Thursday Evening Poster Sessions, November 2, 2017

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room Central Hall - Session HC-ThP

Fundamental Discoveries in Heterogeneous Catalysis Poster Session

HC-ThP-2 Auger Electron Spectroscopy Analysis of Fresh and Aged Alumina Supported Ag Catalysts, *Dennis Paul, J Newman,* Physical Electronics; *W Suchanek,* Scientific Design Company, Inc.

Auger Electron Spectroscopy is a well known surface analysis method optimized for characterization of very small features. The technique has an inherent depth of analysis of ~5 nm and can provide analysis of features as small as ~20 nm. While Auger works well on conducting and semiconducting materials, it is much more challenging to analyze insulating samples due to uncompensated charge buildup that occurs during electron bombardment. Thus, for catalyst analysis on insulating supports (typically metal oxides) Auger can be extremely difficult. However, with careful sample preparation and appropriate Auger operating conditions, excellent data can still be obtained from these challenging materials.

In this investigation Auger elemental mapping and small area spectroscopy were used to study the changes that occur between fresh and aged Cs-promoted, alumina-supported Ag catalyst samples. The results show that while the size of the alumina support particles remains roughly the same during extended use, the Ag catalyst morphology has changed dramatically with the particle size increasing by over an order of magnitude. Conversely, the Cs Auger maps from the Fresh and Aged catalysts show that this constituent remains dispersed across the alumina support during the aging process.

HC-ThP-3 CO Adsorption on Size-selected Pt$_n$ Clusters Uniformly-Deposited on Al$_2$O$_3$/NiAl(110), *Yoshihide Watanabe, A Beniya,* Toyota Central R&D Labs. Inc., Japan

Size-selected metal clusters on oxide surfaces are a subject of considerable interest because of their distinctive size-dependent catalytic properties. The most precise approach to prepare a model catalyst is deposition of size-selected clusters using a mass-filtered cluster ion beam. It is important to prepare a uniformly deposited surface and avoid cluster-aggregations for investigation of size-dependent catalytic activity.

Pt clusters produced using a DC magnetron-sputtering source were mass-selected using a quadrupole mass filter. The parallel plate deflectors were placed to scan the cluster ion beam. When two sine voltage waveforms are applied to the orthogonal deflectors, the ion trajectory on the surface produces a Lissajous pattern. The ion trajectory fills the sample surface uniformly with an irrational frequency ratio. The advantages of this method are simplicity and low cost of setup compared with raster scanning method.

In this study, size-selected Pt clusters were deposited uniformly on surfaces by scanning the cluster ions in the form of Lissajous pattern. We confirmed that size-selected clusters can be deposited uniformly on a surface by Pt 4f intensity mapping. A uniform cluster distribution was also confirmed using a scanning tunneling microscope.

In high-density condition, the Pt clusters deposited without Lissajous scan could aggregate and form different size clusters. Cluster aggregation probability depends on the deposited density. The isolated Pt$_n$ clusters and their aggregates were estimated to be distributed with position-dependence. At 0.1 ML of total coverage, 33% of the clusters coalesce to form larger clusters. This result indicates that the coverage needs to be low enough to neglect the cluster aggregation effect.

The adsorption states of CO molecules on size-selected Pt$_n$ (n = 7, 15, 20) clusters deposited on the Al$_2$O$_3$/NiAl(110) surface were also investigated with and without a Lissajous scan. Two peaks at 2020 and 2040 cm^{-1} are observed in infrared reflection absorption spectroscopy (IRAS) spectra of adsorbed ^{13}CO at saturation coverage. These peaks are assigned to adsorbed CO at the on-top site of slightly cationic Pt atoms interacting with substrate oxygen atoms (2040 cm^{-1}), and of neutral Pt atoms bound by the Pt–Pt bond (2020 cm^{-1}). Temperature programed desorption (TPD) spectra of saturated ^{13}CO were also investigated. Combining the IRAS and TPD results, we determined that CO molecules bind to slightly cationic Pt atoms with an adsorption energy of 0.7–1.0 eV, and bind to neutral Pt atoms with an adsorption energy of 1.4 eV.

HC-ThP-4 Unexpected Formation of Catalytically Active Palladium Nanoparticles on Silica Surface in Organic Solvents, *Megan Bornstein, A Quast, R Park, J Shumaker-Parry, I Zharov,* University of Utah

Supported palladium nanoparticles (PdNPs) have been found to be active catalysts for a variety of organic transformations, with more recent reports showing PdNPs can catalyze chemoselective hydrogenation, as well as the photocatalytic activity of PdNPs can be enhanced plasmonically. Having a method to reliably synthesize small PdNPs on inorganic supports is useful, and we will report on the formation of PdNPs on silica nanospheres in organic solvents, which can be used as a convenient method of PdNPs preparation.

While attempting to immobilize Pd^{2+} ions on ligand-modified silica nanospheres, we observed the formation of small (~5 nm) uniform PdNPs. The only reactants in this process were surface-functionalized silica spheres, Pd(OAc)$_2$, and reagent-grade acetone. This suggests that an impurity in the acetone is responsible for the reduction of Pd^{2+} to Pd^0. We obtained similar PdNPs when using high purity acetone containing a small amount of added ethanol, while no PdNPs formation was observed in acetonitrile. Thus, this suggests that PdNPs is due to the presence of reducing organic compounds, such as alcohols.

The oxidation state of palladium was confirmed using X-ray photoelectron spectroscopy (XPS), and the morphology of the particles was analyzed using Scanning Transmission Electron Microscopy (STEM). The PdNPs formed were very small, typically around 5 nm in diameter when the reaction was done at room temperature, and uniformly distributed on the surface of a silica support that had been functionalized with primary amines or BiPy ligands, which provide stabilization for the PdNPs. For reactions run at 40 °C, the average diameter of the PdNPs was larger than those run at -77 °C or room temperature. The materials synthesized were capable of catalyzing the reduction of 4-nitrophenol to 4-aminophenol and the oxidation of benzyl alcohol to benzaldehyde.

HC-ThP-5 Copper Activated Conversion of Ethanol to Higher Alcohols over Hydrotalcite Derived MgAl Mixed Oxides, *Karthikeyan K. Ramasamy, M Guo, M Gray, S Subramaniam,* Pacific Northwest National Laboratory; *A Karakoti,* Ahmedabad University, India; *V Murugesan, V Shutthanandan,* Pacific Northwest National Laboratory; *S Thevuthasan,* Pacific Northwest National Laboratory, Qatar

Unique physical and chemical properties of layered double hydroxide, hydrotalcite (HT) ($M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}A^{n-}x/n \cdot mH_2O$), derived materials have been used for selective and efficient transformations of organic compounds to higher value products. The catalytic properties of the HT derived mixed oxide material are a function of the morphology, local structure and oxidation state of the participating cations. In this work the effect of addition of copper ions on the catalytic properties of MgAl HT derived materials were studied for selective conversion of ethanol to higher alcohols. The ethanol to higher alcohol conversion goes thru a series of complex intermediate steps. The addition of copper is expected to promote the catalytic dehydrogenation of alcohols to aldehydes which is the first step in the complex cascade reaction and considered as the rate determining step in the overall chemistry. Various concentration of copper loading were attempted from 0 wt% to 6 wt % using different synthesis strategies in an attempt to achieve a homogenous dispersion of copper in the MgAl matrix. The selectivity and efficiency of copper substituted catalysts were analyzed by conversion of ethanol to higher alcohols in an indigenously designed plug flow reactor. Resulting physical and chemical changes in copper substituted catalysts were studied before and after the catalytic reaction using high resolution transmission electron microscopy, x-ray diffraction, x-ray absorption, X-ray photoelectron spectroscopy and nuclear magnetic resonance measurements. It was observed that different oxidation states of copper and the extent of dispersion of copper in the HT matrix influences catalytic efficiency and selectivity of the process by promoting various side reactions. Synthesis of copper substituted HT derived mixed oxide catalyst plays a major role in controlling the dispersion of the copper in the matrix. Fundamental challenges in achieving higher copper substitution without observing significant clustering and aggregation effects will be discussed in context of catalytic selectivity and efficiency.

HC-ThP-6 Methane Dissociation on Ni(111) at High Surface Temperatures: The Observed role of Surface and Subsurface C on Reactivity, *Eric Dombrowski, E High, A Utz,* Tufts University

Steam reforming methane over a Ni catalyst is the chief industrial process for H$_2$ gas production, and activation of methane's C-H bond to form surface-bound CH$_3$ and H is rate limiting. Conventional and vibrational

state-selected molecular beam studies have highlighted the importance of translational (E_{trans}) and vibrational (E_{vib}) energy in promoting this rate limiting step on clean, well-ordered Ni single crystal surfaces. Nearly all of these studies have been performed at low to moderate surface temperatures ($T_{surf} < 700K$), where carbonaceous reaction products remain bound to the surface throughout the measurement.

Here, we describe experiments that extend these state-resolved measurements to the high surface temperatures typically used in the steam reforming process. Under these conditions, the methyl product promptly dehydrogenates to form surface-bound C and H, and H atoms recombinatively desorb, leaving C on the surface. The remaining carbon can dissolve into the nickel subsurface or bulk during the molecular beam dose, with a T_{surf}-dependent dissolution rate. We measured methane uptake onto, and into, a Ni(111) single crystal *in situ* across a range of surface temperatures from $T_{surf} = 680 - 850$ K. We varied incident translational energies and incident methane flux, and measured $S(\theta)$ for both laser-off and state resolved ($v=1$, v_3 antisymmetric C-H stretch) methane. A unique molecular beam reflectivity method allowed us to quantify the initial S_0 as well as $S(t)$ in real time during the dose. Integrating $S(t)$ yielded the integrated amount of C deposited during the dose, (θ) and allowed us to calculate $S(\theta)$.

Over the T_{surf} range studied, we observed drastic differences in carbon dissolution during deposition. At $T_{surf} = 680K$, carbon uptake into the nickel lattice was minimal and about 0.5 ML of C was deposited before the surface became deactivated due to site-blocking. This situation changed dramatically at temperatures above $T_{surf} = 750$ K. At intermediate temperatures, we observed an induction period prior to the onset of site blocking and surface passivation, and, at $T_{surf} = 850$ K, deposition of more than 50 ML of C did not completely passivate the surface. Furthermore, we observed that under some conditions, $S(\theta)$ *increased* with increasing C concentration beneath the surface. A simple two-step dissolution process that includes T-dependent rate constants for C transport between the surface, subsurface, and bulk qualitatively describes our data. We will also describe our most recent efforts to refine this model to more quantitatively describe our experimental measurements to better understand the role of dissolved C on methane activation.

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