## Surface Science Division
## Room 607 - Session SS2-MoM
### Catalysis on Metals

**Moderator:** J.W. Niemantsverdriet, Eindhoven University of Technology, The Netherlands

8:20am **SS2-MoM1 The Influence of a Catalytic Surface on the Gas Phase Ignition and Combustion of H2+O2***, **M. Försth**, F. Gudmundson, J. Persson, A. Rosén,* Chalmers University of Technology, Sweden

The OH concentration outside a Pt catalyst at 1300K, in a stagnation flow of 90% O@sub 2@ and 10% H@sub 2@, has been studied by Planar Laser Induced Fluorescence, PLIF, and compared to measurements outside a heated glass surface. The total pressure in the system was varied from 0.2 to 120 torr. At low pressure, surface reactions were observed for the Pt surface, but not for the glass. At higher pressure, gas-phase ignition occurred for both systems, but not at the same pressure: ignition occurred at a lower pressure outside the inert glass surface. Computer modeling using CHEMKIN confirmed these results. The difference in gas-phase ignition is also seen in the modelling results, and it is due to the removal of atomic O and H from the gas by adsorption and reaction on the catalytic surface. The catalytic reaction mechanism on the surface plays an important role as it enhances the removal of radicals, compared to a surface where only radical recombination back to reactants is allowed.

8:40am **SS2-MoM2 Catalytic Oxidation of Unsaturated C@sub 3@ Hydrocarbons on the Pt (111) Surface***, **A.M. Gabelnick**, A.T. Capitano, D.J. Burnett,* University of Michigan*; D.A. Fischer,* National Institute of Standards and Technology*; J.L. Gland,* University of Michigan

The catalytic oxidation of unsaturated C3 hydrocarbons (propylene and methylacetylene) has been studied in-situ in oxygen pressures ranging from UHV to 0.01 torr on the Pt(111) surface. Using a combination of kinetic and spectroscopic in-situ fluorescence yield soft X-ray techniques, we have characterized the oxidation of these hydrocarbons based on absolute carbon coverage and identified oxidation intermediates spectroscopically. The adsorbed intermediates for oxidation of preadsorbed propylene, propylene catalytic oxidation (both propylene and oxygen in the gas phase), and methylacetylene oxidation have been characterized. Despite differences in these intermediates, skeletal oxidation begins at the same temperature, indicating a common rate limiting step in the oxidation process. In the catalytic oxidation of propylene, dehydrogenation of propylene occurs prior to skeletal oxidation, even with both propylene and oxygen in the gas phase. In pressures of oxygen, a monolayer of propylene and methylacetylene completely oxidize by 450 K, with skeletal oxidation of both hydrocarbons beginning near 320 K. Quantitative kinetic studies of methylacetylene oxidation over a range of conditions enabled the determination of both the activation energy and order of the reaction in oxygen. Experiments performed with coadsorbed oxygen confirm that O(a) is the oxidizing agent.

9:00am **SS2-MoM3 Thermal Conversion of C@sub 3@ Fragments on Pt(111): Evidence for the Formation of Allylic Intermediates***, D. Chrysostomou, C.R. French, J.M. Guevremont, **F. Zaera**,* University of California, Riverside

Platinacyclobutane was selectively formed on Pt(111) via the thermal activation of adsorbed 1,3-diiodopropane, and the mechanism for its conversion to propene was investigated using temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). Thermal desorption of propene from 1,3-diiodopropane occurs at 370 K. The conversion is suggested to involve the formation of a surface bound allylic intermediate. Allyl iodide was used to investigate the further reactivity of that intermediate, and additional experiments were carried out with propyl iodide and propylene as well. Selective deuteration of 1,3-diiodopropane was explored as a mean to determine the C'H bonds active in the metallacycle to propene conversion, but the usefulness of this approach was limited by extensive scrambling in platinacyclobutane prior to the formation of propene. Propene itself was identified to exist on the surface in three different configurations depending on the coverage: di-sigma bonded, pi bonded, and weakly physisorbed. The results from this work provide new insights into the mechanism of hydrocarbon reforming reactions.

9:20am **SS2-MoM4 Reactions of Methyl Groups on Sn/Pt(111) Alloys***, **B.E. Koel**, H. He,* University of Southern California

Reactions of alkyl intermediates are important in many catalytic hydrocarbon reactions over metal and metal alloy surfaces. Reactions of adsorbed CH@sub 3@ (methyl) groups, formed using a pyrolytic azomethane source to produce incident methyl radicals, on two ordered Sn/Pt(111) surface alloys have been studied using HREELS, UPS, TPD, AES and XPS. Chemisorbed CH@sub 3@ species are identified at low doses but longer chain hydrocarbons can be formed at high doses on both Sn/Pt(111) surfaces at 100 K. Chemisorbed methyl groups are characterized by a prominent peak in UPS at 8 eV BE (CH@sub 3@ HOMO) and a strong peak in HREELS at 1240 cm@super -1@ from the @delta@@sub s@(CH@sub 3@) mode. These studies show that alloyed Sn decreases the dehydrogenation rates of akyl groups on Pt(111) surfaces and enables other C-C bond coupling reactions to occur. Alkane and alkene products were desorbed below 200 K in TPD for both Sn/Pt(111) surface alloys. On the (2x2) alloy, only CH species are stable at 300 K, and these react to desorb CH@sub 4@ at 432 K. TPD after methyl dosing on the (@sr@3x@sr@3)R30° alloy at 300 K gave only one very sharp CH@sub 4@ desorption peak at 453 K, and we propose that this arises from decomposition of CH@sub 3@CH species. The chemistry of Pt-Sn alloy surfaces leads to much lower carbon buildup than on Pt surfaces from thermal reactions of alkyl adsorbates.

9:40am **SS2-MoM5 Mechanisms and Dynamics in Millisecond Chemical Reactors***, **L.D. Schmidt**,* University of Minnesota **INVITED**

It is possible to carry out the partial oxidation of alkanes in reactors with residence times less than 10@super -3@ sec above atmospheric pressure and obtain almost complete conversions with high selectivities to products such as H@sub 2@ and CO, olefins, and oxygenated hydrocarbons. These processes involve extremely large temperature and concentration gradients (10@super 6@ K/sec and 10@super 4@ atm/sec), and at temperatures above 1300K where adsorption lifetimes are typically 10@super -9@ sec. For the oxidation of ethane to ethylene, we can obtain 85% selectivity to ethylene with less than 5% CO and CO@sub 2@, even though at equilibrium CO should be the dominant product. These reactions occur on a PtSn catalyst surface which consists of ~10 µm single crystal particles exposing large facets. EDX and XRD of these catalysts show that they consist entirely of intermetallic PtSn compounds with no free Pt phases. This is accomplished by adding large amounts of H@sub 2@ in a ratio of H@sub 2@/O@sub 2@=2. With this feed, the surface reaction forming H@sub 2@O occurs within the first 100 µsec on the first mm of catalyst, while minimizing ethane oxidation. This consumes all O@sub 2@ leaving ethane dehydrogenation which generates as much H@sub 2@ as is fed to the reactor. At 1300K with 10@super -9@ sec adsorption times and very high reactive fluxes, these processes deviate considerably from conventional catalytic reaction conditions, and these processes may involve partially equilibrated internal states of molecules. Implications of nonequilibrium reaction dynamics at extreme these conditions will be considered.

10:20am **SS2-MoM7 In-situ Studies of C-C Hydrogenolysis in Cyclopropane on Platinum using a Combination of Soft X-ray Methods***, A.T. Capitano, A.M. Gabelnick,* University of Michigan*; D.A. Fischer,* National Institute of Standards and Technology*; **J.L. Gland**,* University of Michigan

In-situ studies fluorescence soft X-ray studies clearly show that a propyl intermediate plays an important role during cyclopropane hydrogenolysis to form propane over the Pt(111) surface. Through a combination of spectroscopic and in-situ catalytic studies, a complete picture of hydrogen induced C-C bond breaking mechanisms during cyclopropane hydrogenolysis has been developed. Molecular cyclopropane is adsorbed in a tilted configuration and desorbs in the 130 K temperature range. Preadsorbed cyclopropane desorbs before reacting with hydrogen, even for pressures as high as 0.02 torr. When both cyclopropane and hydrogen are present in the gas-phase, propane is formed above 300 K. In this temperature range, in-situ soft X-ray studies of the adsorbed species show that a propyl intermediate is formed. The coverage and stoichiometry of this intermediate has been characterized over a range of temperatures and reactant ratios. For large excesses of hydrogen, the average hydrogen stoichiometry of the adsorbed species increases with increasing temperature while the amount of carbon remains constant. Characterization of the dominant intermediate at 300 K with FY-NEXAFS indicates that the hydrogenated intermediate is an adsorbed propyl species. Detailed isothermal kinetic studies were used to establish both the activation energy and prefactor for hydrogenation of this intermediate.

During in-situ catalytic studies, an additional C@sub 3@ adsorbed species is observed in the 150 K temperature range. By using FY-NEXAFS, the structure and bonding of this intermediate has been characterized and is consistent with adsorbed cyclopropyl-like. These exciting results have clearly established for the first time under catalytic conditions that C-C bond breaking in cyclopropane proceeds via sequential hydrogen addition.

10:40am **SS2-MoM8 Direct Evidence of Surface Intermediates from the Reactions of C@sub 3@ Hydrocarbons on Cu(100)***, **H. Celio**, K.C. Smith, J.M. White,* University of Texas, Austin

Using reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD), we have characterized important intermediates of the thermal and electron-induced surface chemistry of C3 hydrocarbons on Cu(100). The molecules that have been studied include allyl bromide, allyl chloride, propene, and cyclopropane. We find that the allyl halides dissociate to form pi-bonded allyl groups and halogen atomns at a wide temperature range (110-350 K). Furthermore, we observed an exceptionally facile carbon-carbon coupling between allyl bromide and pi-bonded allyl groups that lead to the formation of 1,5-hexadiene at 110 K. Conversely, allyl chloride principally forms pi-bonded allyl groups, which remained inert in the presence of allyl chloride molecules on the second layer. The implications of the dissimilar surface reactions of these allyl halides are discussed in terms of an Eley-Rideal rather than a diffusion-limited reaction. Electron irradiation (<50 eV) of weakly adsorbed cyclopropane lead to the formation of metallacyclobutane and cyclopropyl groups at 100 K. The thermal chemistry of the latter products yield propene but not pi-bonded allyl groups. The results of the allyl halides and cyclopropane are also compared and discussed for Ag(111).

11:00am **SS2-MoM9 Carbon-Carbon Coupling from Formaldehyde Reaction on Mo(110)***, K.T. Queeney,* Harvard University*; **C.R. Arumainayagam**,* Wellesley College*; C.M. Friend,* Harvard University

Formaldehyde (CH@sub 2@O) reaction on Mo(110) was studied with temperature programmed reaction and infrared reflectance absorbance spectroscopy. We present preliminary results which demonstrate the evolution of gas-phase ethylene from the formaldehyde reaction, to the best of our knowledge the first example of carbon-carbon bond formation on clean Mo(110). This reaction is proposed to proceed via an ethylene dialkoxide intermediate, analogous to that formed during reaction of ethylene glycol on Mo(110). Other reactions include hydrogenation of CH@sub 2@O to form a methoxy intermediate which subsequently undergoes C-O bond scission to evolve gas-phase methyl radicals at ~600 K.

11:20am **SS2-MoM10 Adsorption of Propylene Oxide on Pt(111) Surfaces and its Reactions with Gaseous and Adsorbed H Atoms***, A. Dinger, C. Lutterloh, **J. Biener**, J. Küppers,* Universität Bayreuth, Germany

The adsorption of propylene oxide (PO) on Pt(111) surfaces and its reactions with gaseous and adsorbed H atoms, respectively, was studied with TDS and HREELS methods. Monolayer PO desorbs near 180 K, while multilayer PO desorbs at 130 K. Approximately 50% of the monolayer PO molecules dissociate leading to the desorption of CO and H@sub 2@. The decomposition of PO is initiated by a cleavage of the C-O-C ring. Gas phase H atoms react with PO monolayers on Pt(111) to n-propanol, i-propanol, and acetone with the latter as a minor product and about equal amounts of the alcohols. On the other hand, the reaction between PO and coadsorbed hydrogen leads to the selective formation of acetone.

11:40am **SS2-MoM11 Interaction of Atomic Hydrogen and Deuterium with the Ir(111)-p(1x1)-H, Ir(111)-p(1x1)-D, and Ir(111)-p(1x2)-O Surfaces***, **C.J. Hagedorn**, M.J. Weiss, W.H. Weinberg,* University of California, Santa Barbara

The interaction of gas phase atomic hydrogen and deuterium with chemically modified Ir(111)-p(1x1)-D, Ir(111)-p(1x1)-H, and Ir(111)-p(1x2)-O surfaces at cryogenic temperatures has been studied using thermal desorption mass spectrometry and high-resolution electron energy loss spectroscopy. Although the Ir(111)-p(1x2)-O surface at a temperature of 90 K is passivated with respect to exposure to gas phase H@sub 2@ and D@sub 2@, the interaction of gas phase atomic H and D with this surface at 90 K results in the subsequent desorption of water in thermal desorption spectra. These results suggest that the dissociative chemisorption of molecular hydrogen on Ir(111) is precluded by the presence of the (1x2)-O oxygen overlayer, whereas energetically "hot" gas phase atomic hydrogen reacts readily with this oxygen modified surface. Moreover, a strong isotope effect has been observed in the interaction of gas phase atomic H and D with deuterium and hydrogen modified surfaces. The abstraction cross section for atomic D interacting with the Ir(111)-p(1x1)-H surface to form HD is approximately a factor of two greater than that for atomic H interacting with the Ir(111)-p(1x1)-D surface. This difference between the abstraction cross sections can be explained qualitatively by considering the differences associated with the expected zero point energy of the transition state for the abstraction reaction and the differences associated with the zero point energy between H and D adatoms.

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