

TOWARD AN UNDERSTANDING OF CATALYSIS BY  
SUPPORTED METAL NANOCCLUSERS

PROGRESS REPORT

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**TOWARD AN UNDERSTANDING OF CATALYSIS BY  
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APPENDIX: PREPRINTS/REPRINTS

I. PROJECT ABSTRACT

PROJECT TITLE: TOWARD AN UNDERSTANDING OF CATALYSIS BY  
SUPPORTED METAL NANOCCLUSERS

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YEAR STARTED: 2002

The goal of this program is an atomic-level understanding of catalysis by supported metal nanoclusters. The immediate objectives are: (1) the mechanisms of nanocatalyst sintering and deactivation using *in situ* scanning tunneling microscopy, (2) the design of sinter-resistant supports for metal nanocatalysts; and (3) the surface intermediates in selective oxidation by noble metal nanocatalysts. A focus of this project is the application of scanning tunneling microscopy/spectroscopy (STM/STS), polarization modulation infrared reflection absorption spectroscopy (PM-IRAS), and neutron vibrational spectroscopy (NVS) to the *in situ* characterization of nanocatalysts operating at realistic reaction conditions. Specifically the influence of reactants such as O<sub>2</sub> and H<sub>2</sub>O on the sintering of Au and Ag nanoclusters (1 - 10 nm) supported on single-crystal or thin-film TiO<sub>2</sub>, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> is being investigated by STM/STS. A goal of the work is the synthesis of mixed-oxide supports for the stabilization of metal nanostructures against sintering. Finally, the identification of key reaction intermediates in the selective oxidation of hydrocarbons over gold nanocatalysts is being studied with polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) and neutron vibrational spectroscopy (NVS). The ultimate objective is the seamless integration of model supported metal catalysts and their corresponding practical analogs in fundamental catalytic science.

This experimental program currently utilizes twelve surface analytical systems, all having a microcatalytic reactor contiguous to a surface analysis system. This arrangement allows *in vacuo* transfer of the catalytic surface of interest from one chamber to the other. Surface techniques being used include AES, UPS, XPS, ISS and TPD. LEED is available to probe the order of overlayer metal and impurity atoms used to modify the activity of transition metal catalysts. IRAS and HREELS are currently in use to investigate the vibrational properties of surfaces and adsorbates. Metastable impact electron spectroscopy

(MIES) has recently been added to one of our UHV systems. Two systems are equipped with UHV scanning tunneling microscopes: an Omicron STM-1, and a low/high temperature RHK STM for *in situ* imaging of surface structure. The latter is capable of imaging at realistic reaction temperatures and pressures. Additional STM and AFM capabilities are available for *ex situ* structural measurements.

The ability to carry out high pressure/temperature tunneling microscopy of oxide supported nanoparticles offers the possibility of viewing a working catalytic surface, however, being able to routinely do so presents many significant challenges. During the last two and a half years an experimental approach has been developed in our laboratories that successfully overcomes many of these difficulties. This approach allows us to target pre-selected surface areas and individual supported nanoparticles while spanning the pressure of a reactive gas over twelve orders of magnitude. Thus, for model supported catalyst we are able to bridge the so-called "pressure gap" on a particle-by-particle basis and, in a single experiment, to address such important issues as size effects on cluster stability, deactivation, etc.

Using the STM tip as a nanomask during physical vapor deposition (PVD) converts the tip into a precisely controlled active element in the synthesis of the model catalyst. With this versatile approach, we have demonstrated new, exciting possibilities for nano-patterning the oxide surface with particles of different sizes/compositions and address important issues as nucleation and growth kinetics, alloying, and thermal/chemical particle stability.

The application of these two innovations to the same mesoscopically confined surface area using the same tip and environmental treatments makes these experiments free from the usual artifacts and opens a combinatorial approach for *in situ* STM studies of model catalysts.

#### Related references:

1. "In Situ Scanning Tunneling Microscopic Studies of Supported Metal Clusters: Growth and Thermal Evolution of Individual Particles", A. Kolmakov and D. W. Goodman, Chemical Record, 2, 446-457 (2002).
2. "In situ Scanning Tunneling Microscopy of Individual Supported Metal Clusters at Reactive Gas Pressures from  $10^{-8}$  -  $10^4$  Pa", A. Kolmakov and D. W. Goodman, Review of Sci. Instr., 74, 1-7 (2003).
3. "A combined In-situ Infrared and Kinetic Study of the Catalytic CO + NO Reaction on Pd(111) at Pressures up to 240 mbar", C. Hess, E. Ozonsoy, D. W. Goodman, J. Phys. Chem. B, 107, 2759-2764 (2003).
4. "Model Catalysts: From Imagining to Imaging a Working Surface", D. W. Goodman, J. Catal., 216, 213-222 (2003).

## II. RECENT RESEARCH ACCOMPLISHMENTS (2002-2003)

### 1. CO Oxidation on Supported Nano-Au Catalysts Synthesized from a $[\text{Au}_6(\text{PPH}_3)_6](\text{BF}_4)_2$ Complex

Highly active and stable nano-Au catalysts have been synthesized by the interaction of an Au cluster-phosphine complex with a  $\text{TiO}_2$  support. These catalysts have been characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and tested for CO oxidation. The pre-treatment conditions had a profound influence on the CO oxidation activity of the Au/ $\text{TiO}_2$  catalysts. Under optimum pre-treatment conditions these catalysts showed high catalytic activity. This is noteworthy considering that previous studies by Iwasawa et al. (J. Catal., 1997, 170, 191) on similar systems (different pre-treatment) showed an order of magnitude smaller CO oxidation activity. The catalyst deactivation was very slow and studies showed that the catalyst could be successfully regenerated to regain initial activity. Diffuse reflectance infrared spectroscopy (DRIFTS) studies of CO on these supported catalysts are in excellent agreement with the infrared reflection absorption spectroscopy (IRAS) data obtained on model Au catalysts in our laboratory. The Au/ $\text{TiO}_2$  catalyst prepared by a temperature programmed reduction-oxidation treatment showed high  $\text{CO}_2$  yield for the CO oxidation reaction in the presence of excess hydrogen.

Publication No. 4 in DOE-BES Publication List (Section III)

### 2. $\text{Ru}_3(\text{CO})_{12}$ Adsorption and Decomposition on $\text{TiO}_2$

Triruthenium dodecacarbonyl ( $\text{Ru}_3(\text{CO})_{12}$ ) adsorption and decomposition on titania ( $\text{TiO}_2$ ) were studied using infrared reflection absorption spectroscopy (IRAS), temperature programmed desorption (TPD), Auger electron spectroscopy (AES), and scanning tunneling microscopy (STM). It was found that the vapor-deposited cluster adsorbs with the  $\text{Ru}_3$  plane oriented normal to the surface. The clusters form an amorphous layer at 90 K, order at 195 K, and begin to decompose in vacuum at ca. 250 K. The clusters decompose in two stages, with complete decomposition occurring above 600 K. The clusters are highly dispersed on the surface and decompose cleanly to form small ruthenium clusters up to 3 nm across and single atom rows up to 20 nm long.

Publication No. 5 in DOE-BES Publication List (Section III)

### 3. Interaction of Ag with $\text{MgO}(100)$

The electronic and chemical properties of Ag clusters on  $\text{MgO}(100)$  films grown on  $\text{Mo}(100)$  were studied using metastable impact electron and ultraviolet photoelectron spectroscopies (MIES/UPS), and temperature programmed desorption (TPD). The work function of the as-grown and vacuum-annealed  $\text{MgO}(100)$  surfaces increases monotonically with increasing Ag coverage. In contrast, an initial decrease of the work function upon Ag deposition was found for the sputter-damaged  $\text{MgO}(100)$  surface, implying that small Ag clusters on this surface are electron deficient. Point defects with high electron affinities, such as  $\text{F}^{2-}$  and/or V/V<sup>-</sup>-centers, created by sputtering are believed to be responsible for the initial decrease of the work function upon Ag deposition. For low Ag coverages, the quantity of CO adsorbed at 80 K on a sputter-damaged  $\text{MgO}(100)$  surface is much greater than that adsorbed for a comparable Ag coverage on a relatively smooth,  $\text{MgO}(100)$  surface. These results are consistent with point defects on  $\text{MgO}(100)$

being responsible for altering the electronic and chemical properties of supported Ag clusters.

Publication No. 14 in DOE-BES Publication List (Section III)

#### **4. Ag Growth on Mo(112)-O<sub>ads</sub> and MoO<sub>2</sub> Surfaces**

The growth of Ag clusters on pre-adsorbed oxygen and oxide-covered Mo(112) has been investigated using scanning tunneling microscopy (STM). The objective of these experiments is the synthesis of adjacent areas on a surface with distinctly different metal-support interactions in order to investigate the relationship between the morphology of a supported metal cluster and the strength of the cluster-support interaction. The STM results show that more highly dispersed Ag clusters with a greater number density are obtained on that surface that interacts to a greater extent with the metal. Heating leads to the formation of 2D-Ag nanostructures on oxygen-free Mo(112) (strong metal-support interaction) and 3D cluster growth on oxide-covered Mo(112) (relatively weak metal-support interaction).

Publication No. 19 in DOE-BES Publication List (Section III)

#### **5. In-situ Scanning Tunneling Microscopic Studies of Supported Metal Clusters: Growth and Thermal Evolution of Individual Particles**

An experimental approach has been developed for imaging the nucleation and growth of individual oxide supported nanoparticles and their subsequent *in situ* chemical and thermal treatments by scanning tunneling microscopy (STM). The potential of the method is demonstrated for Au nanoparticles supported on a reduced TiO<sub>2</sub> substrate where a cluster-by-cluster comparison is made of the morphological evolution and stability of nanoparticles during their nucleation and thermal annealing. Using this methodology the details of the nucleation and growth kinetics can be directly observed.

Publication No. 22 in DOE-BES Publication List (Section III)

#### **6. Characterization of C<sub>2</sub>(C<sub>x</sub>H<sub>y</sub>) Intermediates from Adsorption and Decomposition of Methane on Supported Metal Catalysts by In-Situ Inelastic Neutron Scattering Vibrational Spectroscopy**

The article reports the first experimental evidence of the formation of ethylidyne, vinylidene, and methylidyne (C<sub>x</sub>H<sub>y</sub>) species from methane on supported metal catalysts using inelastic neutron spectroscopy (INS). INS data are reported from 100 to 1800 cm<sup>-1</sup> after methane decomposition on Ru/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts and the results compared with recent data acquired by high resolution electron energy loss spectroscopy (HREELS) on single crystal Ru and Ni surfaces.

Publication No. 1 in DOE-BES Publication List (Section III)

#### **7. Identification of Defect Sites on MgO(100) Surfaces**

Methodologies are reported that allow the identification of extended defects on MgO(100) surfaces. The techniques used include low energy electron diffraction (LEED), metastable impact electron spectroscopy (MIES), D<sub>2</sub>O- and CO-temperature programmed desorption (TPD), and MIES of adsorbed Xe. LEED and MIES

data for MgO(100), TPD spectra of D<sub>2</sub>O and CO, and MIES spectra for adsorbed Xe are significantly altered as a function of the density of the extended defects. NO is shown to be an ineffective probe molecule for titration of defect sites on MgO(100).

Publication No. 8 in DOE-BES Publication List (Section III)

#### **8. The Preparation of Ultra-Thin, Ordered SiO<sub>2</sub> Films**

Scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) have been used to optimize the preparation of high quality SiO<sub>2</sub> films. Co-deposition of Si and oxygen at relatively high temperatures followed by an anneal leads to a combination of island and layer-by-layer growth, whereas flat, well-ordered SiO<sub>2</sub> films can be prepared on Mo(112) using a sequential deposition method. Preadsorbed oxygen leads to island growth, therefore, an atomically clean surface is essential for growing flat, well-ordered films. A sharp, hexagonal LEED pattern is shown to be insufficient evidence for a high quality film.

Publication No. 13 in DOE-BES Publication List (Section III)

#### **9. Polarization Modulation Infrared Reflection Absorption Spectroscopy at Elevated Pressures: CO Adsorption on Pd(111) at Atmospheric Pressures**

CO adsorption on a Pd(111) single crystal surface was investigated using *in situ* polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) within the pressure range 10<sup>-6</sup> - 800 mbar. The coverage dependent CO overlayer structures found on the Pd(111) surface are identical throughout this pressure regime, i.e., no new surface species at elevated pressures or adsorbate-induced substrate reconstructions were observed. The transition from an adsorbate superstructure dominated by bridged-bound CO to an adsorbate overlayer having three-fold/atop CO sites was followed by varying the adsorbate pressure over nine orders of magnitude. The derived phase diagram indicates an apparent activation energy of 44.35 ± 1.63 kJ/mol for the bridged-to-three-fold-hollow/atop transition. A comparison between these data and recent sum frequency generation (SFG) results is made.

Publication No. 18 in DOE-BES Publication List (Section III)

#### **10. Decomposition of NH<sub>3</sub> on Ir(100): A Temperature Programmed Desorption Study**

Ammonia adsorption has been studied on a Ir(100) surface in the temperature range 100 - 410 K. In contrast to previous studies on Ir(111), approximately 12% of the chemisorbed ammonia undergoes step-wise decomposition at 200 K. However, decomposition has been found to be an activated process wherein a difference in the activation energy of dissociation and desorption is estimated to be 21 kJ/mol. Recombinative nitrogen desorption has been found to be the rate determining step with an activation energy of 64 kJ/mol. Co-adsorption of hydrogen and ammonia have been carried out to understand the partial pressure dependences for ammonia decomposition----- 0.9 ± 0.1 with respect to ammonia and -0.7 ± 0.1 with respect to hydrogen. Co-adsorption data indicate that the negative order with respect to hydrogen is due to enhancement of the reverse reaction (NH<sub>x</sub> + H ⇌ NH<sub>x+1</sub>, x = 0, 2) as well as reduction in the desorption temperature of ammonia in the presence of excess H-atoms on the surface. In

contrast, co-adsorbed oxygen acts as a promoter for the ammonia dissociation and leads to 100% ammonia conversion. The differences in the decomposition behavior with respect to the previous results for Ir(111) are indicative of the structure sensitivity of the reaction.

Publication No. 2 in DOE-BES Publication List (Section III)

#### **11. Dissociation of D<sub>2</sub>O on MgO(100)**

The adsorption of water on well-ordered MgO(100) surfaces has been studied using metastable impact electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS), and temperature programmed desorption (TPD). Experimental evidence is presented that water adsorbs dissociatively and molecularly within the first monolayer on well-ordered MgO(100) surfaces. These results support recent theoretical predictions [L. Giordano et al., Phys. Rev. Lett. 81, 1271 (1998)] that water partially dissociates on MgO(100) surfaces

Publication No. 3 in DOE-BES Publication List (Section III)

#### **12. Characterization of MgO(100) Thin Film Growth on Mo(100)**

Various MgO thin films grown on Mo(100) have been characterized by using metastable impact electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS), low energy electron diffraction (LEED), and CO as a probe molecule to titrate defects. Using MIES and LEED, the as-grown MgO(100) films (thickness = ca. 15 monolayers) are found to be highly defective. Annealing at 1150 K significantly reduces the density of defects on the MgO(100) surfaces. CO adsorbs on the as-grown MgO(100) film at 90 K, whereas no CO adsorption was detected on the annealed MgO(100) film, in agreement with the MIES and LEED results. For MgO thin films with a thickness of 15 monolayers, no surface charging was observed during the UPS/MIES measurements.

Publication No. 7 in DOE-BES Publication List (Section III)

#### **13. Evidence for Partial Dissociation of Water on Flat MgO(100) Surfaces**

Ab initio calculations of the density of states for adsorbed monolayers of water on a MgO(100) surface are compared with metastable impact electron spectra (MIES) and ultraviolet photoelectron spectra (UPS). The calculations confirm the suggested assignments and in particular show that there is good evidence that some, but not all, molecules have dissociated to hydroxide ions. Density of state calculations are shown for configurations with no dissociated molecules, one third of the molecules dissociated and half the molecules dissociated; the agreement with experiment is best for the configuration with one third of the molecules dissociated.

Publication No. 12 in DOE-BES Publication List (Section III)

#### **14. Adsorption and Reaction of NO on Cu(100): An Infrared Reflection Absorption Spectroscopic Study at 25 K**

The adsorption of nitric oxide (NO) on a Cu (100) surface at 25 K has been studied using infrared reflection absorption spectroscopy (IRAS). Initially, NO adsorbs at the bridge site, however, with an increase in coverage, dimerization of NO occurs. Further dosing of NO at 25 K produces a multilayer of the NO dimer. Annealing this dimer multilayer to 40 K causes a change in the alignment of the



dimers in the multilayer with respect to the Cu(100) surface. Heating to 55 K leads to reorientation of the dimer molecules in the multilayer such that the N-N axis becomes perpendicular to the surface; at 60 K the multilayer NO dimers desorb. Formation of N<sub>2</sub>O was observed upon heating the surface above 60K.

Publication No. 9 in DOE-BES Publication List (Section III)

## **15 Interactions of Ultrathin Pb Films with Ru(0001) and Pd(111)**

The interaction of ultrathin Pb films with Ru(0001) and Pd(111) has been studied with X-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS). XPS and TDS show that at room temperature Pb grows on Ru(0001) via a Stranski-Krastanov (SK) mechanism, *i. e.*, after completion of the first adlayer of Pb on Ru(0001), further Pb deposition leads to the formation of three-dimensional (3D) islands. Upon annealing to 500 K, the overlayer Pb undergoes significant clustering with the extent dictated by the initial coverages. XPS results show that the Pb 4f<sub>7/2</sub> core level binding energy (BE) increases slightly (+ 0.3 eV) as the Pb coverage increases from 0.07 ML to multilayers. When the first monolayer of Pb/Ru(0001) has been completed, the Pb 4f<sub>7/2</sub> BE has nearly reached the BE value for bulk Pb; it is only 0.1 eV lower. At ~ 2 ML, the Pb 4f<sub>7/2</sub> BE is equivalent to that of bulk Pb. In contrast, at room temperature, Pb alloys with the Pd(111) surface, the Pd 3d<sub>5/2</sub> BE increasing ~0.8 eV with coverage from 0.07 to 4.3 ML Pb. The Pb 4f<sub>7/2</sub> BE's also increase with increasing coverage reaching the bulk value of Pb at a coverage of ~ 2 ML. The Pb 4f<sub>7/2</sub> BE at 0.07 ML is 0.55 eV smaller than that of bulk Pb. The lineshape and position of the X-ray induced Pd Auger features (M<sub>4,5</sub>VV) also display significant changes upon alloying. For Pb/Pd alloys, annealing to 500 K does not induce further changes in the Pd (M<sub>4,5</sub>VV) Auger features. The core level BE shifts are discussed in terms of possible initial and final state contributions. In particular, the initial state BE shift mechanisms of hybridization and environmental conduction band charge density are explained in the context of prior theoretical studies. It is shown that 6s-6p hybridization in Pb can be expected to be sufficiently large to contribute to the observed BE shifts.

Publication No. 39 in DOE-BES Publication List (Section III)

## **16 Size Effects in Catalysis by Supported Metal Clusters**

Similar to free clusters in the gas phase, supported clusters often exhibit marked size dependence with respect to chemical activity. However for supported metal clusters the origin of this size effect is intrinsically more complex compared to free clusters and is not well understood. The so-called "structure sensitivity" of metal nanoclusters dispersed on metal oxides is of considerable fundamental interest as well as significant industrial importance for heterogeneous catalysts, gas sensing devices and microelectronics. Great progress has been made in the past two decades in our understanding of those key factors governing the size dependence of cluster reactivity. Several recent examples of the structure sensitivity of metal clusters on oxide surfaces are presented in this review along with recent methodologies to address size effects in supported metal clusters.

Publication No. 29 in DOE-BES Publication List (Section III)

## **17 Non-Oxidative Activation of Methane via its Decomposition**

Effective utilization of methane remains one of the long-standing problems

in catalysis. Over the past several years various routes, both direct and indirect, have been considered for the conversion of methane to value added products such as higher hydrocarbons and oxygenates. This review will focus on the range of issues dealing with thermal and catalytic decomposition of methane that have been addressed in the last few years. Surface science studies (molecular beam methods and elevated pressure reaction studies) involving methane activation on model catalyst systems are extensively reviewed. These studies have contributed significantly to our understanding of the fundamental dynamics of methane decomposition. Various aspects of the non-oxidative methane to higher hydrocarbon conversion processes such as high temperature coupling and two-step low temperature methane homologation have been discussed. Decomposition of methane results in the production of CO<sub>x</sub>-free hydrogen (which is of great interest to state-of-art -low temperature fuel cells) and various types of carbon (filamentous carbon, carbon black, diamond films etc.) depending on the reaction conditions employed; these issues will be briefly addressed in this review.

Publication No. 30 in DOE-BES Publication List (Section III)

**18 Surface Chemistry of Model Oxide-Supported Metal Catalysts: An Overview of Gold on Titania**

Insight into atomic-level surface chemistry of metals on oxide surfaces is vital to understanding heterogeneous catalysis. In this work, scanning tunneling microscopy (STM) in conjunction with traditional surface science techniques is used to study gold metal clusters on a planar titania support. When Au is vapor-deposited onto TiO<sub>2</sub>(110) under ultra-high vacuum (UHV) conditions, it grows as three-dimensional (3D) hemispherical clusters on TiO<sub>2</sub>(110), indicative of a Volmer-Weber (VW) growth mode. However, at very low coverages (0.01-0.05 ML), quasi-two-dimensional (quasi-2D) Au clusters are observed. Annealing studies reveal that Au clusters form large microcrystals with well-defined hexagonal shapes above 1000 K. Furthermore, an oxygen-induced cluster ripening is observed after Au/TiO<sub>2</sub>(110) is exposed to 10.00 Torr O<sub>2</sub> in an elevated pressure reactor. The morphological change of Au clusters induced by O<sub>2</sub> exposure suggests O<sub>2</sub> chemisorption on both the clusters and the TiO<sub>2</sub> substrate at room temperature. Au clusters exhibit a clear bimodal size distribution after O<sub>2</sub> exposure due to Ostwald ripening: some clusters increase in size while others shrink.

Publication No. 26 in DOE-BES Publication List (Section III)

**19 Production of CO<sub>x</sub>-free Hydrogen for Fuel Cells via Step-wise Hydrocarbon Reforming and Catalytic Dehydrogenation of Ammonia**

The stringent CO<sub>x</sub>-free hydrogen requirement for the current low temperature fuel-cells has motivated the development of CO<sub>x</sub>-free hydrogen production alternatives to the conventional hydrogen production technologies. Recently our group has investigated step-wise reforming of hydrocarbons and catalytic decomposition of ammonia for CO<sub>x</sub>-free production of hydrogen. These investigations have employed conventional surface science techniques, model catalysts as well as high surface area supported metal catalysts. This paper presents an overview of the studies undertaken in our laboratory and highlights the important aspects of the proposed CO-free hydrogen production processes.

Publication No. 36 in DOE-BES Publication List (Section III)

## 20 Adsorption of Au on O-deficient MgO(001) Surface

The atomic and electronic properties of the O-deficient MgO(001) surface and effects of Au adsorption (0.25 monolayer) are investigated using the full potential linearized augmented plane wave method. The calculated formation energy of a surface (bulk) O vacancy on MgO(001) is 9.5 eV (10.0 eV). The vacancy induces gap states in a range of 1.8–3.3 eV above the valence band, which is expected to strongly alter the chemical properties of MgO(001). Through total energy and atomic force calculations, the adsorption of Au on the ideal MgO(001) surface is found to be very weak with a Au-O bond length ( $d_{\text{Au-O}}$ ) of 2.16 Å and an adsorption energy ( $E_{\text{ad}}$ ) of 20.13 eV/adatom. On the defective MgO(001) surface, Au adatoms prefer the vacancy sites with a strongly enhanced adsorption energy of -1.93 eV/adatom. The core state energies of Au 4f<sub>7/2</sub> are very sensitive to the change of environment.

Publication No. 24 in DOE-BES Publication List (Section III)

## 21 Acetylene Hydrogenation on Au-based Catalysts

Hydrogenation of acetylene has been investigated on Au/TiO<sub>2</sub>, Pd/TiO<sub>2</sub> and Au-Pd/TiO<sub>2</sub> catalysts at high acetylene conversion levels. The Au/TiO<sub>2</sub> catalyst (avg. particle size: 4.6 nm) synthesized by the temperature programmed reduction-oxidation of Au-phosphine complex on TiO<sub>2</sub> showed a remarkably high selectivity to ethylene formation even at 100 % acetylene conversion. Au/TiO<sub>2</sub> prepared by the conventional incipient wet impregnation method (avg. particle size: 30 nm), on the other hand, showed negligible activity for acetylene hydrogenation. Although the Au catalysts showed a high selectivity for ethylene, the acetylene conversion activity and catalyst stability were inferior to the Pd-based catalysts. Au-Pd catalysts prepared by the redox method showed both high acetylene conversions as well as high selectivity for ethylene. Interestingly Au-Pd catalysts prepared by depositing Pd via the incipient wetness method on Au/TiO<sub>2</sub> showed very poor selectivity (comparable to mono-metallic Pd catalysts) for ethylene. High resolution transmission electron microscopy (TEM) studies coupled with energy dispersive X-ray spectroscopy (EDS) showed that while the redox method produced bimetallic Au-Pd catalysts, the latter method produced individual Pd and Au particles on the support.

Publication No. 37 in DOE-BES Publication List (Section III)

## 22 In situ Scanning Tunneling Microscopy of Individual Supported Metal Clusters at Reactive Gas Pressures from 10<sup>-8</sup> - 10<sup>4</sup> Pa

An experimental apparatus has been designed and an approach developed for imaging *individual* oxide supported nanoparticles with scanning tunneling microscopy (STM) during their nucleation, growth, alloying and "real world" chemical, thermal, and other *in situ* treatments. By careful selection of the tunneling conditions and using the STM tip to index the surface, it is demonstrated that pre-selected individual particles can be imaged at elevated temperatures while changing the reactive gas pressure over twelve orders of magnitude. The experimental challenges due mainly to tunnel junction instabilities, a relatively weak cluster-support interaction, and sample drift are considered and strategies to overcome these obstacles proposed. Using Au and Ag clusters deposited on TiO<sub>2</sub> (110) as a model system, the potential of the method

is demonstrated for exploring on a particle-by-particle basis cluster growth, alloying, thermal coarsening, and the evolution of particle morphology in a reactive gas environment. An additional advantage of the approach is that a wide cluster size distribution can be synthesized and surveyed on the same substrate.

The size effects on cluster morphology therefore can be probed *in situ* for a wide variety of treatments on pre-selected clusters.

Publication No. 38 in DOE-BES Publication List (Section III)

### **23 The Thermal Stability of Pd Supported on Single Crystalline SiO<sub>2</sub> Thin Films**

The effect of annealing temperature on a model Pd/SiO<sub>2</sub> catalyst has been investigated using Auger electron spectroscopy (AES) and scanning tunneling microscopy (STM). Pd clusters on a single crystalline SiO<sub>2</sub> thin film are not altered with respect to size or shape upon heating to 700 K; however, inter-diffusion and sintering of the Pd clusters take place between 750 and 1050 K. At 1000 K, AES data imply the formation of Pd-silicide. Above 1050 K, desorption of Pd occurs concomitant with the decomposition of SiO<sub>2</sub>.

Publication No. 40 in DOE-BES Publication List (Section III)

### **24 Ag Adsorption on Various Silica Thin Films**

Various defect sites on SiO<sub>2</sub> thin films on Mo(112) have been characterized with MIES, and the interaction between deposited Ag and these defects sites investigated with MIES/UPS. MIES/UPS data for low and high defective SiO<sub>2</sub> surfaces acquired as a function of Ag exposure are consistent with 2D Ag growth at low coverage, and 3D growth at higher Ag coverages. With increasing defect density on the SiO<sub>2</sub> surfaces, no significant change is observed in the behavior of the work function with respect to the Ag coverage, suggesting that the interaction between Ag and SiO<sub>2</sub> is not influenced markedly by the presence of defects. This result is consistent with recent theoretical results that indicate a strong covalent bond between an overlayer metal and defect sites of SiO<sub>2</sub>.

Publication No. 41 in DOE-BES Publication List (Section III)

### **25 Growth of Au on TiO<sub>2</sub>(110) on a Cluster-by-Cluster Basis**

In-situ scanning tunneling microscopy (STM) has been used to follow the growth mode of gold clusters on TiO<sub>2</sub>(110) single crystals at room temperature on a cluster-by-cluster basis. Using carefully annealed TiO<sub>2</sub>(110) surfaces with a relatively low defect density it is possible to isolate cluster growth on step sites from that on terraces. Although the overall growth behavior appears invariant with respect to the morphology of the substrate, our results show that the growth rate is much faster on step edges compared to that on terraces, leading to a bimodal cluster size distribution.

Publication No. 42 in DOE-BES Publication List (Section III)

### **26 Understanding Silica-Supported Metal Catalysts: Pd/Silica as a Case Study**

Supported metal catalysts, particularly noble metals supported on SiO<sub>2</sub>, have attracted considerable attention due to the importance of the silica-metal interface in heterogeneous catalysis and in electronic device fabrication. Several important issues, e.g., the stability of the metal-oxide interface at working temperatures and pressures, are not well understood. In this review, the present status of our understanding of the metal-silica interface is reviewed. Recent results of model studies in our laboratories on Pd/SiO<sub>2</sub>/Mo(112) using LEED, AES and STM are reported. In this work, epitaxial, ultrathin, well-ordered SiO<sub>2</sub> films were grown on a Mo(112) substrate to circumvent complications that frequently arise from the silica-silicon interface present in silica thin films grown on silicon.

Publication No. 43 in DOE-BES Publication List (Section III)

**27 Identification of Defect Sites on Oxide Surfaces by Metastable Impact Electron Spectroscopy**

In this review, thin films of SiO<sub>2</sub> on Mo(112) and MgO(100) on Mo(100) have been characterized using metastable impact electron and ultraviolet photoelectron spectroscopies (MIES and UPS). The electronic and chemical properties of the thin films are identical to those of the corresponding bulk oxides. For different prepared defective SiO<sub>2</sub> surfaces, additional features are observed in the band-gap region. These features arise from vacancies or excess oxygen and are consistent with theoretical predictions of additional occupied states in the band-gap due to point defects. Extended defect sites on SiO<sub>2</sub> and MgO are identified using MIES by a narrowing of the O(2p) features with a reduction in the density of extended defect sites. MIES of adsorbed Xe (MAX) is also used to estimate the density of extended defect sites. Furthermore, it is shown that CO is an appropriate probe molecule for estimating the defect density of MgO surfaces. Upon Ag exposure, the change in the work function of a low defect MgO(100) versus a high defect surface is markedly different. For a sputter-damaged MgO(100) surface, an initial decrease of the work function was found, implying that small Ag clusters on this surface are electron deficient. In contrast, for SiO<sub>2</sub> no significant change of the work function upon Ag exposure with increasing defect density was observed. On MgO(100), the presence of defect sites markedly alter the electronic and chemical properties of supported Ag clusters. Such a strong influence of defect sites was not found for Ag clusters on SiO<sub>2</sub>.

Publication No. 44 in DOE-BES Publication List (Section III)

**28 The Influence of Metal Cluster Size on Adsorption Energies: CO Adsorbed on Au Clusters Supported on TiO<sub>2</sub>**

Infrared reflection absorption spectroscopy (IRAS) has been used to study CO adsorption on Au clusters ranging in size from 1.8 to 3.1 nm, supported on TiO<sub>2</sub>. The adsorbed CO vibrational frequency blue-shifts slightly (approximately 4 cm<sup>-1</sup>) compared to that adsorbed on bulk Au, whereas the heats of adsorption (-ΔH<sub>ads</sub>) increase sharply with decreasing cluster size, from 12 to 19 kcal/mol.

Publication No. 47 in DOE-BES Publication List (Section III)

**29 CO Dissociation at Elevated Pressures on Supported Pd Nano-clusters**

*In situ* polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) is used to study CO adsorption at elevated pressures and temperatures on Pd nano-clusters deposited on crystalline SiO<sub>2</sub> thin films. The PM-IRAS data indicate that CO dissociates on the Pd nano-clusters at 185 mbar and at temperature >600K. Combined STM and PM-IRAS data show that the Pd nano-clusters are three-dimensional and consist predominantly of <111> facets with an average diameter and height of 3.5 nm and 0.7 nm, respectively. STM data indicate no change in the morphology or sintering of the Pd nano-clusters between 300 and 650 K. For comparison, CO adsorption was investigated on a Pd(111) single crystal surface using PM-IRAS under similar conditions (P<sub>CO</sub> = 133 mbar, T = 175 - 750 K).

Comparison of the PM-IRAS data for CO adsorption on Pd (111) and Pd nano-clusters indicate that in contrast to the Pd nano-clusters, CO adsorbs molecularly on the Pd(111) surface in a reversible manner, i.e. no dissociation.

Publication No. 48 in DOE-BES Publication List (Section III)

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#### **IV. OBJECTIVES FOR 2004**

There are three major thrusts planned for the coming year: i) the synthesis and characterization with high resolution STM of ensembles of one oxide, i.e.  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ , on a single crystalline support, followed by decoration with metal clusters, i.e. Au, Pd, Cu, etc. Preliminary results from our laboratories show these mixed-oxide supports to offer great potential for making sinter-resistant, supported nanocatalysts; ii) completion of an extensive study of the CO/NO reaction over single crystalline and supported Pd clusters using principally PM-IRAS; this vibrational technique is being exploited for use at elevated temperature and pressures typically used in technical environments; and (iii) characterization of nanostructured  $\text{TiO}_2$  ensembles supported on silica by HREELS, ISS, XPS, UPS, and MIES, emphasizing the unique structural and electronic properties of supported  $\text{TiO}_2$  films in the context of their special catalytic properties.

#### **V. UNSPENT FUNDS FOR THE YEAR (2003)**

At the current rate of expenditures we anticipate there to be no unspent funds on this project for the period January 1 to December 31, 2002.