

# Tuesday Morning, October 16, 2007

## Surface Science

Room: 608 - Session SS1-TuM

## Catalytic Chemistry of Hydrocarbons

Moderator: B.E. Koel, Lehigh University

8:00am SS1-TuM1 **Impact of Surface Analysis in Hydrocarbon Catalysis: Examples from Industry**, A.S.Y. Chan, S.R. Bare, UOP - Honeywell

Isomerization of straight chain alkanes to their branched isomers is an important industrial process to upgrade the octane value of gasoline. A solid acid catalyst that is effective for the isomerization of light alkanes is sulfated zirconia. In 1990, Sun Refining and Marketing Co. patented a modified sulfated zirconia catalyst containing transition metals (e.g. Mn, Fe) as promoters. More recently, in 2003, UOP patented an improved catalyst that was promoted by at least one lanthanide. In this talk, we will focus on the surface characterization of model sulfated zirconia catalysts that are Mn-promoted and lanthanide-promoted. By using a combination of X-ray Photoelectron Spectroscopy (XPS) and Low Energy Ion Scattering (LEIS), the location of promoters and their subsequent effect on the structure of the zirconia support will be elucidated. In addition, the accessibility of active metal and acid sites on these two promoted catalysts will be discussed. Finally, we will generalize the combined XPS and LEIS studies to provide a more complete picture of other catalytic systems: examples will be drawn from novel zeolites used in alkylation reactions, and Pd-based selective hydrogenation catalysts.

8:20am SS1-TuM2 **The Influence of Steps on the Adsorption, Fragmentation, and Reactions of Ethylene and Ethanol on Rh Surfaces**, J.N. Andersen, E. Lundgren, A. Resta, Lund University, Sweden

We have used high resolution core level photoemission to study how the adsorption, fragmentation, and reaction of ethylene and ethanol are influenced by low coordinated atoms found at the steps of vicinal Rh surfaces. The talk is naturally divided in two parts. In part 1, we describe how detailed analysis of the C1s spectra including the vibrational fine-structure of this level often facilitates determination of the adsorbed fragments of these molecules. In part 2, we use this method of identification to monitor the influence of steps. This was done by comparing results from Rh(111) and some of its vicinals. For ethanol adsorption, we find large differences in the fragmentation pattern at 300K between the Rh(111) and the Rh(553) surfaces, in particular, the steps on Rh(553) are found to be very effective in dehydrogenation reactions. We also find differences in the oxidation of ethanol, where Rh(553) is found to be more reactive. For ethylene adsorption we have studied the temperature induced ethylidyne formation and subsequent decomposition. Also in this case do we find that the steps increase the reactivity regarding fundamental reactions involved in both the formation and the decomposition pathways. In addition, comparison between Rh(553) and Rh(322) demonstrated a larger reactivity of (100)-type than of (111)-type micro-facets. Finally, we discuss the importance of the present results in the context of catalytic reactions on small metal particles.

8:40am SS1-TuM3 **Mechanistic Insights on Fischer-Tropsch Synthesis**, M. Mavrikakis, University of Wisconsin - Madison **INVITED**

First-Principles methods can provide useful information regarding detailed reaction mechanisms. In this talk, we will present our recent work on the early steps of Fischer-Tropsch synthesis on iron and cobalt based catalysts. A number of elementary reaction steps leading to CO dissociation and hydrogenation of carbon-containing species have been analyzed both in terms of their thermochemistry and minimum energy paths. A comparison between our results and recent experimental results on realistic FTS catalysts leads to some interesting conclusions, including the role of hydrogen in CO dissociation on Fe and Co catalysts, and the possible role of identified surface reaction intermediates in the FTS polymerization reaction.

9:20am SS1-TuM5 **H Induced CO Dissociation on Nickel Surfaces**, M.P. Anderson, F. Abild-Petersen, J. Engbaek, O. Lytken, S. Horch, J.H. Nielsen, Technical University of Denmark, J. Sehested, J.R. Rostrup-Nielsen, Haldor Topsoe A/S, Denmark, J.K. Norskov, I. Chorkendorff, Technical University of Denmark

The dissociation of CO is both a model test reaction on clean single crystals and a relevant reaction step for industrial methanation. Much attention has therefore been dedicated to understanding the details of the mechanism. First of all, there seems to be a lack of consensus on whether CO can dissociate on Nickel at low temperatures (400 K) in a UHV experiment. In this work we have used a Ni(14,13,13) crystal which is mis-cut in such a way that there is an atomic step for each 26 terrace atoms. We show that CO (which has carefully been cleaned from Ni(CO)<sub>n</sub>) does not dissociate unless the temperature is larger than 400 K and there are atomic steps present on the surface. If the steps are blocked by sulfur no dissociation could be measured under UHV conditions. The activation energy for dissociation is found to be 1.6 eV, which is slightly larger than that for desorption. This observation is found to corroborate with DFT calculations indicating a barrier for dissociation of 1.7 eV. This is, however, in contrast with the activation energy of 1.07 eV and 1.01 eV observed for the methanation reaction on single crystals and real supported catalysts, respectively. Furthermore, surprisingly small prefactors for those reactions have been reported in both cases. By investigating the possible pathways using DFT, a much lower barrier for CO dissociation of 1.08 eV was identified when considering a COH intermediate. By incorporating this intermediate in the reaction pathway, the low activation energy and low prefactors can be explained in terms of a COH intermediate dissociating on step sites both in the single crystal experiments and on the nanoparticles constituting the real catalysts. In the latter case the conclusion is further confirmed by investigations of the relation between the particle size and the catalytic rate, where a strong deviation from a simple surface area effect is found.

9:40am SS1-TuM6 **Density Functional Theory Study of the Interconversion between HCO (formyl) and COH Surface Reaction Intermediate on Pt(111)**, L. Arnadottir, E.M. Stuve, University of Washington, H. Jónsson, University of Iceland

Two forms of the reaction intermediate with H:C:O stoichiometry were studied on Pt(111) using density functional theory. Three cases were studied: the intermediate on a clean surface, the intermediate and one water molecule on the surface and the intermediate with a water bilayer. Both the H-C=O (formyl) and C-OH configurations were found to be stable on clean Pt(111) and when coadsorbed with a water molecule. Interconversion between the two configurations was studied using the nudged elastic band method. On the clean surface interconversion between the two forms goes through a CO<sub>ads</sub> and H<sub>ads</sub> intermediate, meaning that although both HCO and COH are stable on the clean surface they will not interconvert. In the presence of coadsorbed water molecule the activation barrier for the interconversion from HCO to COH was found to be 0.62 eV. While the HCO configuration is stable in the presence of a water bilayer, the COH configuration dissociates to CO<sub>ads</sub> and H<sub>ads</sub>. These results suggest that, in the presence of water, the HCO form will be the only stable form of the reaction intermediate of H:C:O stoichiometry.

10:40am SS1-TuM9 **Enantioselectivity and Structure of Naturally Chiral Metal Surfaces**, A.J. Gellman, Y. Huang, L. Baker, Carnegie Mellon University

The high Miller index surfaces of single crystal metals have chiral structures and have been shown to interact enantiospecifically with chiral adsorbates. There are many demonstrations of this phenomenon originating from several laboratories around the world. One specific example is the adsorption of R-3-methylcyclohexanone on Cu(hkl)<sup>R&S</sup> surfaces. Several years ago we demonstrated that the adsorption of R-3-methylcyclohexanone on the Cu(643)<sup>R&S</sup> surfaces was enantiospecific. The desorption energies of R-3-methylcyclohexanone adsorbed at R and S kinks differed and the orientation of the molecule at the R and S kinks differed. Over the past two years we have completed a study of the adsorption of R-3-methylcyclohexanone on a set of 16 single crystal surfaces spanning the entire stereographic projection. In spite of the complex variety of surface structures, we find that the adsorption sites on all surfaces can be classified as terraces, step and kink type sites and have adsorption energies for R-3-methylcyclohexanone that are quite distinct from one another. One of the important observations is that some of the nominally straight step edges such as those found on the Cu(410) surface exhibit behavior similar to that of the kinks on the Cu(643) surface. This arises because these (410) step edges are in fact quite rough and are not formed by close packed rows of

atoms. Recent work has focused on the structure of chiral Cu surfaces. Molecular simulation by various other groups has demonstrated that the kinked step edges of these surfaces are roughened by annealing to high temperatures and that such step edges expose a variety of different kinks sites that are not found on the ideally terminated high Miller index surfaces. Scanning tunneling micrographs of these surfaces that have been reported by other groups bear out this description of the structure of the high Miller index surfaces. Over the past year we have developed the use of Xe TPD and Xe UV photoemission as a means of obtaining spectroscopic characterization of the kink step and terrace site densities on these surfaces.

**11:00am SS1-TuM10 Tunneling Contributions in  $\beta$ -Hydride Elimination of Ethyl Groups on Cu(111) and Cu(100) surfaces, Y. Huang, A.J. Gellman, D. Sholl, Carnegie Mellon University**

Ethyl groups decompose into ethylene through the  $\beta$ -hydride elimination on Cu(111) and Cu(100) single crystal surfaces. Density Functional Theory calculations for  $\beta$ -hydride elimination of ethyl groups on Cu(111) and Cu(100) have been conducted by Sholl et al. These calculations suggested that hydrogen tunneling influences the kinetics of  $\beta$ -hydride elimination of ethyl groups on Cu(111) but not on Cu(100). Based on the calculations the Deuterium isotope effect in  $\beta$ -hydride elimination of ethyl groups should be greater on Cu(111) than on Cu(100). To verify this temperature programmed desorption (TPD) spectra of ethyl iodide and ethyl-2,2,2- $d_3$  iodide on both Cu(111) and Cu(100) were obtained. The pre-exponential and activation barrier to  $\beta$ -hydride elimination reactions were determined and compared on both Cu(111) and Cu(100) surfaces.

**11:20am SS1-TuM11 CO Chemisorption on Cu(111) via Embedded Configuration Interaction Theory, S. Sharifzadeh, P. Huang, E.A. Carter, Princeton University**

Although density functional theory (DFT) is often considered the electronic structure method of choice to study surfaces, situations exist where DFT fails, e.g. strongly correlated electrons and descriptions of unoccupied states. As an example, CO adsorption on Cu(111) is poorly described within DFT because the CO bond to Cu(111) involves Cu back-donation to the empty CO  $2\pi^*$  orbitals, which are at too low an energy in DFT, leading to an overestimation of  $\pi$  back-bonding. Measurements at low coverage are consistent with on-top site CO adsorption on Cu(111), whereas pseudopotential-based DFT methods predict hollow site adsorption, due to the overestimation of the importance of  $\pi$ -back-bonding. In this work, we study CO/Cu(111) with a density-based embedding strategy, where a local region of interest, described by accurate ab initio quantum chemistry calculations, is embedded into a background described by DFT. The region of interest is represented by a cluster of atoms that includes CO and nearby metal atoms. A self-consistent, DFT-based embedding potential accounts for the effect of the background on this cluster. Since ab initio quantum chemistry methods, e.g. configuration interaction (CI), give a better description of the CO LUMO, we expect an improvement on the description of CO chemisorption. We will present site preferences and adsorption energies from embedded CI, as well as comparing to periodic DFT and finite cluster calculations.

**11:40am SS1-TuM12 Mechanistic Insights Into Methane Activation from State-Resolved Beam-Surface Scattering Measurements, A.L. Utz, D.R. Killelea, V.L. Campbell, D.F. Del Sesto, N.S. Shuman, Tufts University**

State-resolved surface scattering experiments provide detailed insight into the mechanistic basis for methane activation. We use infrared laser excitation of molecules in a supersonic molecular beam to prepare reagents with a well-defined internal and translational energy. The state-resolved reaction probabilities that we measure reveal which molecular motions (methane stretching and bending, translation, and surface atom motion) best promote reaction. Earlier work in our lab has shown that on Ni(111), C-H stretching excitation is significantly more effective than translational energy or bending excitation in promoting methane dissociation. Recent measurements demonstrate our ability to exert bond-selective control over methane dissociation. We excite the C-H stretch in CHD<sub>3</sub> and detect exclusively reaction products from the C-H bond cleavage channel. In contrast, thermal excitation of CHD<sub>3</sub> vibrations leads to a preference for C-D bond cleavage. This observation contradicts statistical pictures of gas-surface activation and indicates that energy exchange during direct dissociation is not complete on the timescale of reaction. The presentation will highlight recent experimental results from our lab, discuss how these results teach us about the reaction coordinate for methane activation, and explore how limited energy flow during reaction impacts our understanding of the energetics of hydrocarbon activation.

**12:00pm SS1-TuM13 Preparation of Nickel Nanoparticles and their Catalytic Activity in the Cracking of Methane., J.C. De Jesus, I. Gonzalez, PDVSA-Intevep, Venezuela, M. Garcia, C. Urbina, Universidad Central de Venezuela**

In this study, a facile method for the preparation of nickel nanoparticles is employed to investigate the catalytic decomposition of methane into carbon nanotubes. Nickel acetate tetrahydrate decomposes readily below 350°C to form metallic nanoparticles (average size 10-80 nm), and weight changes measured inside a thermogravimetric analyzer (TGA) in methane streams can be related quantitatively to the production of carbon nanotubes by catalytic cracking. C to Ni atomic ratios (C/Ni) estimated directly from TGA data provided a systematic approach to study in-situ the catalytic activity of the nickel nanoparticles. Methane cracking starts at temperatures as low as 400°C and continues efficiently until approximately 600°C. Between 600°C and 660°C, methane decomposition momentarily breaks off, while presumably the catalytic system undergoes a self-reorganization. Cracking resumes at 660°C and continues slowly up to 950°C. The amount of carbon deposited in the 600-660°C interval shows a lineal dependence with methane concentrations, with C/Ni ratios ranging from 6 to 31. Transmission electron microscopy (TEM) images of the different C/Ni residues collected at 660°C showed that during cracking narrower carbon nanotubes are produced at elevated methane concentrations, suggesting dispersion of nickel nanoparticles.

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