Surface Science
Room: Hall D - Session SS-TuP

Surface Science Poster Session

SS-TuP1 A Study of a Hydrogen Atom on Pd-Ag Alloy Surfaces Via First Principles Calculation, ***N. Ozawa***, *T. Roman, H. Nakanishi, H. Kasai*, Osaka University, Japan

Technology for extracting hydrogen gas with high purity from natural gases is necessary for the establishment of a hydrogen fuel system. At present, since materials used for permeable films such as Pd are rare and expensive, a fundamental understanding about reaction processes of hydrogen on metal surfaces is necessary for developing an alternative material replacing with them. On the time, we have studied the elementary reaction processes of a hydrogen atom on Pd surfaces and its subsurface[1-4] using first principles calculations. In particular, we have given focus on quantum mechanical behaviors of the hydrogen atom motion, which appear due to the small mass of hydrogen. In this study, we investigate the quantum states of the hydrogen atom on the PdAg alloy surface and in its subsurface by calculating the wave functions and the eigen energies for the hydrogen atom motion within the framework of the variation method on an adiabatic potential energy surface (PES) obtained from the first principles calculations.[5,6] From these researches, we discuss the behavior of the hydrogen atom such as adsorption and diffusion. We find that the adsorption energy of the hydrogen atom on the surface and activation energy for diffusion into the subsurface area are smaller than on pure Pd surfaces. In this conference, we also discuss the hydrogen atom behavior on the other kinds of Pd-based alloy surfaces.

[1] H. Kasai and A. Okiji, Prog. Surf. Sci. 44, 101 (1993).

[2] K. Nobuhara, H. Kasai, W. A. Diño, H. Nakanishi and A. Okiji, Jpn. J. Appl. Phys. 42, 4630(2003).

[3] N. B. Arboleda Jr., H. Kasai, K. Nobuhara, W. A. Diño, and H. Nakanishi, J. Phys. Soc. Jpn. 73, 745 (2004).

[4] N. Ozawa, N. B. Arboleda Jr., K. Nobuhara, W. A. Dino, H. Nakanishi and H. Kasai, J. Appl. Phys. 101, 123530 (2007).

[5] N.Ozawa, N. B. Arboleda Jr., T. A. Roman, W. A. Diño, H. Nakanishi and H. Kasai, J. Phys.: Condens. Matter 19, 365214 (2007).

[6] N. Ozawa, N. B. Arboleda Jr., H. Nakanishi, S. Shimoji, and H. Kasai, Surf. Interface Anal. In print.

SS-TuP2 Size-Dependent Surface Chemistry of Alumina Nanoparticles, ***P.L. Brazee***, Smith College, *D.M. Dukes, L. Schadler*, RPI, *K.T. Queeney*, Smith College

The particle size of a number of different oxide materials has been found to influence cell adhesion and growth; specifically, nanophase (rather than conventional micron-sized) particles enhance these processes. The increased adsorption of proteins to nanophase particles has been implicated in this size-dependent phenomenon. The current study focuses on the surface chemistry of alumina particles as a function of average particle size, specifically to determine whether or not there are size-dependent differences in surface chemical species that may affect protein (and other biomolecule) adsorption. Alumina nanoparticles of varying phase and diameter were spin-coated onto silicon substrates and their uniformity characterized via SEM and XPS. The distribution of surface hydroxyl (OH) species was analyzed via transmission infrared (IR) spectroscopy. The OH stretches observed for all alumina samples are signficantly redshifted (~200 cm^{-1}) from the frequencies observed for dried alumina powders (e.g. using diffuse reflectance IR). While a common cause of such redshifting in ν(OH) peaks is hydrogen bonding with surface water, the spin-coated samples do not exhibit the concomitant peak broadening associated with this kind of hydrogen bonding. We propose that the unique ν(OH) signatures of spin-coated alumina particles arise from discrete hydrogen bonding interactions between alumina hydroxyls and surface silanols on the underlying silicon substrate. Differences in the OH-stretching peaks for different phases (e.g. γ vs. α) of alumina provide evidence that these features do, in fact, arise from the alumina particles themselves. We do in fact see a size dependence in the distribution of surface hydroxyl species, with distinct populations of different OH species arising from conventional vs. nanophase alumina of all phases studied. These differences are likely to arise from different relative populations of edge vs. facet sites as a function of particle size.

SS-TuP3 Surface Electronic Structure of Epitaxial La_2NiMnO_6 and La_2CoMnO_6 Films Grown on $SrTiO_3$(100), ***H. Geisler***, *C.A. Ventrice*, Texas State University, *Y. Losovyj*, Louisiana State University, *K. Chetry, A. Gupta*, University of Alabama

The surface electronic structure of thin films of the double perovskites La_2NiMnO_6 and La_2CoMnO_6 have been measured using ultra-violet photoelectron spectroscopy at the CAMD synchrotron. Both La_2NiMnO_6 and La_2CoMnO_6 are magnetic semiconductors with magnetic transition temperatures in their bulk phases of 280 K and 226 K, respectively. The thin films were grown on $SrTiO_3$(100) substrates using pulsed laser deposition. To prepare the clean surfaces before photoemission measurements, the samples were sputtered with 1 keV Ar ions and annealed at ~400 °C in an O_2 atmosphere of 10^{-6} Torr. Angle-resolved photoemission measurements of both surfaces show very little dispersion of the valence emissions. Annealing the surfaces in ultra-high vacuum results in a shift of the valence features away from the Fermi level, indicating that loss of surface oxygen results in an n-type doping of these surfaces.

SS-TuP4 X-ray Photoelectron Study of Polycrystalline Samples Type $SeCuO_3$ and $SeMnO_3$ Perovskites, ***L. Huerta***, *R. Escamilla*, Universidad Nacional Autónoma de México, *M. Flores*, Universidad de Guadalajara, México, *E. Morán, M. Alario-Franco*, Universidad Complutense, España

Polycrystalline samples type $SeCu_{1-x}Mn_xO_3$ perovskites were studied by x-ray photoelectron spectroscopy (XPS). The XPS spectra revealed Se, Cu and Mn oxides on the surface of the samples, mainly SeO_2, CuO and MnO. After with great periods of etching time the intensity of SeO_2, CuO and MnO decreased. The Se 3d, Me $2p_{3/2}$ (Me = Cu, Mn), Me 3d and O 1s spectral lines associated to the chemical states $SeMO_3$ were identified and they do not change with increased of etching time.

SS-TuP5 A STM Study of Pt Nanoparticles Deposited on CeO_x(111) Thin Films, ***P.J. Riedel***, *J. Zhou*, University of Wyoming

Ceria-supported Pt nanoparticles are widely used in many important applications, including three-way automobile emission-control catalysis and fuel cells owing to the peculiar redox properties and oxygen storage capacity of ceria as well as the synergistic effect between the Pt and ceria. Previous chemistry studies using XPS and TPD in the literature have demonstrated that the reactivity of ceria-supported Pt nanoparticles is dependent on the cerium oxidation state. To elucidate the nature of their reactivity, we investigated their structure and morphology using STM. Reducible CeO_x(111) thin films were grown in situ on Ru(0001) under ultrahigh vacuum conditions. Our data demonstrate that surface structures of ceria thin films are dependent on the degree of ceria reduction. Fully oxidized CeO_2(111) film exhibits a fairly low density of point defects due to the formation of oxygen vacancies. However, the number of surface defects increases as the ceria film is reduced. Pt particles were vapor-deposited onto ceria thin films at 300 K. The growth of Pt particles was investigated by STM as a function of metal coverage, post-deposition annealing temperatures, as well as Ce oxidation state, which were further compared to the growth of Rh and Pd. The research is sponsored by the start-up fund at the University of Wyoming and the Wyoming NASA Space Grant.

SS-TuP6 Growth and Reactivity of Pt-Au Bimetallic Nanoclusters Supported on TiO_2(110), ***J.S. Ratliff***, *J.B. Park, S.A. Tenney, S.F. Conner, D.A. Chen*, University of South Carolina

Pure Pt, pure Au, and bimetallic Pt-Au clusters were deposited on TiO_2(110) at room temperature and studied with scanning tunneling microscopy, low energy ion scattering, and temperature programmed desorption. Pt forms smaller clusters with higher cluster densities than Au for the same metal coverage. Bimetallic Pt-Au clusters were formed by seeding Au at existing Pt clusters. The growth of Au on Pt seed clusters was confirmed by a decrease in cluster density upon dosing Au onto 0.25 monolayers (ML) of Pt. For the growth of Au on Pt seed clusters, the average cluster size increases and cluster density decreases with increasing Au coverage. Low energy ion scattering spectroscopy confirms that both Pt and Au are at the surface of the clusters, even at 300K. Carbon monoxide was used to probe the activity of the bimetallic clusters. With a constant total metal coverage, CO desorption scales linearly with the Pt percentage. Upon dosing increasing amounts of Au onto 0.25ML of Pt, CO desorption decreases but does not reach zero, even with 3ML of Au, suggesting that CO may be able to pull Pt to the surface of the clusters. CO_2 production from bimetallic clusters exposed to O_2 prior to CO exposure decreases much more rapidly with increasing Au coverage than does CO desorption due to decreased number of Pt surface sites for O_2 dissociation.

SS-TuP7 Temperature Program Desorption Study of Cu_x on Reduced TiO_2(110), ***J.C. Lofaro, Jr.***, Stony Brook University, *M.G. White*, Brookhaven National Laboratory and Stony Brook University

Copper catalysts supported on metal oxides have been used as a heterogeneous catalysts in industrial setting for various chemical processes.[1,2] Recent works have shown that copper nanoparticles supported on metal oxides (ZnO, CeO_2, TiO_2) have higher activity for the water gas shift reaction (WGSR) as well as other chemical processes.[3,4] Here, copper nanoparticles are deposited on a TiO_2(110) single crystal using a homemade thermal evaporator, which is used as a model system. Auger electron spectroscopy (AES) is used to characterize the copper coverage and temperature programmed desorption (TPD) is used to probe the clusters reactivity and thermal stability. Copper coverages ranging from 0.25ML to 10ML are investigated. Probe molecules including carbon monoxide and water since those are the starting points for the WGSR, which copper is known to catalyze at high temperatures.[5]

[1] K. Klier, Adv. Catal., 1982, 31, 243.

[2] J. C. Bart and R. P. A. Sneedon, Catal. Today, 1987, 2, 124.

[3] J. A. Rodriguez, P. Liu, J. Hrbek, J. Evans, M. Pérez, Hetero. Catal. 2007, 46.

[4] X. Zhao, J. A. Rodriguez, J. Hrbek, M. Pérez, Surface Science, 2005 , 600, 229.

[5] J. Nakamura, J. M. Campbell, C. T. Campbell, J. Chem. Soc. Faraday Trans., 1990, 86, 2725.

SS-TuP8 Photooxidation of Acetone and Butanone on Rutile TiO_2(110), ***D.P. Wilson****, D. Sporleder,* Stony Brook University, *M.G. White*, Stony Brook University, Brookhaven National Laboratory

Interest in the photooxidation of organic compounds on heterogeneous surfaces such as TiO_2 has increased in recent years. Here, acetone and butanone, two common organic ketones, are studied under UHV conditions to determine what fragmentation occurs during photooxidation and to gain insight as to the predictability of desorbing species. The data was collected using a pump-probe time-of-flight (TOF) method. Excitation occurs via exposure to 3.7 eV photons followed by ionization with 13.05 eV photons. Preheating the surface to ~200K facilitated the formation of an organic-diolate species needed for photoactivity. During butanone photooxidation, different desorption mechanisms between mass 30 and masses 27-29 are evident. Background thermal results and preliminary translational energy distributions are calculated for acetone and some butanone fragments and are presented here.

SS-TuP9 Significant Reduction in Adsorption Energy of CO on Platinum Nanoparticles on Graphite, ***J.P. Oh****, T. Kondo,* University of Tsukuba, Japan*, Y. Suda,* Toyohashi University, Japan*, D. Sekiba, H. Kudo, J. Nakamura*, University of Tsukuba, Japan

Adsorption and desorption of CO on Pt vapor-deposited on highly oriented pyrolytic graphite (HOPG) have been investigated by temperature programmed desorption (TPD) of CO and in-situ helium atom scattering (HAS). Pt particles deposited on HOPG with sub-monolayer coverage are found to exhibit lower temperature desorption peak of CO at ~300 K at a heating rate of 0.5 K/sec. With increasing Pt coverage on HOPG, the desorption peak of CO at 450 K becomes dominant as observed on Pt single crystals. It was confirmed by Rutherford backscattering spectroscopy (RBS) measurements that any impurities other than carbon and Pt do not exist in the HOPG sample. These results indicate that the Pt particles deposited on a graphite surface with sub-monolayer coverage has significantly different properties for CO adsorption from that of Pt single crystal: lower adsorption energy of CO on Pt of Pt/HOPG than that for Pt single crystal. The reduction in the adsorption energy has been attributed to the interface interaction between Pt particles and graphite surface based on the separately conducted scanning tunneling microscopy experiment. Simultaneous measurement of HAS with CO-TPD indicated, the morphological change of the specific Pt particles at ~350 K. Scanning electron microscope observation before and after annealing the Pt/HOPG sample also reveals that Pt particle is mobile at higher temperatures above 350 K. However, sintering of Pt leading to an increase of particle size was not observed.

SS-TuP10 Low-Temperature Reaction of Cl_2 and C_2H_4 on ZnO(000-1) Single Crystal Surfaces, ***W.H. Doh****, C.M. Kim*, Kyungpook National University, South Korea

We studied the reaction of Cl_2 and C_2H_4 co-adsorbed on ZnO single crystal surfaces. It is observed that C_2H_4 is molecularly adsorbed on ZnO at 110 K and desorbed intact from the surface when the surface temperature is increased. Cl_2 is molecularly adsorbed on ZnO at 110 K and decomposed to atomic chlorine when the surface is heated to higher than 200 K. When the ZnO surface is co-adsorbed with Cl_2 and C_2H_4, desorption of 1,2-dichloroethane is observed. We studied the mechanism of low-temperature addition of Cl to C_2H_4 on ZnO. We propose that “hot” atoms are produced in the process of Cl_2 dissociation and these “hot” chlorine atoms attack co-adsorbed C_2H_4 to produce 1,2-dichloroethane before thermodynamic equilibrium is reached.

SS-TuP11 Effect of Al_2O_3 and ZrO_2 Supports on Rh for Reaction Properties of NO, ***I. Nakamura****, A. Takahashi, T. Fujitani*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

The reduction of the noble metal content in the three-way automotive catalyst (Rh, Pt, Pd/Al_2O_3-ZrO_2-CeO_2) is currently required. In order to reduce noble metal loading, the enhancement of atomic efficiency and suppression of oxidation and sintering of noble metal are important subjects. To overcome these subjects, the clarification of the supported metal state is necessary. In this study, we investigated the influence of oxide support on the structure of Rh and the NO reactivity using the Rh/Al_2O_3 and Rh/ZrO_2 model catalysts. The model catalysts were prepared by deposition of Rh onto the Al_2O_3 and ZrO_2 thin films. The NO dissociation activity on the Rh/Al_2O_3 model catalyst was higher than that on Rh(111). In contrast, the activity for the Rh/ZrO_2 model catalyst was the same as Rh(111). Furthermore, the dissociation activity on the Rh/Al_2O_3 model catalyst increased by heating, but no enhancement by heating treatment was observed for the Rh/ZrO_2 model catalyst. We thus considered that the Al_2O_3 support promotes the NO dissociation activity by changing the Rh surface structure. To clarify the effect of Al_2O_3 support on Rh, we examined the NO adsorption state on the model catalysts. The IRAS peak due to NO adsorbed on bridge site was observed at 1645 cm^{-1} for the Rh/Al_2O_3 model catalyst. For the Rh/ZrO_2 model catalyst, the peak was seen at 1616 cm^{-1}, which was attributed to NO on hollow site. These results indicate that the surface structures of Rh are (100) and (111) faces for the Rh/Al_2O_3 and Rh/ZrO_2 model catalysts, respectively. We also confirmed that the exposed surfaces of Rh supported on Al_2O_3 and ZrO_2 are the (100) and (111) face from a comparison with the rate and apparent activation energy for NO dissociation on Rh(100) and Rh(111). Thus, we found that the effect of Al_2O_3 support on Rh for an enhancement of NO dissociation activity is to stabilize the surface structure of the (100) face with a high NO dissociation ability. AFM measurements confirmed that the small Rh particles with 2.5 nm diameter were formed on the Rh/Al_2O_3 model catalyst. We concluded that the Al_2O_3 support affected the morphology of the Rh surface by stabilization of small Rh particle, resulting in the enhancement of NO dissociation activity.

SS-TuP12 Au-N Synergy and N-Doping of Metal Oxide-Based Photocatalysts, ***J. Graciani****, A. Nambu,* Brookhaven National Laboratory*, J. Evans,* Universidad Central de Venezuela*, J.A. Rodriguez,* Brookhaven National Laboratory*, J.F. Sanz*, Universidad de Sevilla, Spain

N-doping of titania makes possible photocatalytic activity for the splitting of water, and other reactions, under visible light. Here we show from both theory and experiment that Au preadsorption on TiO2 surfaces significantly increases the reachable amount of N implanted in the oxide. The stabilization of the embedded N is due to an electron transfer from the Au 6s levels toward the N 2p levels, which also increases the Au-surface adhesion energy. Theoretical calculations predict that Au also can stabilize embedded N in other metal oxides with photocatalytic activity such as SrTiO3 and ZnO, producing new states above the valence band or below the conduction band of the oxide. In experiments, the Au/TiNxO2-y system was found to be more active for the dissociation of water than pure TiO2 or TiO2-y. Furthermore, the Au/TiNxO2-y surfaces were able to catalyze the production of hydrogen through the water-gas shift reaction (WGS) at elevated temperatures (575- 625 K) displaying a catalytic activity superior to that of pure copper (the most active metal catalysts for the WGS) or Cu nanoparticles supported on ZnO.

SS-TuP13 Bimetallic Pt/Metal Nanocatalysts for the Decomposition of Methanol: Effect of Secondary Metal on Oxidation State, Activity, and Selectivity, ***J.R. Croy****, S. Mostafa, L. Hickman, H. Heinrich, B. Roldan Cuenya*, University of Central Florida

Bimetallic Pt-Metal (Pt-M) catalysts are important in a wide range of applications including the direct methanol fuel cell (DMFC). In order to take full advantage of Pt/M systems in the design of new and efficient nanocatalysts, we must understand the structural, chemical, and electronic modifications brought about by the addition of the secondary metal M. We present here an investigation of the influence that the addition of secondary metals (M=Au, Pd, Ru, and Fe) has on the oxidation state, activity, and selectivity of ZrO_2-supported Pt nanoparticles. We use as a probe reaction the decomposition of MeOH. Size-selected bimetallic Pt nanoparticles were obtained by diblock-copolymer encapsulation and deposited on nanocrystalline ZrO_2 powder. The chemical composition of the particles was studied by X-ray photoelectron spectroscopy and structural characterization was done by atomic force microscopy and transmission electron microscopy. The reactivity of the bimetallic systems for MeOH decomposition was monitored in a packed-bed mass flow reactor by mass spectrometry. Distinct atomic segregation trends were observed upon annealing these nanoparticles in an oxygen-rich environment. The affect these trends have on the oxidation state of Pt and how this state influences reactivity will be discussed.

SS-TuP14 Reaction Properties of O_3 and CO Over Gold Surface, ***T. Fujitani****, I. Nakamura, A. Takahashi*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Gold nanoparticles supported on TiO_2 exhibit high catalytic activity for CO oxidation. Although numerous investigations have been carried out to elucidate the source of this enhanced activity, there are still controversies concerning the active sites and the role of support for the Au/TiO_2 catalyst. In addition to the aforementioned studies, reactions of O_2, O_3 and CO on gold surfaces have been investigated by means of surface science techniques. Recently, we found that O_3 dissociation and CO adsorption depend strongly on the gold surface structure. Here, we report the adsorption and desorption properties of atomic oxygen produced from O_3 exposure and CO adsorption properties on gold single crystals as well as gold deposited on TiO_2(110). XPS measurements confirmed that no dissociative adsorption of O_2 occurred on surfaces of Au(111), Au(100) and Au(311). On the other hand, atomic oxygen was observed on Au(111) and Au(311) upon exposure to O_3, but no atomic oxygen was detected on Au(100). The saturation coverage of atomic oxygen on Au(311) was half of that observed on Au(111), where the exposed (111) face on Au(311) was half of that on Au(111). Furthermore, the initial formation rate of atomic oxygen for Au(311) was half of that for Au(111). These results clearly indicate that O_3 dissociation over gold surfaces proceeded selectively on the (111) face. We found that the adsorption behavior of CO also depended on the gold surface structure. PM-IRAS peaks of CO at 2070-2080 cm^{-1} were observed for Au(111) and Au(100) at CO pressures above 0.5 Torr; these peaks were assigned to the CO adsorbed on atop sites (atop-CO). In contrast, the peak due to atop-CO adsorbed on step sites was seen at 2117 cm^{-1} for Au(311) at 0.01 Torr. It was thus shown that the step sites on the gold surface were effective for CO adsorption under low CO pressure. Next, we investigated the CO adsorption state for the gold nanoparticles on TiO_2(110). PM-IRAS peak of CO adsorbed on atop sites of gold atom was observed at 2120 cm^{-1}, which was higher than the frequency of the CO adsorbed on Au(111). The CO frequency observed for the Au/TiO_2 model catalyst agreed with that on step sites for Au(311). We thus found that the TiO_2 support influences the electronic state of the supported gold, resulting in the formation of positively charged gold nanoparticles.

SS-TuP15 Formation and Thermal Stability of Gold Oxide and Platinum Oxide Shells on Nanoparticles: Size and Support Effects, ***L.K. Ono***, *J.R. Croy*, *B. Roldan Cuenya*, University of Central Florida

Gold and Pt nanoparticles (NPs) with two different size distributions (average sizes of ~1.5 and ~5 nm) have been synthesized by inverse micelle encapsulation and deposited on reducible (TiO_2) and non-reducible (SiO_2, ZrO_2) supports. The thermal stability of oxidized Au and Pt species formed upon cluster exposure to atomic oxygen has been investigated in ultrahigh vacuum using a combination of temperature-, time- and CO dosing-dependent X-ray photoelectron spectroscopy (XPS), as well as temperature programmed desorption (TPD). Our work on gold clusters demonstrates that (a) low temperature (150 K) exposure to atomic oxygen leads to the formation of surface, as well as sub-surface gold oxide, (b) the presence of the reducible TiO_2 substrate leads to a lower gold oxide stability compared to that on SiO_2, possibly due to a TiO_2 oxygen vacancy-mediated decomposition process, (c) heating to 550 K (Au/SiO_2) and 300 K (Au/TiO_2) leads to a near-complete reduction of small (~1.5 nm) NPs while a partial reduction is observed for larger clusters (~5 nm), and (d) the desorption temperature of O_2 from pre-oxidized Au clusters deposited on SiO_2 depends on the cluster size, with smaller clusters showing stronger O_2 binding. Preliminary data on the formation and thermal stability of different Pt oxide species (PtO_2 and PtO) on size-selected Pt clusters will be shown. Emphasis will be given to how the nature of the oxide support affects this stability. Furthermore, the distinct reactivity of similarly-sized, pure Pt and Au nanoparticles versus their oxidized counterparts will be discussed.

SS-TuP16 3D Concentration and Structure Maps of Heterogeneous Surfaces Determined by LEEM-IV Analysis, ***J. Sun****, University of New Hampshire, *J.B. Hannon*, IBM T. J. Watson Research Center, *G.L. Kellogg*, Sandia National Laboratories, *K. Pohl*, University of New Hampshire

Controlling compositional heterogeneity is important in ultrathin films growth, but determining exactly how and why heterogeneity develops is extremely challenging. The reason is that the three-dimensional compositional and structural profile of the film is difficult to measure because of the lack of surface techniques that combine high spatial resolution, subsurface sensitivity, chemical identification capability and high temporal resolution. For example, STM is not sensitive to the subsurface region and LEED averages over a large surface area. To overcome these limitations, we have developed a novel analysis approach[1] that allows us to measure the evolution of the 3D compositional and structural profile of a heterogeneous alloy surface in real time. We do this by quantitatively analyzing the pixelated intensity in the low-energy electron microscopy (LEEM) images. In the dynamical IV (intensity-vs.-voltage) analysis, a proper model for the inner potential, representing the atomic muffin-tin constant and the inelastic optical scattering, was adapted to overcome the challenges in very low-energy electron scattering. The structural and non-structural parameters are optimized simultaneously in search of the real surface structure that gives a best fit between the calculated and experimental IV curves. We have measured the composition of a CuPd surface alloy in the three topmost atomic layers, during growth, with 8.5 nm lateral resolution and monolayer depth resolution. From the 3D compositional and structural profiles, we have identified a generic step-overgrowth mechanism that leads to inherent alloy heterogeneity at steps. The heterogeneity can be traced to the difference between bulk and surface diffusion of Pd. Furthermore, Monte Carlo simulations are described to reproduce the time evolution of the compositional heterogeneity and give support to the step-overgrowth model. By the LEEM-IV analysis technique, the surface structural and compositional information measured in situ can be correlated with other surface properties, such as surface strain, diffusion mechanisms, and growth and decay processes. This work is supported by the National Science Foundation, the Department of Energy, Office of Basic Energy Sciences, and the Petroleum Research Fund.

[1] Sun, J., Hannon, J. B., Kellogg, G. L. & Pohl, K., Phys. Rev. B 76, 205414 (2007); Hannon, J. B., Sun, J., Pohl, K. & Kellogg, G. L., Phys. Rev. Lett. 96, 246103 (2006).

SS-TuP17 Reactivity of Diatomic Molecule on Bimetallic Surface: The Case of O_2 Adsorption and Dissociation on Pt/Fe, ***M.C.S. Escano****, *H. Kasai*, Osaka University, Japan

Bimetallic surfaces have been receiving increasing catalytic interest. Aside from using strain to tune reactivity, to a large extent, metal overlayers exhibit modified surface electronic structure due to interfacial interactions.[1,2] While dissociative adsorption of small molecules on metal surfaces has been studied extensively, theoretical studies on gas-bimetallic surface interaction have been sparse. Previous ab-initio calculations on atomic and electronic structure of Pt/Fe(001) show small lattice mismatch and a charge transfer from Pt and Fe atom sites towards Pt-Fe interface.[3] Layer by layer density of states curves against Pt(001) and Fe(001) show increase of d states at the Fermi level and a spin polarization of Pt d_{zz} states. Such changes with respect to the pure components call for investigation on O_2 surface reactivity. Spin-polarized density functional theory calculations were performed to investigate adsorption and O_2 dissociation on Pt/Fe(001). The adsorption characteristics of atomic and molecular oxygen are compared with clean Pt(001). The energetics of O_2 adsorption and dissociation are discussed in terms of two-dimensional cuts of the six-dimensional potential-energy surface. Results show "no barrier" O_2 molecule preferential adsorption on bridge with O-O axis directed towards top sites (t-b-t). A barrierless dissociation over one trajectory, O-O axis parallel and spanning over bridge-hollow-bridge (b-h-b) site, is also predicted. The potential energy decreases monotonically along this lowest energy reaction path indicative of strong O_2 interaction with the surface. A proposed pathway for dissociation may take molecular adsorption along t-b-t and a translation and dissociation towards b-h-b. Detailed analysis of the transition state reveals ease of translation towards the b-h-b. Local density of states (LDOS) of O_2 arriving over bridge for the molecular state and at the transition state support strong hybridization between O_2 p_x-states and Pt d_{zz} states. In the meeting, we will detail the mechanism of O_2 reactivity based on charge redistribution, total charge flow integrals and partial charge density plots.

[1] M. Mavrikakis, B. Hammer and J.K. Nørskov, Phys. Rev. Lett. 81, 2819 (1998).

[2] J.A. Rodriguez, Surf. Sci. Rep. 24, 223 (1996)

[3] MC Escaño, H. Nakanishi and H.Kasai, J. Phys.: Cond. Matt. 19, 482002 (2007).

SS-TuP18 Surface Chemistry of Carboxylic Acids on Si(100)2×1, ***M. Ebrahimi****, *J.F. Rios*, *K.T. Leung*, University of Waterloo, Canada

Organic functionalization of Si(100)2x1 has attracted a lot of recent attention due to its potential applications in organic-inorganic hybrid semiconductor devices, molecular electronics, chemical and biological sensors, and optical materials. Understanding of the behaviour of organic molecules on Si(100)2×1 surface is fundamentally important, because the electronic and chemical properties and selectivity of the inorganic substrate are modified by the organic adsorbate. Among the wide range of organic functional groups, the carboxyl group is one of the key constituents of amino acids, the building blocks of peptides and proteins. Under appropriate cleaning preparation, the Si(100) surface reconstructs to the 2×1 surface, on which the dangling bonds of adjacent Si atoms pair to create surface Si=Si dimer rows. The interaction of the carboxyl group with the Si=Si dimers, composed of a full σ bond and a partial π bond, is therefore of special interest to understanding the chemical reactivity and selectivity of biomolecules in general with this widely industrially used semiconductor. The present work investigates the dissociative adsorption of acetic acid and acrylic acid on the UHV prepared Si(100)2×1 surface at room temperature using X-ray photoelectron spectroscopy (XPS), temperature programming desorption (TPD), and density-functional theory (DFT) calculation. Selectivity of the surface towards acrylic acid, bifunctional molecule, has been investigated as well. Our DFT calculation by using B3LYP/6-31++G(d,p) shows several possible adsorbate-substrate configurations (ASCs) for the adsorption of these carboxylic acids on Si(100)2×1 surface. Acetate and acrylate resulting from the O-H dissociation of the related carboxylic acid on the Si(100) bind to the surface through oxygen atom.

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* Morton S. Traum Award Finalist

Our DFT and XPS results enable the identification of the adstructures arising from bonding involving either one oxygen atom (the unidentate ASC) and two oxygen atoms (the inter-dimer and intra-dimer bidentate ASCs). Our C 1s features prove the formation of bidentate adstructure at the early stage and of both unidentate and bidentate adtructures at the saturation level of exposure. The thermal evolution of the adsorbates studied by TPD and XPS of the flash-annealed surface confirm desorption of some species detected by Q-mass spectroscopy and formation of SiC on Si.

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