

# Thursday Morning, November 3, 2011

Surface Science Division  
Room: 107 - Session SS-ThM

## Oxide Surface Structure & Reactivity

Moderator: G.A. Kimmel, Pacific Northwest National Laboratory

8:00am **SS-ThM1 Bond Activation of Alkanes on CaO(100)**, A. Chakradhar, U. Burghaus, North Dakota State University

The molecular and dissociative adsorption kinetics, respectively, of ethane, butane, pentane, and hexane are studied on CaO(100) using thermal desorption spectroscopy (TDS) and Auger electron spectroscopy (AES). After adsorption/desorption cycles, AES scans show no carbon residuals on the surface. Molecular adsorption as well as bond breaking is observed for all alkanes studied, except for ethane. Molecular desorption of these alkanes is characterized by two TDS peaks while recording the parent mass. These two features are assigned to different adsorption sites/configurations of the alkanes. In addition, the binding energies of the bound alkanes, based on their desorption temperatures, are calculated by using Redhead equation. The bond activation is evident from desorption of hydrogen and mostly methane and ethylene fragments in multi-mass TDS experiments. Bond activation of hydrocarbons is pertinent for the petroleum industry, providing transportation fuels and other petrochemical products.

8:20am **SS-ThM2 Reaction Chemistry of Methyl and Methylene Species on Cr<sub>2</sub>O<sub>3</sub>(0001)**, Y. Dong, D.F. Cox, Virginia Tech

The reactions of methyl (CH<sub>3</sub>) and methylene (CH<sub>2</sub>) surface species formed from the dissociation of halogenated methanes have been studied with temperature programmed desorption over Cr<sub>2</sub>O<sub>3</sub>(0001). Methyl fragments undergo a rate-limiting dehydrogenation to methylene and produce methane (CH<sub>4</sub>) and ethylene (CH<sub>2</sub>=CH<sub>2</sub>) as the primary products. Comparison to earlier results for the Cr<sub>2</sub>O<sub>3</sub>(1012) surface show that methyl dehydrogenation is a structure-insensitive reaction, with the barrier to dehydrogenation being insensitive to the surface cation coordination number and/or local Cr-O site pair geometry. The ethylene formed from the dehydrogenation of CH<sub>3</sub> is associated with the surface diffusion of methylene species and subsequent coupling (C-C bond formation) reactions.

Separate studies of the reaction of methylene show that surface diffusion and coupling to ethylene can occur at lower temperatures than required for CH<sub>3</sub> dehydrogenation. The diffusion-limited coupling of CH<sub>2</sub> appears to be a structure-sensitive reaction, with the barrier to surface diffusion about 25 kJ/mol higher on Cr<sub>2</sub>O<sub>3</sub>(0001) than the (1012) surface.

8:40am **SS-ThM3 Organometallics as Probes of Functional Group Distribution on Oxide Surfaces**, S.L. Scott, University of California, Santa Barbara **INVITED**

The reactivity of the hydroxyl-terminated surface of silica is important for constructing tailored interfaces in many applications, including catalysis, separations, and microelectronics. Amorphous silicas are particularly interesting because of their high surface areas. The hydroxyl content of their surfaces can be reduced thermally, but it decreases slowly because the hydroxyls have very low mobility. Their mutual condensation requires proximity, and, frequently, the formation of strained siloxane rings. Since these silicas have no long-range order, it is often postulated that the hydroxyl groups are distributed randomly, and that when the nominal hydroxyl density is low (e.g., after thermal treatment at temperatures exceeding 500 °C), these hydroxyls can be considered essentially isolated. Curiously, the Ga K-edge EXAFS shows that the reaction of Ga(CH<sub>3</sub>)<sub>3</sub> with such a silica pretreated at 800 °C generates only digallium sites, requiring that the hydroxyls be organized pair-wise, likely as vicinal silanols linked by a single siloxane bond. The origin of the preferred vicinal disposition may be hydrolysis of a strained siloxane bond. Where isolated hydroxyls do exist, they appear to be located on reactive 2-rings whose reactivity resembles that of a masked silanol. Consequently, it is unwise to assume that site isolation results from grafting onto these silicas, although the vicinal disposition of silanols provides an opportunity to create tailored bifunctional surfaces.

9:20am **SS-ThM5 Are MgO Thin Films More Reactive Than Bulk MgO Surfaces?**, G. Cabailh, R. Lazzari, H. Cruguel, J. Jupille, UPMC and CNRS, France, L. Savio, IMEM-CNR, France, M. Smerieri, A. Orzelli, L. Vattuone, M. Rocca, Università di Genova, Italy and IMEM-CNR, France  
The ubiquity of the interface between water and oxide materials has prompted a tremendous activity to determine the adsorption mechanisms at

the microscopic scale on crystalline surfaces of simple oxides. Among these, magnesium oxide MgO offers the advantage of having various morphologies of good crystalline quality, involving cleaved crystal surfaces, high surface area samples and supported films, all of these dominated by the low index (100) orientation. On bulk MgO, the fivefold coordinated atoms of the basal (100) surface do not dissociate isolated H<sub>2</sub>O molecules. Conversely, H<sub>2</sub>O is easily dissociated at low-coordinated sites such as steps and kinks. A puzzling case is the adsorption of H<sub>2</sub>O on metal-supported MgO films in the submonolayer range of which coverage by OH groups has been estimated to be 60 to 70% of a monolayer [1,2]. Similar OH coverages were obtained by aging freshly prepared films in the residual atmosphere of the vacuum chamber [1], although the observation was contradicted by the finding of a more modest effect that cast doubt on OH being the cause of aging [2]. The extraordinary uptake of OH groups was attributed to the peculiarities of the electronic properties of the thin supported MgO films [3]. However, density functional theory hardly supports this view. Little changes in both the electronic structure and the capacity to dissociate H<sub>2</sub>O are predicted for monolayer-thick MgO(100) islands that, at variance with experiment, are only expected to dissociate H<sub>2</sub>O molecules along their borders [4].

In an attempt to solve the discrepancies between experiments and between experiment and simulation, MgO films of different stoichiometry were grown on Ag(100) by reactive deposition of Mg in an O<sub>2</sub> partial pressure, prior to being exposed to H<sub>2</sub>O vapor and/or aged in vacuum [5]. Films were observed by scanning tunneling microscopy (STM) and water uptake was analyzed by x-ray photoemission spectroscopy (XPS). The stoichiometry and, consequently, the chemical activity towards hydroxylation of the MgO(100) films, was shown to strongly depend on the O<sub>2</sub> pressure during the film growth. Oxygen-deficient films undergo dramatic oxygen uptake either by exposure to H<sub>2</sub>O or by aging in vacuum. Conversely, on stoichiometric MgO islands, XPS analysis and STM images are consistent with the prediction that H<sub>2</sub>O only dissociates at the island edges.

- [1] S. Altieri et al., Phys. Rev. B. 76 (2007) 205413.
- [2] L. Savio et al., J. Phys. Chem. B 108 (2004) 7771.
- [3] S. Altieri et al., Thin Solid Films 400 (2001) 9.
- [4] A. M. Ferrari et al., Phys. Chem. Chem. Phys. 9 (2007) 2350.
- [5] G. Cabailh et al., J. Phys. Chem. C, in press (2011).

9:40am **SS-ThM6 The Adsorption of Silver on Fe<sub>3</sub>O<sub>4</sub>(111) Studied by Adsorption Microcalorimetry, LEIS, and AES**, J.C. Sharp, Y.X. Yao, C.T. Campbell, University of Washington

Noble metals supported on oxide surfaces are of interest due to their catalytic activity and their sintering resistance is a subject of concern in terms of their long-term stability under reaction conditions. The heat of adsorption of silver on Fe<sub>3</sub>O<sub>4</sub>(111) grown on Pt(111) was measured using adsorption microcalorimetry, and its growth morphology was measured with low-energy ion scattering spectroscopy (LEIS) and Auger electron spectroscopy (AES). The initial sticking was 0.96 rising to 0.99 after 1 monolayer of Ag deposited. The LEIS and AES data were fitted to a hemispherical cap model for the Ag nanoparticles, which were found to grow with a particle density of  $4 \times 10^{12}$  particles per cm<sup>2</sup>. The initial heat of adsorption was found to be 220 kJ/mol, rising to 285 kJ/mol after 1 monolayer of deposited Ag. From these data, we extracted the energy of metal atoms versus the Ag particle size to which they attach on Fe<sub>3</sub>O<sub>4</sub>(111), and compare it to results on other single crystalline oxide surfaces.

10:40am **SS-ThM9 Properties of TiO<sub>2</sub> Nanoparticle Arrays Functionalized with Pt Photodeposition**, Y. Liu, J. Taing, M. Cheng, University of California, Irvine, H. Bluhm, Lawrence Berkeley National Laboratory, J.C. Hemminger, University of California, Irvine

Titanium(IV) oxide (TiO<sub>2</sub>), acting as a stable support for photocatalysts and sensitizers, has applications in catalysis and energy science. Metal nanoparticles supported on TiO<sub>2</sub> have been shown to have unusual reactivity. The deposition of metal nanoparticles can alter the electronic properties of the TiO<sub>2</sub> nanoparticles. To understand the influence of metal deposition, we photodeposit platinum (Pt) onto ordered linear arrays of TiO<sub>2</sub> nanoparticles grown at the step edges of highly oriented pyrolytic graphite. X-ray photoelectron and absorption spectroscopies were used to explore the electronic structure of the TiO<sub>2</sub> nanoparticle arrays with and without photodeposited Pt. The titanium L-edge spectra, supported by multiplet calculations, provide crucial information about crystal field effects, atomic multiplet interactions, and the phase of the TiO<sub>2</sub> particles. Valence photoemission results and band structure calculations using density-functional theory indicate a narrowing of the TiO<sub>2</sub> band gap when Pt is loaded onto the TiO<sub>2</sub> nanoparticle surface. This suggests that Pt

photodeposition onto linear TiO<sub>2</sub> nanoparticle arrays may enhance the solar absorption of TiO<sub>2</sub> due to narrowing of the TiO<sub>2</sub> bandgap.

11:00am **SS-ThM10 Atomic-scale Structure of the Polar Spinel MgAl<sub>2</sub>O<sub>4</sub>(100) Surface**, *M.K. Rasmussen, K. Meinander*, Aarhus U., Denmark, *A.S. Foster*, Tampere Univ. of Tech., Finland, *B. Hinemann*, Haldor Topsøe A/S, Denmark, *F.F. Canova*, Tampere Univ. of Tech., Finland, *S. Helveg*, Haldor Topsøe A/S, Denmark, *N.M. Martin, J. Knudsen*, Lund U., Sweden, *A. Vlad*, Max-Planck-Institut für Metallforschung, Germany, *E. Lundgren*, Lund U., Sweden, *A. Stierle*, Max-Planck-Institut für Metallforschung, Germany, *F. Besenbacher, J.V. Lauritsen*, Aarhus U., Denmark

Metal oxide spinels are an important class of materials in both ceramics technology and materials science. Although the prototypical ternary metal oxide spinel, magnesium aluminate spinel (MgAl<sub>2</sub>O<sub>4</sub>), is widely used, for instance, as a membrane in solid oxide fuel cells and in heterogeneous catalysis, either as a support for active metal nanoclusters or as a catalyst in its own right [1], many of the intricate details of its surface structure still remain unresolved. The atomic-scale surface characterization of similar spinel-type metal oxides has generally been challenging, due to the insulating nature of these materials, a property which limits the use of many standard surface science techniques.

Using a combination of non-contact atomic force microscopy (NC-AFM) and surface X-ray diffraction (SXRD), coupled together with density functional theory (DFT) structure calculations and NC-AFM simulations based on DFT, we have unraveled the complex structure of the polar MgAl<sub>2</sub>O<sub>4</sub> (100) surface. Surprisingly, we find that the surface is terminated by an Al and O-rich structure, with a thermodynamically favored amount of Al atoms interchanged with Mg. These cation antisites, which are low-density defects in the bulk, may be a key element in determining the substrate properties of MgAl<sub>2</sub>O<sub>4</sub>, among others its basicity and the likelihood for formation of OH-groups, which are believed to be anchoring sites for metallic nanoclusters, such as Ni, commonly used in steam reforming catalysts.

[1] J. R. Rostrup-Nielsen, J. Sehested, and J. K. Nørskov, *Adv. Catal.* **47**, 65 (2002).

11:20am **SS-ThM11 Growth and Characterization of Cu/ZnO on Au(111) as a Model Catalyst System**, *X. Deng, J. Lee, C. Matranga*, National Energy Technology Laboratory

Model Cu/ZnO catalysts have been grown on a single crystal Au(111) substrate and characterized with X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). Growth of ZnO on Au(111) is achieved by oxidation of Zn that has been deposited onto the substrate or by reactive evaporation of Zn in the presence of an oxidizer. XPS confirms that Zn has been oxidized and STM reveals that ZnO forms a uniform overlayer on Au(111) with an apparent height of ~6 Å. STM also reveals that the ZnO overlayer on Au(111) forms an ordered hexagonal Moiré pattern with a periodicity of 25 Å, possibly due to the lattice mismatch between the oxide and growth substrate. The atomic structure of the ZnO overlayer is also resolved with STM, showing a hexagonal unit cell with a lattice constant of 3.2 Å. Cu is then deposited onto the ZnO overlayer by evaporation, and STM is used to characterize the structure and morphology of the Cu/ZnO system. The model Cu/ZnO on Au(111) system will be compared to “real world” Cu/ZnO catalysts used for CO<sub>2</sub> hydrogenation and low temperature water gas shift reactions.

11:40am **SS-ThM12 Iron Oxide Growth on YSZ(001) and YSZ(111)**, *I. Ermanoski, G.L. Kellogg*, Sandia National Laboratories

We have used low energy electron microscopy (LEEM) to study in real time the growth of iron oxides on the fully oxidized and partially reduced (001) and (111) surfaces of yttria-stabilized zirconia (YSZ). The FeO<sub>x</sub>-YSZ system is currently used as a working material for solar thermochemical splitting of H<sub>2</sub>O and CO<sub>2</sub> [1], but little fundamental information is available concerning the structure and composition of the mixed oxides and their surfaces. Upon Fe deposition in ~10<sup>-6</sup> Torr of O<sub>2</sub> background pressure, iron oxides grow on the surface. Low energy electron diffraction (LEED) patterns, dark field LEEM imaging, and LEEM I-V measurements show that the composition and morphology of the surface oxide is very diverse, and depends on the substrate stoichiometry, crystallographic orientation, as well as on the deposition conditions and film thickness.

This work was supported by the LDRD program at Sandia National Laboratories, in the form of a Grand Challenge project entitled Reimagining Liquid Transportation Fuels: Sunshine to Petrol. Sandia is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Company, for the U.S. Department of Energy's NNSA under contract DE-AC0494AL85000.

[1] Diver, R.B., Miller, J.E., Allendorf, M.D., Siegel, N.P., Hogan, R.E., “Solar thermochemical water-splitting ferrite-cycle heat engines”, *Journal of Solar Energy Engineering*, **130** (2008) 041001

# Authors Index

**Bold page numbers indicate the presenter**

## — B —

Besenbacher, F.: SS-ThM10, 2  
Bluhm, H.: SS-ThM9, 1  
Burghaus, U.: SS-ThM1, 1

## — C —

Cabailh, G.: SS-ThM5, 1  
Campbell, C.T.: SS-ThM6, 1  
Canova, F.F.: SS-ThM10, 2  
Chakradhar, A.: SS-ThM1, **1**  
Cheng, M.: SS-ThM9, 1  
Cox, D.F.: SS-ThM2, 1  
Cruguel, H.: SS-ThM5, 1

## — D —

Deng, X.: SS-ThM11, **2**  
Dong, Y.: SS-ThM2, **1**

## — E —

Ermanoski, I.: SS-ThM12, **2**

## — F —

Foster, A.S.: SS-ThM10, 2

## — H —

Helveg, S.: SS-ThM10, 2  
Hemminger, J.C.: SS-ThM9, 1  
Hinnemann, B.: SS-ThM10, 2

## — J —

Jupille, J.: SS-ThM5, **1**

## — K —

Kellogg, G.L.: SS-ThM12, 2  
Knudsen, J.: SS-ThM10, 2

## — L —

Lauritsen, J.V.: SS-ThM10, 2  
Lazzari, R.: SS-ThM5, 1  
Lee, J.: SS-ThM11, 2  
Liu, Y.: SS-ThM9, **1**  
Lundgren, E.: SS-ThM10, 2

## — M —

Martin, N.M.: SS-ThM10, 2  
Matranga, C.: SS-ThM11, 2  
Meinander, K.: SS-ThM10, **2**

## — O —

Orzelli, A.: SS-ThM5, 1

## — R —

Rasmussen, M.K.: SS-ThM10, 2  
Rocca, M.: SS-ThM5, 1

## — S —

Savio, L.: SS-ThM5, 1  
Scott, S.L.: SS-ThM3, **1**  
Sharp, J.C.: SS-ThM6, **1**  
Smerieri, M.: SS-ThM5, 1  
Stierle, A.: SS-ThM10, 2

## — T —

Taing, J.: SS-ThM9, 1

## — V —

Vattuone, L.: SS-ThM5, 1  
Vlad, A.: SS-ThM10, 2

## — Y —

Yao, Y.X.: SS-ThM6, 1