

Moderators: Arthur Utz, Tufts University, **Jason Weaver**, University of Florida

8:00am **HC+SS-ThM-1 Dehydration and Dehydrogenation of Formate on Fe_3O_{-4-}(001)**, ***Marcus Sharp,*** Pacific Northwest National Laboratory / Washington State University*; C. Lee, S. Smith, B. Kay, Z. Dohnálek,* Pacific Northwest National Laboratory

Interest in improving the activity and selectivity of catalysts has been persistent due to their importance in numerous chemical industries. Yet the mechanistic understanding of the active site structure, coordination environment, and stability is often lacking. Using a combination of temperature programmed reaction spectroscopy (TPRS), molecular beam scattering (MBS), and X-ray photoelectron spectroscopy (XPS) we investigate the reactivity of formic acid on the Fe_3O_4(001) that serves as a model reducible oxide support for single-atom catalysts. XPS shows that formic acid deprotonates at low temperature (~80 K), forming a formate intermediate and a protonated lattice oxygen (hydroxyl). At higher temperatures (400–600 K), the formate undergoes dehydration to CO and H_2O via two desorption channels, while dehydrogenation to CO_2 is a minor channel. Angle-resolved TPRS and MBS experiments show that CO leaves the surface with excess kinetic energy closely focused along the surface normal. Surprisingly, not all formate species can react through the low-temperature channel. XPS, however, does not indicate a change in surface species throughout reaction temperatures. The addition of isotopically labeled formic acid (DCOOD) after the depletion of the low-temperature reaction channel show a complete mixing of all surface formate species. Similarly, the addition of atomic hydrogen after the depletion of the low-temperature reaction shows that surface hydroxyls are important in guiding the decomposition reaction to various reaction channels. Fe deposition on top of Fe_3O_4(001) reveals that Fe based-structures also act as the active sites for the high-temperature desorption of CO. This study illustrates the complexity of reaction intermediates at catalyst surfaces where changes in surface morphology can lead to differences in product selectivity and activity.

8:20am **HC+SS-ThM-2 The Effect of No and Co on the Rh(100) Surface at Atmospheric Pressure***, D. Boden, J. Meyer,* ***Irene Groot,*** Leiden University, Netherlands

Rhodium is used in automotive catalysis to reduce NO and CO emissions in the exhaust by catalyzing the reduction of NO to $N_2$and the oxidation of CO to CO_2. This means the rhodium nanoparticles in the catalyst are exposed to high pressures of NO and CO, both known to be highly corrosive gases, which leads to disintegration and sintering of the rhodium catalyst. It is important to understand the effect high pressures of NO and CO have on the rhodium surface at the nano scale, in order to design strategies to impede catalyst deactivation. Here, one of the most active rhodium facets, Rh(100), is studied at atmospheric pressures of NO and CO with scanning tunnelling microscopy (STM), in order to observe the roughening of the surface in situ. Additionally, atomistic thermodynamics, based on density functional theory (DFT) calculations, is used in combination with ex situ ultrahigh vacuum techniques (low-energy electron diffraction and Auger electron spectroscopy) to understand the behavior of adsorbates on the surface during the STM experiments, at the atomic scale. The formation of rhodium islands on the (100) terraces is observed at high CO pressures, in conjunction with roughening of the step edges. Interestingly, roughening does not occur at the same pressures of NO. The surface roughening is also less severe when co-dosing NO and CO, even at identical CO partial pressures. The results from atomistic thermodynamics show that NO likely inhibits CO adsorption by blocking the CO adsorption sites, thereby preventing carbonyl formation and decreasing surface roughening.

8:40am **HC+SS-ThM-3 Sustainable Production of Aromatics via Methane Dehydroaromatization: Role of Dynamic Carbon Accumulation***, M. Hossain,* Virginia Tech*; M. Rahman,* Southwest Research Institute, San Antonio Texas*; D. Maiti, E. Sobchinsky, M. Kunz, R. Fushimi,* Idaho National Laboratory*;* ***Sheima Khatib,*** Virginia Tech **INVITED**

Natural gas, mainly composed of methane, constitutes an available and cheap resource that can be used as a building block to produce chemicals. Methane dehydroaromatization (MDA) is a reaction capable of directly converting methane to value-added aromatics, without an intermediate syngas step. The reaction happens in non-oxidative conditions, producing mainly benzene and hydrogen, 6 CH4(g) → C6H6(g) + 9H2(g). Zeolite-supported Mo catalysts have so far been the most widely studied catalysts in MDA, but they do not fulfill the conversion and stability requirements for commercialization. During the reaction induction period, Mo oxide species gradually reduce to Mo carbides, which are responsible for methane activation and subsequent conversion to aromatics. We have developed a strategy to improve benzene yield and catalyst stability by controlling the activation of the Mo species to optimize their reduction and dispersion before exposure to reaction conditions. Our results indicate that when activation of catalysts is performed by reduction in pure hydrogen under temperature-controlled conditions, the carbides formed (ex situ) lead to more selective catalysts that deactivate more slowly compared to carbides formed during reaction (in situ). To explain this difference, we studied the dynamic carbon accumulation kinetics on varying redox states of MoOx/HZSM-5 catalyst via strategic molecular probe experiments in the Temporal Analysis of Products (TAP) reactor. Incremental pulse-by-pulse TAP investigation helps to distinguish different surface reactions and paves the way for elucidating the role of catalyst state towards preferential soft coke formation, as opposed to hard coke that results in catalyst deactivation. These intrinsic kinetic fingerprints of the catalyst will provide guidance towards better MDA reaction protocols for sustained high aromatics production from waste greenhouse gas, methane.

9:20am **HC+SS-ThM-5 Mechanistic Understanding of Methanol Synthesis on an In_2O_3 Catalyst***,* ***Yong Yang,*** ShanghaiTech University, China

Indium oxide (In_2O_3) became a very promising catalyst in recent years for its high selectivity of CO_2 hydrogenation to methanol, an ideal fuel for green energy. The reaction normally requires elevated temperature from 220 to 330°C and relative high pressure around 50 bar. Deep mechanistic insight with experimental evidence is still in demand for effective development in catalyst rational design. The widely applied direct kinetics investigation by *in situ* IR of this reaction is difficult due the formation of In_2O_3blackunder H_2reduction condition.

Here based on a recent optimized c-In_2O_3 catalyst, we investigate methanol synthesis reactivity correlated spectroscopic and kinetics properties at up to 16 bar and 270°C by online MS isotope kinetics measurements, *in situ* time resolved FT-IR and XPS (ThermoFishier ESCALab250Xi), in both in steady-states and transients. In all kinetics experiments reported here, the input total flow rate is controlled around 15 sccm with H_2/D_2:CO_2:Ar ratio at 10.5 sccm:3.5 sccm:1.4 sccm and the resulted gas hour space velocity is around 17 L/g/Hr.

Both steady-states and transients isotope input results clearly indicate a normal kinetic isotope effect (KIE). In addition pressure dependence study indicates that the reaction rate is nearly proportional to the input pressure and Arrhenius plot yield activation energies with both inputs remain almost constant at different pressures, with a higher activation energy (E_a) for D_2/CO_2 than H_2/CO_2 (120 vs. 100 kJ/mol). The KIE and pressure dependence behaviors are essentially different from Cu based catalyst in the same reaction, although E_a values are close. Auniversal reaction rate equation with parameters of pressure and temperature is thus provided. Based on results from two series of isotope switching transients experiments from D_2/CO_2 to H_2/CO_2, quantitative transient products analysis of exchanged D/H isotopic species reveals that there are up to 2.5 monolayers of dissociated deuterium involves in the D isotopomer methanol products. This indicates that the active surface is highly reduced with a high efficiency of surface hydrogenation to methanol. The surface species characterization by *in situ* FT-IR and XPS investigate sample *in situ* prepared as pre-oxidized, pre-reduced and further exposed with water vapor or CO_2. The combined results provide key evidence for main XPS features assignments.

These results helps elucidating the kinetics and spectroscopic fundamentals in this reaction and hopefully will provide useful information toward the rational design of active and stable catalysts based on In_2O_3 for CO_2 hydrogenation to methanol.

9:40am **HC+SS-ThM-6 The Strong Metal-Support Interaction Under Reactive Conditions and Its Influence on the Hydrogen Evolution Reaction Over Pt/TiO$_2$(110)***, **Philip Petzoldt**,* Technical University of Munich, Germany*; M. Eder,* TU Wien, Austria*; M. Blum,* Lawrence Berkeley National Laboratory (LBNL)*; T. Kratky,* Technical University of Munich, Germany*; S. Günther,* Technical University Munich, Germany*; M. Tschurl, B. Lechner, U. Heiz,* Technical University of Munich, Germany

Covering reactive nanoparticles with thin metal oxide films is a promising strategy to improve their stability and catalytic selectivity. Reductive heating of noble metal particles supported on reducible oxides initiates their encapsulation due to the strong metal-support interaction (SMSI). This phenomenon has been studied under well-defined UHV conditions on single crystals and on more applied, structurally inhomogeneous catalysts. However, only few studies provide insight at the atomic scale under reactive conditions which is crucial for the systematic optimization of catalytic systems.

In this contribution, we investigate the dynamic behavior of the SMSI state on Pt-loaded TiO$_2$(110) under reactive conditions and its influence on the catalyst's activity in the photocatalytic hydrogen evolution reaction. Employing near ambient pressure XPS, we show that the SMSI kinetics may be tuned by choosing the oxygen pressure. Monitoring the hydrogen evolution reaction by mass spectrometry, we further demonstrate that the impact of the noble metal encapsulation on the catalyst's chemistry depends on the complex interplay of reaction conditions and catalyst preparation.

Our results provide new mechanistic insights into the interaction of noble metal particles with the support and may foster the development of catalysts with improved stability and selectivity.

11:00am **HC+SS-ThM-10 Rotational Orientation Effects in Hydrogen-Surface Scattering***, **Helen Chadwick**, Y. Alkoby, G. Alexandrowicz,* Swansea University, UK **INVITED**

The interaction of hydrogen with surfaces plays an important role in many heterogeneously catalysed reactions, for example converting ortho-hydrogen to para-hydrogen for the safe storage of liquid H-$_2$ fuel, in the Haber Process for making ammonia and in the Fischer-Tropsch synthesis for making longer chain hydrocarbons. Carefully controlled, quantum state resolved experiments play a pivotal role in providing benchmarks which can be used to help develop accurate, predictive theoretical models of these important interactions. The influence of the rotational orientation projection quantum state of the molecule (m_J), which can be considered classically to describe whether the hydrogen is rotating like a helicopter or cartwheel when it collides with the surface, has been less well characterised due to the challenges associated with preparing these quantum states, particularly in closed shell, ground state molecules. Here I will present a unique magnetic manipulation interferometry technique [1] that allows us to control and manipulate the rotational orientation and nuclear spin projection (m-$_I$) quantum states of small molecules both before and after they collide with a surface. Using the elastic scattering of H_2 from LiF as an example [2], I will demonstrate that we can extract empirical scattering matrices from the data which can be compared directly to those from theoretical calculations. I will also show new results for H_2 scattering from the stepped Cu(511) surface, where signals for several different diffraction channels have been measured which exhibit different dependencies on the rotational orientation states, as well as observations which suggest that H_2 can dissociate when it collides with the surface. All of these results combined, provide very stringent experimental benchmarks which will help develop accurate theoretical models.

Acknowledgments: This work was supported by the Horizon 2020 Research and Innovation Programme Grant Number 772228 and an EPSRC New Horizons Grant Number EP/V048589/1.

References

[1] O. Godsi et al., Nat. Comm. 8, 15357 (2017).

[2] Y. Alkoby et al., Nat. Comm. 11, 3110 (2020).

11:40am **HC+SS-ThM-12 Studies of Pt-Sn Catalysts for Methylcylcohexane Dehydrogenation to Toluene***, **Donna Chen**,* University Of South Carolina*; M. Qiao, A. Ahsen, A. Heyden, J. Monnier,* University of South Carolina

The use of H_2 as an energy carrier has emerged as an attractive alternative to fossil fuels, but a major challenge for the H_2-based economy lies in the efficiency of storage and transportation. The use of liquid organic hydrogen carriers (LOHC) would allow for the reversible storage of H_2 through hydrogenation-dehydrogenation reactions. The toluene-methylcyclohexane (MCH) pair is ideal for this purpose because MCH has a relatively high gravimetric storage density, and both compounds are widely available, low-toxicity liquids at ambient temperature. While catalytic hydrogenation of LOHCs is exothermic and facile, a major problem with using LOHCs for hydrogen storage is that catalytic dehydrogenation is endothermic and not always reversible due to side reactions. Pt catalysts are active for dehydrogenation of MCH to toluene, but undesirable C-C bond breaking reactions also lead to coking and deactivation. In this work, model Pt-Sn bimetallic surfaces are studied for MCH dehydrogenation in order to understand the role of Sn in preventing the deactivation of Pt surfaces. Pt-Sn alloy surfaces were prepared by depositing Sn on Pt(111) and annealing to various temperatures to form ordered overlayers, which were characterized by low energy electron diffraction, scanning tunneling microscopy (STM), and X-ray photoelectron spectroscopy (XPS) in an ultrahigh vacuum (UHV) chamber. The model surfaces were then transferred into a flow reactor coupled directly to the UHV chamber for kinetic studies under realistic pressure conditions; after MCH reaction, the surfaces were transferred back to the UHV chamber for characterization by XPS and STM. The activity of the model single-crystal surfaces are also compared with the conventional catalysts consisting of supported Pt-Sn particles. Computational work will help identify the role of the various active sites and determine reaction mechanisms, as well as the rate and selectivity controlling steps at the active sites.

12:00pm **HC+SS-ThM-13 Platinum@Hexaniobate Nanopeapods: A Directed Photocatalytic Architecture for Dye-Sensitized Semiconductor H$_2$ Production Under Visible Light Irradiation***, **Clare Davis-Wheeler Chin**,* Sandia National Laboratories, USA*; P. Fontenot,* Tulane University*; T. Rostamzadeh,* University of New Orleans*; L. Treadwell,* Sandia National Laboratories, USA*; R. Schmehl,* Tulane University*; J. Wiley,* University of New Orleans

Platinum@hexaniobate nanopeapods (Pt@HNB NPPs) are a nanocomposite heterogeneous photocatalyst that was selectively engineered to increase the efficiency of hydrogen production from visible light photolysis.Pt@HNB NPPs consist of linear arrays of high surface area Pt nanocubes encapsulated within scrolled sheets of the semiconductor $H_xK_{4-x}Nb_6O_{17}$, and were synthesized in high yield via facile one-pot microwave heating method that is fast, reproducible, and more easily scalable than multi-step approaches required by many other state-of-the-art catalysts.The Pt@HNB NPPs unique 3D architecture enables physical separation of the Pt catalysts from competing surface reactions, promoting electron efficient delivery to the isolated reduction environment along directed charge transport pathways that kinetically prohibit recombination reactions.Pt@HNB NPPs catalytic activity was assessed in direct comparison to representative state-of-the-art Pt/semiconductor nanocomposites (extPt-HNB NScs) and unsupported Pt nanocubes.Photolysis under identical conditions exhibited superior H_2 production by the Pt@HNB NPPs, which exceeded other catalyst H_2 yields (µmol) by a factor of 10.Turnover number (TON) and apparent quantum yield (AQY) values showed similar dramatic increases over the other catalysts.Overall, the results clearly demonstrate that Pt@HNB NPPs represent a unique, intricate nanoarchitecture among state-of-the-art heterogeneous catalysts, offering obvious benefits as a new architectural pathway towards efficient, versatile, and scalable hydrogen energy production.Potential factors behind the Pt@HNB NPPs superior performance are discussed below, as are the impacts of systematic variation of photolysis parameters and the use of a non-aqueous reductive quenching photosystem.

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Author Index

Bold page numbers indicate presenter