Thursday Evening Poster Sessions, October 24, 2019

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room Union Station AB - Session HC-ThP

Fundamental Discoveries in Heterogeneous Catalysis Poster Session

HC-ThP-1 The Role of Boron in Supported Platinum Dry Reforming Catalysts*, **Carly Byron**, S Bai, A Teplyakov,* University of Delaware

Dry reforming of methane (DRM) has been proposed as an alternative to coal or natural gas production of synthesis gas, and the process has been optimized with various metal catalysts to enhance catalytic activity and reduce surface carbon contamination. In this work, boron was paired with platinum, a highly active DRM catalyst, on a silica support material, and surface characterization techniques were used to determine how the presence of boron affected the metal catalyst and the catalytic performance. X-ray photoelectron spectroscopy (XPS) revealed the existence of trigonal (BO_3 structures) and tetrahedral (BO_4 structures) B-containing surface species, which agreed with solid-state ^{11}B NMR results. Density functional theory (DFT) calculations were performed to determine the thermodynamically stable configuration of the B/SiO_2 species, as well as the most favorable species for platinum adsorption. Tetrahedrally coordinated boron was found to be the most favorable species for platinum adsorption. A butane dehydrogenation reaction was utilized to produce fully deactivated $Pt/B/SiO_2$ catalysts samples for further analysis. After complete catalyst deactivation, ^{11}B NMR combined with theoretically-predicted isotropic chemical shifts calculated by Amsterdam Density Functional (ADF) revealed that, in addition to BO_3 and BO_4 fragments, a boron-carbon surface species had been formed during butane dehydrogenation, but this was only observed on catalysts containing platinum. From this observation, it has been concluded that platinum causes carbon contamination during this reaction, but it is mitigated by the presence of boron.

HC-ThP-2 Spectroscopic Characterization of Ethylidyne formed from Acetylene on Pd(111)*, **Ravi Ranjan**, M Trenary,* University of Illinois at Chicago

The surface species formed following the adsorption and hydrogenation of acetylene (C_2H_2) on Pd(111) in the temperature range of 90-450 K are identified and characterized. The techniques used to detect the species are reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD). Acetylene was adsorbed at low temperature and then heated to 300 K where it converts to ethylidyne (CCH_3), which is identified by its $\delta(CH_3)$ bending mode at 1327 cm^{-1}. The reaction mechanism for this conversion is quite complex; in the literature there are discrepancies in the identification of the intermediates with both vinyl ($CHCH_2$) and vinylidene (CCH_2) having been proposed. The experimental data available to date favors the formation of vinylidene as an intermediate in the conversion of acetylene to ethylidyne (CCH_3). Evidence for vinylidene is seen in the appearance of its bending mode ($\delta(HCH)$) at 1425 cm^{-1}. The possible mechanism of ethylidyne (CCH_3) formation is through isomerization of acetylene to vinylidene (CCH_2) followed by hydrogenation of vinylidene. In the temperature range of 400 to 450 K, C_2H_2 decomposes and forms a C_xH_y species as verified by TPD spectra showing an H_2 peak at 440 K following C_2H_2 adsorption at low temperature. The low energy electron diffraction (LEED) pattern of acetylene adsorbed at 95 K gives rise to a $(\sqrt{3}\times\sqrt{3})R30^\circ$ pattern. The experimental result is also supported by quantum mechanical computational calculations based on density functional theory.

HC-ThP-3 XPS, TOF-SIMS, and AES Analysis of Fresh and Aged Alumina-Supported Silver Catalysts*, **John Newman**, D Carr, D Paul, L Swartz,* Physical Electronics*; M Di Mare, W Suchanek,* Scientific Design Company, Inc.

Alumina supported silver catalysts have been used for decades for the direct oxidative conversion of ethylene to ethylene oxide. Ethylene oxide is used in many cleaning and sterilizing products; however, its major industrial application is in the production of ethylene glycol used in the generation of antifreeze, polyesters, liquid coolants and solvents. Global production of ethylene oxide is estimated to grow to 28 million metric tons in 2019 at an estimated market value of over $48 billion (1, 2).

Due to the huge size of this market, incremental improvements in the efficiency and longevity of the catalyst can be very beneficial. Many companies continuously explore ways in which to improve the various aspects of the catalyst system – the physical and chemical properties of the catalyst, the preparation technology, and the reaction conditions.

In this investigation, three surface sensitive (outermost ≤ 5 nm) techniques, X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), and Auger Electron Spectroscopy (AES) were used to study the changes that occur between fresh and aged Cs-promoted, alumina-supported Ag catalyst samples. XPS provided insights into the overall surface concentrations of the elements present as well as chemical state changes that occurred during aging. TOF-SIMS was used to detect and spatially locate elements at concentrations often too low to detect with XPS or AES, and AES high magnification elemental mapping and small area spectroscopy were used to study the localized elemental changes that occurred between fresh and aged catalyst samples. Information gained from these experiments provides valuable insights on the physical and chemical transformations taking place during aging of the catalyst. This information can then be used to suggest further modifications to improve the performance of the catalyst system.

References

1. PR Newswire, *Global Ethylene Oxide Market Report 2018 - Forecast to 2023: The Growing Demand for PET Bottles from the Packaging Industry*, Nov 26, 2018

2. Business Wire, *Global Ethylene Oxide Market Report By Application*, April 24, 2018

HC-ThP-4 Infrared Spectroscopy of Carbon Dioxide Hydrogenation over the Cu(111) and Pd/Cu(111) Single Atom Alloy Surfaces under Ambient Pressure Conditions*, **Arephin Islam**, M 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 ambient pressures of carbon dioxide, a peak is observed at 1295 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 $H_2(g)$ at 300 K, the spectra change and new peaks due to surface species appear. By performing the experiment with polarized infrared radiation, the gas phase and surface species are easily distinguished. The results demonstrate that CO_2 hydrogenation is readily achieved over a Cu(111) model catalyst and that surface intermediates can be detected with RAIRS.

HC-ThP-5 Morphology of an Oxide Formed on Au(111) at High Temperatures under Ambient Pressure Conditions*, **Jordon Baker**, H Kaleem, E Maxwell, A Baber,* James Madison University

The deactivation of heterogeneous catalysts occurs via several mechanisms such as poisoning, coking, and sintering, among others. In order to maintain the high chemical reactivity of heterogeneous catalysts, the process for catalyst deactivation must be well understood and avoided. The effect of high temperature annealing cycles on the morphology of TiO_2/Au(111) model catalysts has been studied. When modified with TiO_2 nanoparticles, the morphology of the model catalyst can vary based on differences in the annealing cycle parameters. Atomic force microscopy (AFM) was used to image the morphology of the surface before and after annealing TiO_2/Au(111) to 1000 K. TiO_2 nanoparticles sintered and Au(111) step edges smoothed, but surprisingly a new surface feature was observed with AFM under ambient conditions, resembling mixed metal oxides formed under UHV conditions. X-ray photoelectron spectroscopy was used to characterize the surface species remaining after the high temperature exposure. The stabilization of a mixed metal oxide on Au(111) has not previously been observed, and future work will investigate the chemical reactivity of these materials.

HC-ThP-6 Machine-Learning Enabled Search for The Next-Generation Catalyst for Hydrogen Evolution Reaction*, **Sichen Wei**, S Baek, K Reyes, F Yao,* University at Buffalo

As a zero-emission, eco-friendly fuel, hydrogen gas can be generated via electrochemical (EC) water splitting. Achieving high-efficiency water splitting requires the use of a catalyst to minimize the overpotential to drive the hydrogen evolution reaction (HER). Noble metals such as platinum (Pt) can provide an excellent catalytic activity for HER but are too expensive and scarce for broad applications. Therefore, the development of active HER catalysts made from low-cost materials constitutes a crucial challenge in the utilization of hydrogen energy.

Earth-abundant transition metal dichalcogenides (TMDs), such as molybdenum disulfide (MoS_2), have been discovered recently, which exhibit good activity and stability for electrocatalytic reactions. In order to fully explore the untapped potential of MoS_2, the synthesis recipe for MoS_2 needs to be optimized. Such an optimization process needs scientists to search through a combinatorically large space of experimental parameters, which will be time-consuming and costly if using conventional trial-and-error approaches.

In this report, MoS_2 HER catalytic activity optimization is performed by examining different combinations of synthesis parameters during the hydrothermal process. To investigate the structure-activity relationship, scanning electron microscope (SEM), X-ray diffraction (XRD), Raman spectroscopy and various electrochemical characterizations have been conducted. A strong correlation between hydrothermal conditions and HER performance matrix has been observed. In order to accelerate the search for the best synthesis recipe, machine-learning (ML) techniques have been introduced to help identify the optimal parameter combinations for producing MoS_2. The hydrothermal parameters with the corresponding onset potentials and Tafel slopes are adopted as prior knowledge and are incorporated into the Bayesian Optimization model. The model will be able to guide the wet chemical synthesis of $MoS_2$and yield the most effective HER catalyst eventually.

HC-ThP-7 Intermolecular Interactions of Small Alcohols on Au(111)*, **Eric Maxwell**, J Baker, H Kaleem, A Baber,* James Madison University

Metal oxide nanoparticles supported on Au(111) are active catalysts for the oxidation of small alcohols to form industrially significant products and intermediates such as aldehydes. In a systematic study to better understand the adsorption behavior of these small alcohols, coverage studies of methanol, ethanol, and 1-propanol have been conducted on Au(111) using ultrahigh vacuum temperature-programmed desorption (TPD). These three alcohols molecularly adsorb to distinct terrace, step edge, kink, and multilayer sites, for which desorption energies are calculated by Redhead’s peak maximum method. The use of complete analysis as a more accurate method for the calculation of desorption energies is also explored for the case of methanol. TPD experiments and subsequent analysis uniquely allow for the investigation of both adsorbate-surface interactions and adsorbate-adsorbate intermolecular interactions. This provides a more robust understanding of surface phenomena and affords valuable data for modelling and predicting the adsorption behavior of small alcohols on Au(111)-based catalysts. It is shown that, for all adsorption sites, desorption energy is directly proportional to carbon chain length. However, the rate at which desorption energy increases varies distinctly between adsorption sites. This study indicates that the role of intermolecular interactions in the adsorption behavior of small alcohols varies between adsorption sites, and can be predicted for other small alcohols.

Author Index

Bold page numbers indicate presenter