Surface Science
Room 210B - Session SS1-TuA
Hydrocarbon Reactions on Metal Surfaces

Moderator: D.E. Barlow, Naval Research Laboratory

1:20pm **SS1-TuA1 Thermodynamics and Kinetics of Elementary Steps on Surfaces, and their Applications in Modeling Complex Reactions***, **C.T. Campbell**,* University of Washington **INVITED**

Some useful concepts for describing elementary reaction steps on surfaces will be reviewed, and illustrated with example applications to catalytic reactions. First, the characteristics which define a true "elementary step" will be considered. In general, the reaction order is well defined for true elementary steps, and their prefactors can be theoretically estimated with reasonable accuracy using transition state theory and simple concepts of statistical mechanics. Once the prefactor is known, a single absolute rate measurement provides the activation energy, which is thus obtained with good accuracy even when the prefactor used is in error by two orders of magnitude. The net reaction energy often can be measured independently. Examples of doing this with adsorption calorimetry will be reviewed. Recent developments promise to make calorimetric measurements of adsorption energies on single crystal surfaces more common, since they now can be applied to crystals as thick as obtainable by simple mechanical thinning (80 ï�-m). Once the net reaction energy is known for an elementary step, a measurement of its activation energy directly provides that for its reverse step and, through knowledge of statistical mechanics, its equilibrium constant. These kinetic and thermodynamic parameters are invaluable in examining or modeling the rates of complex reaction mechanisms, which in general turn out to depend on the kinetic and thermodynamic parameters of only a few of the many elementary steps involved. A simple method for determining which of the elementary steps are critical, based on the â?odegree of rate controlâ?�, will be described. Work supported by DOE-OBES and NSF.

2:00pm **SS1-TuA3 Recent Advances in the Surface Chemistry of Hydrocarbon Fragments on Transition Metals***, **F. Zaera**,* University of California

A brief review of recent results from our efforts to elucidate the mechanistic details of the surface chemistry of hydrocarbons on transition metal surfaces will be presented. The chemistry of C4 hydrocarbons on Pt(111) single-crystal surfaces will be highlighted, with focus on the steps responsible for double bond migration and cis-trans isomerization in olefins. A comparison will be provided with our previous studies using shorter moieties, and the role of different key intermediates such as alkyls and allyls will be discussed. Insertion reactions will be addressed next. Specifically, the mechanism of chain growth on Ni(110) surfaces will be analyzed in terms of the chemistry of methylene and methyl on that surface. The effect of coadsorbed oxygen on these reactions, as well as the opening of new oxygen incorporation steps, will be discussed. Finally, reference will be made to the surface chemistry of chiral compounds on metals as it relates to enantioselective catalysis.

2:20pm **SS1-TuA4 Enantioselective Reactivity of R-2-bromobutane on Chiral Copper Surfaces***, **D.M. Rampulla**, A.J. Gellman,* Carnegie Mellon University

Enantioselective reactions are integral to most biological chemistry and large-scale pharmaceutical production. Enantioselective reactions require chiral media such as solvents, surfaces, or catalysts of a single handedness. Enantioselective heterogeneous catalysis is a promising method for the preparation of chiral compounds but requires catalytic surfaces with inherently chiral structure. The stepped and kinked high Miller index surfaces of metals are naturally chiral and have been shown to interact enantiospecifically with chiral adsorbates. Enantioselective desorption of small chiral molecules from such surfaces has been demonstrated and studied, but enantioselective reactivity on naturally chiral metal surfaces has not been explored. Temperature Programmed Reaction Spectroscopy (TPRS) has been used to study the decomposition of R-2-bromobutane on the chiral Cu(643)@super R@ and Cu(643)@super S@ surfaces. Alkyl halides, such as R-2-bromobutane adsorb dissociatively to form R-2-butyl groups, which decompose via @beta@-hydride elimination to yield 1- and 2-butenes. The temperatures at which these desorb and the selectivity to 1- and 2-butenes are influenced by the chirality of the copper surfaces. Earlier results of R-2-bromobutane on Cu(531)@super R&S@ surfaces will be discussed and compared with more recent results obtained on the Cu(643)@super R&S@ surfaces.

2:40pm **SS1-TuA5 Stereochemistry in Surface Explosion***, **K.-H. Ernst**, B. Behzadi, R. Fasel, S. Romer,* EMPA Duebendorf, Switzerland

The vast majority of chiral compounds crystallize into racemic crystals. It has been predicted early and was later experimentally established as a rule, that chiral molecules on surfaces are more easily separated into homochiral domains due to confinement into a 2D-plane and lower entropic contributions. We investigated the formation and stability of two-dimensional tartrate lattices on a Cu(110) surface for the racemic mixture by means of temperature programmed desorption (TPD), low energy electron diffraction (LEED), and X-ray photoelectron spectroscopy (XPS). At low coverage, the bitartrate species becomes separated into homochiral domains, but with increasing surface density the monotartrate species forms a closed-packed racemic 2-D crystal. Consequently, the 2-D conglomerate bitartrate phase does not show differences to the enantiopure bitartrate phase with respect to thermal stability. However, the thermally induced autocatalytic decomposition reaction, so-called surface explosion, of the monotartrate species is influenced by the chirality of the adjacent molecules. The racemic mixture undergoes decomposition at a lower temperature than the enantiopure lattice at same coverage and lateral arrangement. This is in contrast to the higher stability of 3D tartaric acid crystals, but is consistent with the observation that homochirality is preferred in hydrogen-bonded self-assembled biomolecular structures.

3:00pm **SS1-TuA6 The Ullmann Coupling Reaction: Atomic Scale Study of the Reactive Intermediates and Products of a Surface Catalyzed Reaction***, **S.U. Nanayakkara**, E.C.H. Sykes, L.C. Fernández-Torres, P. Han, P.S. Weiss,* The Pennsylvania State University

We present an atomic-scale study of the Ullmann coupling reaction on Cu{111} using low temperature scanning tunneling microscopy and spectroscopy. We have studied the reactive intermediates and the products of the Ullmann coupling reaction between bromobenzene molecules, which form biphenyl at room temperature (293 K). Chemical identification of the surface-bound species has been achieved using their tunneling spectroscopic signatures. We demonstrate that bromobenzene molecules dissociatively chemisorb at 293 K and form phenyl intermediates, which travel distances of up to a few 1000 @Ao@ over Cu{111} terraces to bind preferentially at step edges. This preference is due to the anisotropic electron density distribution at the step edges. We identify the surface step edge as the active site of this reaction on Cu{111} for C-C bond formation. Once two phenyl intermediates combine to form biphenyl, these product molecules diffuse onto the terraces and arrange as clusters. Our interpretations of the preferred adsorption sites and the intermolecular interactions of adsorbates are explained in terms of the local electronic perturbations on the surface by surface steps and adsorbates.

3:20pm **SS1-TuA7 Adsorption Energies of Small Alkane Molecules on MgO(100), Pt(111), and C(0001)/Pt(111) by Temperature Programmed Desorption***, **S.L. Tait, Jr.**,* University of Washington*; Z. Dohnálek,* Pacific Northwest National Laboratory*; C.T. Campbell,* University of Washington*; B.D. Kay,* Pacific Northwest National Laboratory

The adsorption of small hydrocarbon molecules at oxide and metal surfaces represents an important scientific problem with applications in catalysis and sensors. We have used molecular beams and temperature programmed desorption (TPD) to study the adsorption of small alkane molecules, C@sub n@H@sub 2n+2@ (n=1-10), on MgO(100), Pt(111), and a two-dimensional graphite film on Pt(111). Hydrocarbon molecules are deposited on the surface by a highly collimated molecular beam with a well-defined incident angle and kinetic energy. The adsorption energies and pre-exponential factors are extracted from TPD data. Simulations based on the results of this analysis show excellent agreement with experiment. The desorption prefactors increase with alkane chain length by more than five orders of magnitude over the range of alkane molecules studied. Adsorption energy on each surface increases linearly with alkane chain length with a y-intercept value near zero. Prior studies have found a non-zero intercept by treating the pre-exponential factor as constant with alkane chain length. This increase in pre-exponential factor can be attributed entirely to the increase in the rotational entropy in the transition state theory, assuming that the adsorbed initial state is not a free rotor but that the transition state is. Pacific Northwest National Laboratory is a multiprogram National Laboratory operated for the U. S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

SLT supported by a UW/PNNL Joint Institute for Nanotechnology fellowship.

3:40pm **SS1-TuA8 Characterization of Ethylidene and Methylidyne on Pt(111) with Infrared Spectroscopy***, **R. Deng**, E. Herceg, M. Trenary,* University of Illinois at Chicago

Hydrocarbon intermediates formed in the adsorption and decomposition of ethylene (C@sub 2@H@sub 4@), diiodomethane (CH@sub 2@I@sub 2@) and iodomethane (CH@sub 3@I) on Pt(111) were investigated using reflection absorption infrared spectroscopy (RAIRS) and mass spectrometry. The ethylidene (CHCH@sub 3@) species is identified on the basis of RAIRS peaks at 2960 cm@super -1@ and 1387 cm@super -1@ that are assigned to the CH@sub 3@ asymmetric stretch and the CH@sub 3@ symmetric bend, respectively. It is found that the highest ethylidene coverage can be produced by ethylene exposure to the surface at temperatures around 280 K. Ethylidene undergoes rapid hydrogenation upon exposure to 2x10@super -7@ Torr of H@sub 2@ at 250 K to produce gas phase ethane, as detected by a mass spectrometer. The results indicate that ethylidene could be an intermediate in ethylene hydrogenation on transition metal surfaces near room temperature. Surface methylidyne can be formed in multiple ways: thermal decomposition of diiodomethane and iodomethane; ethylene decomposition at a temperature of about 500 K; and surface carbon hydrogenation. Methylidyne is identified by a CH (CD) stretch mode at 2956 (2206) cm@super -1@. The co-adsorption of surface hydrogen and iodine causes this band to shift to higher frequency. The observation of methylidyne at 500 K indicates that C-C bond scission of the initially adsorbed ethylene occurs at this temperature.

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