

Surface Science

Room 2002 - Session SS1-MoM

Catalytic Chemistry of Hydrocarbons

Moderator: J.N. Andersen, Lund University, Sweden

8:00am **SS1-MoM1 Activation of Au for Nitrogen Addition Reactions, X. Deng, T.A. Baker, C.M. Friend**, Harvard University

Aziridination, nitrilation and hydrogenation of styrene are promoted on Au(111) pre-covered with NHx groups. NH, N and H were formed on Au(111) at 110 K by electron bombardment of condensed ammonia. 2-phenylaziridine is the major product, accounting for 63% of the total styrene conversion; it is attributed to the addition of NH to styrene. In addition, benzonitrile, benzyl nitrile and ethylbenzene are produced due to reactions with adsorbed N and H atoms, respectively. These observations establish a clear guide for the possible application of supported Au catalysts in the future.

8:20am **SS1-MoM2 Toward Computational Screening in Heterogeneous Catalysis: Pareto-Optimal Methanation Catalysts, M.P. Andersson**, Technical University of Denmark, Denmark; *T. Bligaard, A. Kustov, K.E. Larsen, J. Greeley, T. Johannessen, C.H. Christensen*, Technical University of Denmark; *J.K. Norskov*, Technical University of Denmark, Denmark

In this work we make the first step towards a computational screening for catalyst materials based on density functional theory and apply it to find new metal alloy materials for the methanation reaction ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$), see e.g. footnote 1. We do so by using the following procedure: First we establish a descriptor for the reaction, which we then use to screen new alloy materials for high activity. The most interesting candidates are investigated in more detail using density functional theory and their methanation activities are finally tested experimentally. The descriptor is chosen based on the fact that there are two key parameters for methanation: The CO dissociation barrier and the stability of the intermediates C and O. These two properties are furthermore linearly related in a so-called Brønsted-Evans-Polanyi (BEP) relation (footnote 3) and we are able to reduce them to a single descriptor, the dissociation energy of CO, which gives the expected volcano shaped curve. We have screened 117 binary alloys by estimating activity and price from interpolation of the bulk composition. We make a simultaneous optimization of both activity and price via a pareto plot (footnote 2) and we predict FeNi and FeNi₃ alloys to be both more active and cheaper than pure Ni catalysts (the current industrial catalysts). Full density functional theory calculations confirm the results of the interpolation scheme. Finally we have investigated the activity towards methanation for Fe-Ni alloys and have found that alloys with 50-75% Ni have an activity better than pure Ni by about a factor of two to three. (FootnoteText@ footnote 1@Sehested J, Dahl S, Jacobsen J, et.al. J. Phys. Chem. B 109, 2432-2438 (2005)@footnote 2@Bligaard T, Johannesson GH, Ruban AV, et.al. Appl. Phys. Lett. 83, 4527-4529 (2003).@footnote 3@Nørskov JK, Bligaard T, Logadottir A. et.al. J. Catal. 209, 275-278 (2002).

8:40am **SS1-MoM3 Double-Bond Isomerization in Cyclic Olefins Adsorbed on Platinum Surfaces., R. Morales, F. Zaera**, University of California, Riverside

The migration & cis-trans isomerization of C=C in olefins is central to many processes in oil refining and food processing. It has been well established that those reactions follow simple half hydrog. and dehydrog. steps according to the Horiuti-Polanyi mech., but that still leaves a number of subtle issues associated with the stereo- & regioselectivity of the reactions involved. For instance, the branched alkyls that may form as intermediates after half hydrog. of substituted olefins may have beta-H in different environments, and elimination of those in the step that regenerates the olefin may lead to different products. Here we show that this is certainly the case with methyl cyclopentenes & methyl cyclohexenes, where the C=C may be in either exo and endo positions. We have studied the chemistry of those compounds on Pt(111) single-crystal surfaces under UHV by means of TPD & RAIRS. Those molecules were chosen because of the particular lability of their allylic H, and because they may offer significance hindrance towards normal olefin adsorption and alkyl-alkene interconversion reactions. It was found that both the C5- and C6-cyclic molecules undergo dehydrog. in a stepwise manner, but with different kinetics depending on the position of the C=C. For instance, while methylene cycloalkanes decompose in four dehydrogenation stages, 1-methyl-1-cycloalkenes display only three distinct

decomposition stages. Also, the molecules with internal C=C proved more stable than those with the unsaturation in the external position, a fact that facilitates the hydrog. of methylene-C5 and methylene-C6 to the corresponding cycloalkanes and their isomerization to 1MC5= and 1MC6=, resp. In addition, it was shown that aromatization reactions, to form benzene or toluene, can be driven at higher temps. It was determined by using RAIRS that ring expansion for the 1MC5= and methylene cyclopentane does not take place via an allylic intermediate, but by the formation of a methylcyclopentadiene species instead.

9:20am **SS1-MoM5 Catalysis Science of Surface Metal Oxide Catalytic Active Sites, I.E. Wachs**, Lehigh University **INVITED**

Surface metal oxide sites represent the catalytic active sites present in oxide-based catalytic materials (zeolites, supported metal oxides, heteropolyoxo anions, bulk mixed metal oxides and clays). Recent in situ and operando Raman, IR and UV-Vis DRS characterization advances are allowing for the complete determination of the molecular and electronic structures of the surface metal oxide catalytic active surface sites under reaction conditions. Combination of the molecular and electronic structural information with the corresponding kinetics of the surface chemistry is allowing, for the first time, the establishment of molecular/electronic structure-activity/selectivity relationships. These fundamental studies with molecularly designed metal oxide catalysts are allowing for the direct determination of the number of catalytic active sites involved in a specific catalytic reaction (one, two or greater), the relative contributions of isolated and polymeric surface metal oxide sites as well as oxide nanoparticles, the role of the oxide support ligand, the effect of cation oxidation state, and the mechanism by which promoters influence specific catalytic reactions.

10:20am **SS1-MoM8 Methanethiol Desulfurization on Titania-Supported Ni Clusters, O. Ozturk, J.B. Park, D.A. Chen**, University of South Carolina

The hydrodesulfurization chemistry of methanethiol has been studied on Ni clusters supported on TiO₂(110). Ni clusters of different sizes and with uniform size distributions have been deposited on the titania substrate and characterized by scanning tunneling microscopy (STM). After heating methanethiol adsorbed on the Ni clusters to various temperatures, high resolution X-ray photoelectron spectroscopy (XPS) studies demonstrate that methyl thiolate is formed as a surface intermediate, and atomic sulfur remains on the surface after methyl thiolate decomposition. Furthermore, the S(2p) binding energies suggest that the surfaces of the Ni clusters have predominantly (110) structure. Temperature programmed desorption (TPD) experiments show that methane and hydrogen are the major gaseous products formed from methanethiol decomposition on Ni clusters of all sizes, and CO is also formed as a minor product via oxidation of atomic carbon by lattice oxygen. Both XPS and TPD studies indicate that the larger, annealed Ni clusters have decreased activity compared to the smaller clusters deposited at room temperature; this loss of activity may be related to partial encapsulation of the Ni clusters by TiO_x upon heating.

10:40am **SS1-MoM9 Chiral Surface Structure and Enantioselectivity, A.J. Gellman**, Carnegie Mellon University; *J.D. Horvath*, Milliken Corp.; *Y. Huang*, Carnegie Mellon University; *A. Koritnik*, University of Michigan

High Miller index metal surfaces with structures lacking mirror symmetry are naturally chiral and have enantiospecific interactions with chiral adsorbates. This set of surfaces spans the interior of the stereographic projection of surface structures. In the case of fcc lattices the chiral surfaces are those that have kink-step-terrace structures. The adsorption of R-3-methylcyclohexanone is enantiospecific in the sense that its desorption energies from the chiral kinks are dependent on the handedness of the kink. The kinks, steps and terraces on the high Miller index surfaces are formed by the (100), (110) and (111) microfacets. Thus there are, in principle, only six types of kinked surfaces dictated by which of the three microfacets forms the kink, step and terrace. R-3-methylcyclohexanone adsorption and temperature programmed desorption has been studied on a set of 9 achiral Cu surfaces and on both the R- and S-enantiomers of a set of 7 chiral Cu surfaces. Six of the chiral surfaces have been chosen to fall within the six zones of the stereographic projection having surface structures formed of the six combinations of kink, step and terrace formed by (100), (110) and (111) microfacets. The desorption spectra of R-3-methylcyclohexanone can be resolved into components arising from desorption from the kinks, the step edges and form the terraces of each of the surfaces. The desorption from the kink sites is enantiospecific in the sense that the R-3-methylcyclohexanone has different desorption energies from the two enantiomers of the surfaces. The enantiospecificity of the

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desorption energies varies from @DELTA@@DELTA@E@sub des@ = 0.2 to 1.0 kJ/mole.

11:00am **SS1-MoM10 Diffusion of Adsorbates: on "Walking" and "Dancing" Molecules**, *K.-Y. Kwon, K.L. Wong, G. Pawin, X. Lin, R. Frisbee, L. Bartels*, University of California at Riverside **INVITED**

We report on the diffusion of individual 9,10-dithioanthracene (DTA) and CO molecules on Cu(111). DTA adsorbs with the aromatic backbone lying flat on the substrate and with both sulfur atoms attached to it. In variable-temperature STM studies, we find that DTA possesses the notable property, that it diffuses exclusive in the direction of its aromatic ring system. It achieves this by moving its substrate linkers in an alternating fashion much resembling bipedal locomotion. Over a wide temperature range we neither find rotation of the molecule in the surface plane nor diffusion perpendicular to the aromatic system. Consequently, an individual molecule is confined to shuttle forward and backward along a straight line albeit the sixfold symmetry of the top substrate layer. We will discuss possible extensions of this work towards breaking of the forward/backward symmetry, transport, etc. DTA forms molecular rows rather than islands on Cu(111). Exchange of the thiol linkers by carbonyl causes these rows to form a mesh resembling a honeycomb with regular "pore" sizes of ca. 50 Angstrom, much larger than the molecule itself. We contrast the behavior of DTA with that of CO on the same surface: CO diffusion was found to be generally isotropic, as expected, and depending on the local coverage. At a local coverage corresponding to one molecule per 20 substrate atoms, CO has a 3 times higher diffusion rate than an isolated molecule. The diffusion barrier for isolated CO molecules was found to be $75 \text{ \AA} \pm 5 \text{ meV}$ at a prefactor of 10 MHz. Time-lapsed STM measurements provide 2D trajectories of the motion of CO molecules and pairs of them. The latter exhibit dominantly tangential diffusion at close CO-CO proximity. Taking into account the diffusion directions as well as the intermolecular distances, the 2D diffusion potential of a CO in the vicinity of another CO can be reconstructed.

11:40am **SS1-MoM12 Comparison of the Stability of Small Molecules On Rh(111) and Rh(553)**, *A. Resta, J. Gustafson, R. Westerström, E. Lundgren, A. Mikkelsen, J.N. Andersen*, Lund University, Sweden

We have studied the adsorption and thermally induced reactions of C@sub 2@H@sub 4@ and C@sub 2@H@sub 5@OH, on Rh(111) and Rh(553) with particular emphasis on the differences induced by the atomic steps present on the vicinal Rh(553) surface. The development of surface species was followed at temperatures ranging from 100 K to 680 K by chemically sensitive high resolution core level photoemission (HRCLS) applied to the adsorbate C1s and O1s and the substrate Rh 3d levels. Comparing results from the two surfaces, we find a number of differences which can be ascribed to reactions occurring in the vicinity of the steps on Rh(553). For C@sub 2@H@sub 4@ we monitor the formation and subsequent decomposition of ethylidyne (CCH@sub 3@) by saturating the surfaces with C@sub 2@H@sub 4@ at 100K followed by annealing at increasingly higher temperatures. We find that both the formation as well as the decomposition of ethylidyne occur at a lower temperature on Rh(553) than on Rh(111). Although HRCLS spectra indicate similar decomposition products on both surfaces, a more detailed analysis suggests significantly different decomposition scenarios on the two surfaces. In similar annealing experiments of a few layers of C@sub 2@H@sub 5@OH we find that the formation of CO, which indicates the breaking of the C-C bond in ethanol, occurs at lower temperature on Rh(553) than on Rh(111). We never observe atomic O or OH-like groups on neither surface. In addition to the temperature differences we also find significantly different fragmentation patterns on the two surfaces. For instance, ethylidyne is shown to form on Rh(111) but is absent from Rh(553).

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