

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room A213 - Session HC+SS+TL-ThA

Reaction Pathways and Addressing Challenges for Energy Production in the 21st Century & Heterogeneous Catalysis Graduate Student Award Presentation

Moderators: Sanjaya Senanayake, Brookhaven National Laboratory, Arthur Utz, Tufts University

2:20pm **HC+SS+TL-ThA1 High Resolution XPS to Identify C₂H₂ Surface Species on a Cobalt Model Catalyst: New Experimental Evidence for the Importance of Alkylidyne as Growth Intermediates in Fischer-Tropsch Synthesis**, *Kees-Jan Weststrate*, Syngaschem BV, Netherlands; *D. Sharma, D. Garcia Rodriguez, M.A. Gleeson*, DIFFER, Eindhoven University, The Netherlands, Netherlands; *H.O.A. Fredriksson, H.J.W. Niemantsverdriet*, Syngaschem BV, Netherlands

Supported cobalt catalysts find their most widespread application in low temperature Fischer-Tropsch synthesis (FTS), a process in which C-C bond forming reactions produce long chain saturated hydrocarbon chains from synthesis gas, a mixture of CO and H₂. The versatile FTS process may very well continue to play a role in future energy scenarios: synthesis gas can be derived from any carbon-containing source, e.g. biomass or even CO₂ may be used. These renewable carbon sources offer a sustainable alternative to replace petroleum as the principal feedstock of chemicals and liquid transportation fuels.

The FTS reaction mechanism can be ranked among the most complex in the chemical industry. CO and H₂ are converted into long chain hydrocarbons in a sequence of bond-breaking and bond-making steps that are catalyzed by metals such as cobalt, ruthenium and iron (the latter is active in the carbide form). As the steady state concentration of chain growth intermediates is below the detection limits of in-situ spectroscopies simplified model studies are needed to elucidate the mechanism by which long hydrocarbon chains grow on the cobalt catalyst surface. Since chains grow on a surface that is packed with CO, it is of crucial importance to consider how CO spectators influence the reactivity of hydrocarbon adsorbates. We use a Co(0001) single crystal surface as a model system to study how C₂H_x adsorbates react on a cobalt surface, both in ultrahigh vacuum (~10⁻¹⁰ -10⁻⁷ mbar) as well as at near-ambient pressure (~0.1 mbar). By using the high resolution available of x-ray photoemission spectroscopy at the SuperESCA beamline of ELETTRA (Trieste, Italy), and the unique opportunity to combine these qualities with measurements at near-ambient pressure at the HIPPIE beamline of MAX IV (Lund, Sweden), we were able to elucidate the reaction mechanism by which carbon-carbon bonds form on a cobalt surface. We find that CO's presence is of essential importance: It promotes hydrogenation of acetylene, HC≡CH [the most stable C₂H_{ad} without CO] to ethylidyne, ≡C-CH₃, a facile reaction that occurs around 250 K. Ethylidyne dimerization around 310 K produces 2-butyne (H₃C-C≡C-CH₃), a strongly bound alkyne adsorbate that hydrogenates to 2-butene (g) above 400 K. Extrapolated to FTS, the findings speak in favour of the alkylidyne chain growth mechanism: long chain alkylidynes (≡C-R), stabilized by the presence of CO spectators, react with a methylidyne (≡CH_{ad}) monomer to produce a 1-alkyne (R-C-CH) adsorbate. Partial hydrogenation of the 1-alkyne product is promoted by CO_{ad} and produces the alkylidyne species needed for the next CH insertion step.

2:40pm **HC+SS+TL-ThA2 Beam Reflectivity Measurements of Carbon Dissolution on Nickel Single Crystal Catalysts**, *Eric High, D.G. Tinney, A.L. Utz*, Tufts University

The interaction of carbon with metal catalysts is of significant interest. In methane steam reforming, the build-up of carbon in the nickel subsurface leads to a gradual reduction in reactivity on the surface and ultimately results in deactivation of the metal catalyst. Additionally, the initial dissolution and subsequent reemergence of carbon from the subsurface are key steps in the growth of well-ordered graphene on nickel substrates via chemical vapor deposition (CVD). Researchers have previously used Auger and X-ray photoelectron spectroscopy to investigate the dynamics of carbon dissolution into nickel surfaces. We instead employ beam reflectivity measurements to monitor the process of carbon diffusion into the nickel subsurface in real-time. We will present data collected via exposure of a Ni(997) single crystal to supersonically expanded CH₄ molecules at surface temperatures above 600 K. We observe significant changes in the reaction profile by increasing surface temperature as the

rate of dissolution approaches the reactive flux of the high energy gas molecules. We use these results to further develop kinetic models for methane reactivity as a function of surface coverage as well as carbon diffusion into the stepped nickel crystal. The major parameters from these models include the site-blocking coverage and its subsequent dependence on surface temperature as well as an updated measure of the barrier to diffusion for the C/Ni system.

3:00pm **HC+SS+TL-ThA3 Fundamental Research Opportunities to Advance Energy Technologies**, *Bruce Garrett*, Department of Energy INVITED
The U. S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES) supports fundamental research in chemical and materials sciences to provide the foundations for new energy technologies and to support DOE missions in energy, environment, and national security. This presentation will discuss opportunities for fundamental research to impact DOE's energy mission "to catalyze the timely, material, and efficient transformation of the nation's energy system and secure U.S. leadership in energy technologies" with a focus on the way we generate, store and use energy nationally. I will provide an overview of BES strategic planning over the past decade that identified priority research directions for advancing energy applications, highlight key scientific advances in these areas, and discuss some future opportunities for modern science, particularly studies of interfacial processes, to accelerate the transformation of the U. S. energy portfolio.

4:00pm **HC+SS+TL-ThA6 Oxidation and Redox-Mediated Transformation of a Tb₂O₃ Thin Film from the Cubic Fluorite to Bixbyite Structure**, *Christopher Lee, J.F. Weaver*, University of Florida

The terbium oxides, a member of the rare earth oxide family, exhibit favorable properties in selective oxidation catalysis due to the high mobility of oxygen stored and released within the lattice. Of particular note is the ease of structural rearrangement into highly stable, well-ordered intermediates between the Tb₂O₃ and TbO₂ stoichiometries in addition to a continuum of nonstoichiometric states. As opposed to ceria, which stabilizes strongly in the CeO₂ stoichiometry, thin film terbia is very stable in the Tb₂O₃ stoichiometry and can exist in an oxygen deficient cubic fluorite arrangement (CF-Tb₂O₃) as well as the bixbyite structure (c-Tb₂O₃).

We discovered a redox-mediated mechanism for the transformation of thin film CF-Tb₂O₃(111)/Pt(111) to c-Tb₂O₃(111)/Pt(111) in ultrahigh vacuum (UHV). Low energy electron diffraction (LEED) and temperature programmed desorption (TPD) shows that repeated oxidation and thermal reduction to 1000 K transforms an oxygen deficient cubic fluorite Tb₂O₃(111) thin film to the well-defined bixbyite, or c-Tb₂O₃(111) structure. In addition, TPD measurements show the development of several distinct O₂ desorption peaks arising from the oxidation of c-Tb₂O₃ domains to the stoichiometrically-invariant ι -Tb₇O₁₂ and δ -Tb₁₁O₂₀ phases and demonstrates the more facile oxidation of c-Tb₂O₃ relative to CF-Tb₂O₃. We present evidence that nucleation and growth of c-Tb₂O₃ domains occurs at the buried TbO_x/CF-Tb₂O₃ interface, and that conversion of the interfacial CF-Tb₂O₃ to bixbyite takes place mainly during thermal reduction of TbO_x above ~900 K and causes newly-formed c-Tb₂O₃ to advance deeper into the film. The avoidance of low Tb oxidation states may facilitate the CF to bixbyite transformation via this redox-mechanism.

Further oxidation of a well-ordered c-Tb₂O₃ film provides evidence of the sequential phase stabilization of ι -Tb₇O₁₂, δ -Tb₁₁O₂₀, and α -TbO_{2-x} stoichiometric structures along with lower temperature peaks corresponding with more weakly-bound surface oxygen. Oxidation at temperatures between 300-500 K reveals an apparent Arrhenius activation barrier of ~7.4 kJ/mol for the initial conversion of c-Tb₂O₃ to ι -Tb₇O₁₂. Furthermore, oxidation at 100 K creates an additional oxygen species stable at lower temperatures that has a much more pronounced effect on oxidation of the film surface over the bulk of the film. The ability to control the surface termination of the TbO_x(111) thin films along with selectively creating surface bound oxygen species provides the structural basis necessary to clarify the partial oxidation mechanisms associated with terbia-based catalysis.

4:20pm **HC+SS+TL-ThA7 Discrimination of Surface Storage and Mechanistic Pathways Using Dynamic Pulse Response Experiments**, *Y. Wang, M.R. Kunz*, Idaho National Laboratory; *G. Yablonsky*, Washington University in Saint Louis; *Rebecca Fushimi*, Idaho National Laboratory
Pulse response experiments in a pure diffusion reactor significantly increase the number of gas/solid collisions for probing kinetic interactions but maintain straightforward transport modeling by avoiding gas phase dynamics. Using inverse-diffusion methods [1] the millisecond time-

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dependence of the reaction rate can be calculated as it responds to the forced concentration dynamic. More importantly, in this experiment the gas and surface concentrations are decoupled and their influence on the transformation rates of reactants and products can be studied.

Vacuum pulse response studies of ammonia decomposition on polycrystalline Fe, Co and a CoFe bimetallic preparation were conducted to investigate the microkinetic features that lead to very distinct global performance [2]. We present dynamic atomic accumulation; a new measure used to characterize the ability of a complex surface to regulate adsorbed species. We find Fe can support hydrogenated species with a longer surface lifetime than either CoFe or Co. From the time-dependence of the rate we find Co can support two mechanistic pathways for H₂ production. The quantitative rate, gas and surface concentration data of microkinetic reaction steps explain why materials with cobalt perform better at a global level.

1. Redekop, E.A., et al., *The Y-Procedure methodology for the interpretation of transient kinetic data: Analysis of irreversible adsorption*. Chem. Eng. Sci., 2011. **66**(24): p. 6441-6452.

2. Wang, Y., et al., *Transient Kinetic Experiments within the High Conversion Domain: The Case of Ammonia Decomposition*. Catalysts, 2019. **9**(1): p. 104.

4:40pm **HC+SS+TL-ThA8 Nuclearity Effects in Supported Zinc and Gallium Catalysts for Alkane Dehydrogenation, Susannah Scott**, University of California at Santa Barbara **INVITED**

The selective dehydrogenation of alkanes to alkenes is an important process in the valorization of shale gas liquids and in the production of on-demand olefins. Ga- and Zn-modified aluminosilicates have been extensively studied as catalysts for these reactions. In the presence of Brønsted acid sites (BAS), the olefins undergo subsequent aromatization to more valuable BTX. The nuclearity of the metal active sites, the proximity between the metal sites and the BAS, and the nature of the support, may influence the catalytic activity but detailed structure-property relationships are difficult to ascertain in conventional catalysts with many types of sites. The reactions of GaMe₃ and ZnMe₂ with the hydroxyl-terminated surfaces of dehydrated silica and alumina, as well as with the internal and external surfaces of H-ZSM-5, are particularly simple. They generate methane and isolated dimethylgallium and methylzinc sites. K-edge X-ray absorption spectra, analyzed via inspection of the wavelet transform EXAFS (WT-EXAFS) and curvefitting of the Fourier transform EXAFS (FT-EXAFS), reveal that the silica and zeolite materials contain dinuclear grafted sites, regardless of the thermal pretreatment of the support, while alumina gives dispersed mononuclear grafted sites. Differences in reactivity and stability appear to originate in these structural variations.

5:20pm **HC+SS+TL-ThA10 Fundamental Insights into Hydrocarbon Conversion Mechanisms in Lewis and Brønsted Acid Zeolites using Temporal Analysis of Products, Hari Thirumalai¹, J.D. Rimer, L.C. Grabow**, University of Houston

The surge in natural gas production has incentivized the search for processes that can utilize methane and light olefin derivatives in the manufacture of useful products such as benzene, toluene and xylene (BTX). These are important commodity chemicals that are used as fuel additives and as raw materials in the synthesis of specialty chemicals. Industrial demand is met through processes such as the synthesis of BTX through dehydroaromatization of light olefins or through alkylation of aromatics, typically with the use of zeolites as catalysts. Complex reaction mechanisms determined by the presence of a hydrocarbon pool dominate hydrocarbon chemistry and are challenging to study. These challenges hinder the in-depth understanding of the role of the catalyst and its eventual design for tailored applications.¹

In this work, we use the transient kinetics technique, temporal analysis of products (TAP), to probe hydrocarbon conversion and upgrade in the transient regime of reaction. TAP experiments help probe the intrinsic kinetics of reactant conversion in a well-defined Knudsen transport regime under high-vacuum conditions. We studied the dehydroaromatization of ethylene and the methylation of toluene as case-studies for hydrocarbon conversion reactions. The precise control of reactant molecules entering the reactor and responses recorded by a high-resolution mass spectrometer at the reactor outlet in the dehydroaromatization of ethylene suggest that a Lewis acid such as Ag⁺ or Ga³⁺ in the zeolite accelerate the retention of long lived carbonaceous species in the zeolite, thus attaining the autocatalytic arene cycle more rapidly. Pulse responses provide qualitative evidence that olefins are strongly bound to the metal-

exchanged zeolite samples with delayed desorption, enhancing the rate of hydrocarbon conversion and carbon retention. Finally, experiments investigating the methylation of toluene to xylene provide valuable information on competitive binding of reactants to the zeolite acid sites and the ensuing primary reactions that drive the reaction.

Overall, our experiments under semi-idealized conditions help provide insight into the crucial primary reactions that initiate the hydrocarbon pool mechanism, thus elucidating the role of extra-framework species such as Ag⁺ or Ga³⁺ and their synergy with the Brønsted acid sites in hydrocarbon conversion. The fundamental understanding gained from these experiments will be crucial in deciphering the role of the different zeolitic active sites in model hydrocarbon conversion reactions.

References

1. Hsieh, M. F., Zhou, Y., Thirumalai, H., Grabow, L. C., & Rimer, J. D. *ChemCatChem*, (2017), **9**(9), 1675-1682.

¹ Morton S. Traum Award Finalist

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