DIVISION OF PHYSICAL CHEMISTRY

Final Program, 226th ACS National Meeting, New York, NY, September 7-11, 2003

Size-Selected Clusters on Surfaces

Abstracts

PHYS **17 [654994]: Clusters, facets and edges: Site-dependent selective chemistry on model catalysts**
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No abstract available.

PHYS **18 [639176]: Size selected metal clusters on surfaces and in the gas phase**
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A new source has been developed for generating broad distributions of metal clusters with n up to about 100. These clusters can be mass selected and gently deposited on semiconductor surfaces under ultra high vacumn conditions. Preliminary results for a range of sizes of silver and gold clusters deposited on TiO2 will be given, where characterization is done using high resolution STM/AFM analysis. Results will also be given for gas phase reactions of smaller coinage metal clusters reacting with propene, ethylene, oxygen and other ligands. Ligand induced fragmentation is induced in some systems and mechanisms will be given. Where possible equilibrium constants are measured as a function of temperature in order to obtain thermochemical quantities. High level ab initio calculations are done on all systems for comparison with experiment.

PHYS **19 [655052]: Anionic gold clusters, and their reactivity**
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Reactions of size selected anionic gold clusters with CO and O_2 were investigated using Fourier Transform Ion Cyclotron Resonance Mass Spectroscopy (FT-ICR MS). The clusters display an amazing variety and selectivity in their chemistry, with clusters of different sizes differing not only in terms of their reaction rates, but also in the reaction pathways, sequence and chemical behavior. The bimolecular CO adsorption on the gold clusters exhibits in general very low reaction rates, with overall, odd clusters reacting faster than the even species. On the other hand, the even clusters seem to exhibit higher propensity towards reaction with O_2. Interesting sequential absorptions, ligand exchanges, and cooperativity effects between the adsorption of CO and O_2 are observed. No clear evidence for oxydation of CO is detected. The implication of the observations for the catalytic activity of gold will be discussed.

PHYS **20 [643632]: Gas-phase transition metal cluster catalysis: Energetics of reaction intermediates**
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Palladium and gold clusters catalyze the oxidation of CO to CO_2. Guided ion beam tandem mass spectrometry techniques are employed to investigate the reactivity of small gas-phase metal cluster anions. The energetics of intermediates along the catalytic reaction path are examined by synthesizing beams of the clusters anions with adsorbed CO, O_2, or CO_2 molecules, or O atoms. Energy-resolved collision-induced dissociation of these intermediate species allows determination of the threshold energies for desorption. The reactivity and energetics of the gas-phase palladium and gold cluster anions are compared with previous work on platinum clusters, and with the reactions on bulk surfaces and supported clusters. Issues of the efficiency of gas-phase catalysis are considered.

PHYS **21 [644138]: Catalytic water formation on free platinum clusters**

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A pulsed beam of platinum clusters is generated with a laser vaporization source. The cluster beam passes through two reaction cells and the clusters are detected with laser ionization and time-of-flight mass spectrometry. By measuring the abundance of pure clusters and reaction products as a function of reaction cell pressure, the reaction probability in a cluster-molecule collision can be determined. The reaction probability of Pt_n (n=7-30) with oxygen is for most sizes between 0.2 and 0.3, and appears somewhat lower with hydrogen (deuterium). When the clusters first react with oxygen and then with hydrogen the number of oxygen atoms adsorbed on the clusters decreases as the number of cluster-hydrogen collisions increases. The only reasonable explanation for this is that water molecules form on the clusters and desorb. The efficiency of the reaction is high on the cluster sizes investigated (7-30 atoms), with only a weak size dependence.

PHYS **22 [644298]: Gas-phase molybdenum carbide and sulfide clusters and nanocrystallites: Production and reactivity**

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We are investigating the reactivity of molybdenum carbide and sulfide nanoparticles generated in the gas-phase. In the bulk, MoS_2 is widely used as a catalyst for hydrodesulfurization and molybdenum carbide surfaces have been shown to be effective for promoting reactions involving C-H bond activation. The wider range of stoichiometries and particle structures afforded by nanoparticle synthesis is expected to provide a means to further tailor their activity. We have recently used a laser ablation plasma source to generate gas-phase Mo_mX_n (X=C, S) clusters and nanocrystallites and are currently developing an ion beam apparatus to study size-selected free and deposited ions of the same material. Preliminary mass spectroscopy results show the production of a wide range of nanoparticle stoichiometries slightly different from those observed using laser ablation. The most recent data from this apparatus will be presented along with results from our laser ablation studies. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract No. DE-AC02--98CH10886

PHYS **44 [632858]: Hydrocarbon reactions on oxide-supported metal nanoparticles**

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Oxide-supported metal catalysts have been studied here using well-defined surfaces involving vapor-deposited metal films on single-crystal oxides. Angle-resolved Xray photoelectron spectroscopy (ARXPS), low-energy He+ ion scattering spectroscopy (ISS), non-contact atomic force microscopy (nc-AFM), low-energy electron diffraction (LEED) and temperature programmed desorption (TPD) were used to characterize the resulting metal nanoparticles formed and their chemisorption properties toward hydrocarbons. The heats of adsorption of metal atoms on MgO(100), measured calorimetrically as a function of the resulting metal particle size, show a dependence on particle size that is much stronger than suggested by the Gibbs-Thompson relation. This strong dependence helps explain the observed strong variation in chemisorption properties with particle size. This result will be contrasted with the frequent observation of structural insensitivity in hydrocarbon dehydrogenation and hydrogenation reactions on metal particles. The reasons for this apparent discrepancy will be discused. ·Work supported by NSF and DOE-OBES, Chemical Sciences Division.

PHYS **45 [643861]: Chemistry and catalysis of metal clusters on surfaces**

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The reactivity of nanoscale systems are mainly dominated by quantum-size effects that govern the electronic spectra of clusters, by the structural dynamical fluxionality of clusters, as well as by impurity-doping effects. In this talk these fundamental and unique cluster properties are illustrated by specific examples obtained from molecular beam

experiments in the gas phase and experiments on size-selected clusters on surfaces. Where possible, concepts for their understanding are given. Specifically, the nanoscale reactivity of free, small metal clusters will be presented. It will be shown how the interaction and chemical reactivity can be changed with cluster size. On a specific example it will be shown how the reaction mechanism and the energetics of a catalytic cycle can be extracted from the measured, temperature-dependent kinetics. The experimental results are then compared to extensive ab-initio calculations. In a second set of experiments metal atoms and small metal clusters are formed in the gas phase, size-selected and then deposited on thin oxide films grown on metal surfaces. Chemical reactions and catalytic properties on the obtained cluster-assembled materials are then investigated under UHV conditions by means of thermal desorption, infrared spectroscopy and pulsed molecular beams. The oxidation and polymerisation reactions are strongly dependent on cluster size and on the cluster-support interaction, and not only the number of product molecules per cluster is changed, but also the branching ratio of the certain reactions. In many cases the measured reactivities are different from the ones obtained for the corresponding bulk systems. By combining the obtained experimental results with ab-initio calculations, a picture of the size-dependent behavior of cluster-assembled materials is now emerging.

PHYS **46 [662346]: Structural, electronic, and doping effects in nanocatalysis by supported and free gold clusters**

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The unique properties of size-selected metal nano-clusters, underlie the remarkable newly found catalytic activity of small gold clusters (both when supported on metal oxide surfaces as well as in the gas-phase). These include: (i) structural dynamical fluxionality, (ii) quantum size effects reflected in size-dependence of the electronic energy-level spectra and charging characteristics, and (iii) impurity-doping effects that allow modification and control of the chemical reactivity. We discuss research efforts aimed at these “nanocatalytic factors” (see H. Hakkinen, et. al., Angew. Chem. Int. Ed. 42, 1297 (2003)), and illustrate them through joint experimental and theoretical investigations.

PHYS **47 [633590]: Bond energies of molecular fragments to transition metal clusters**

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In this work, we examine the kinetic energy dependences of the reactions of Fe_n^+ and Ni_n^+ (n=2-15) with CD_4 and ND_3 in a guided ion beam tandem mass spectrometer over the energy range of 0-10 eV. Metal cluster cations are formed in a laser vaporization/supersonic expansion source and reactions are performed under single collision conditions. The kinetic energy dependences are analyzed to determine thresholds for various primary and secondary reactions. From these thresholds, bond energies for iron and nickel cluster cation bonds to C, CD, CD_2, CD_3, N, ND, ND_2, and ND_3 are determined. For other atomic systems, bond energies to modest size metal clusters (10-15 atoms) reach bulk phase values. Thus, values for the molecular fragments provide some of the very FIRST data for the thermochemistry of such species bound to surfaces, information that is virtually non-existent even though these are key intermediates in a variety of catalytic processes.

PHYS **48 [642352]: Surface scattering studies of gold nanocluster chemistry**

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Gold nanoclusters supported on a titania single crystal are probed by molecular beam surface scattering methods in order to investigate their catalytic activity toward the carbon monoxide oxidation reaction. We typically populate the surface with adsorbed oxygen using a plasma-jet, radio-frequency powered oxygen source. Neat beams of CO are then impinged on the surface at various temperatures and oxygen coverages to test the oxidation reactivity. In particular, we will report on the reactivity of CO towards molecularly adsorbed oxygen as well as atomically adsorbed oxygen. We will also report on the effect of cluster size on oxidation activity over a temperature range from 77 - 400 K.

PHYS **71 [634890]: Influence of oxygen vacancies on surface and interface reactions on the rutile TiO_2(110) surface**

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Defects such as oxygen vacancies often dominate the electronic and chemical properties of transition-metal oxide surfaces. I will review recent studies on a prototypical model oxide surface - rutile TiO_2(110) - where we have exploited our high-resolution STM to study how oxygen vacancies influence surface and interface reactions. A novel and surprising O_2-mediated diffusion mechanism of oxygen vacancies on TiO_2(110) will be presented. Bridging oxygen vacancies are found to be the active nucleation sites for Au clusters on the rutile TiO_2(110) surface and we find that each vacancy site can bind 3 Au atoms on average. The change in morphology of the gold nano-clusters, exposed to CO and O_2, both under UHV and high pressure conditions, will be discussed.

PHYS **72 [639814]: Structure and reactivity of metal clusters at oxide surfaces characterized by time-resolved DXAFS and STM**

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In this study we attempted to obtain the information on how and when cluster structures change during chemical processes, which will help to discover unidentified chemistry of dynamics of catalytically active metal clusters at surfaces. We have succeeded in monitoring time-dependent Ru and Rh cluster structures at oxide surfaces in a molecular scale by time-resolved energy-dispersive X-ray absorption fine structure (DXAFS). This paper also reports the structure and reactivity of Pt nano-clusters prepared by metal-organic chemical vapor depositin (MOCVD) and metal vapor deposition (MVD) on TiO_2(110) surfaces, which were characterized by scanning tunneling microscopy (STM).

PHYS **73 [635032]: Structures and complexes of size-selected silver clusters**

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Size-selected metal cluster were prepared by mass-filtering cations from a sputtered cluster beam, retarding the clusters so as to minimize fragmentation upon impact, then neutralizing the positively charged clusters in a stream of thermionic electrons in the presence of cold rare gas such as argon. Using this technique we were able to determine unequivocal structures for Ag_5 and Ag_7, show that the dimetalcarbonyl formed from size-selected Fe dimers is the octacarbonyl rather than the eneacarbonyl and determine upper bounds for the SERS enhancement resulting from resonance enhancement alone (<1000).

PHYS **74 [659061]: The structure of Au in Au/titania catalysts, used in the epoxidation of propene in H_2/O_2 mixtures**

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Traditionally, gold has been regarded as a beautiful metal without any potential in catalysis. Recently, this picture has changed completely. It was discovered that nanosize clusters of gold are exceptionally active. For instance, in the presence of the rightly prepared Au catalysts CO oxidation occurs at high rates below 0 ^{o}C. Au/titania catalysts show potential in a commercially extremely important reaction, viz., the production of ethene epoxide from propene and a mixture of hydrogen and oxygen.
Results will be presented from a thorough characterization of the gold clusters by a combination of XPS, TEM and ^{197}Au Mössbauer absorption spectrometry. The deposition-precipitation method used lead to gold particle sizes ranging from 3 to 6 nm. The mechanism is based on bifunctional catalysis: Au catalyses the formation of hydroperoxide-like species from oxygen and hydrogen, while the epoxidation of propene takes place at the titania support. It will be shown that all information indicates that metallic gold is the active phase during epoxidation.

PHYS **75 [644377]: Shape, sintering and SERS from size-selected metal clusters on oxide supports**
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I will discuss our recent progress in probing the shape and sintering of size-selected Ag and Au clusters supported on titania surfaces using STM. We probe the evolution of the cluster shape as a function of temperature, surface conditions and defect density. We have also probed the cluster shape under catalytic conditions in the oxidation of unsaturated hydrocarbons such as ethylene and propylene. In addition we have used a metal tip over individual clusters to enhance the electric field within the tip-cluster gap by several orders of magnitude. We have used this enhanced field to record the SERS spectrum of molecules within the gap.

PHYS **97 [654974]: Clusters: Insights into surface reactions and catalyst involving oxygen transfer processes**
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Small clusters are comprised mainly of surface atoms or molecules and their study can provide useful information related to surface science. As a complementary approach to conventional surface studies widely used in the field of catalysis, it is becoming increasingly recognized that cluster science can also help elucidate the physical and chemical properties of condensed phase catalysts and, can provide detailed information on the mechanisms of reactions and the nature of various reaction sites that enables certain catalytic materials to be especially effective. In addition, the possible direct use of clusters as catalysts has aroused interest due to the difference in reactivities often observed for nanoscale materials compared to conventional bulk catalysts.

PHYS **98 [641163]: Infrared spectroscopy of size-selected cluster-adsorbate complexes**
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Weakly bound complexes of the form Mx+-(L)y (M=Fe, Ni, etc.; L=CO2, C2H2, H2O, benzene, etc.) are prepared by laser vaporization in a pulsed-nozzle cluster source. These species are mass analyzed and size-selected in a reflectron time-of-flight mass spectrometer. Clusters are photodissociated at infrared wavelengths with a Nd:YAG pumped infrared optical parametric oscillator/amplifier (OPO/OPA) laser or with a tunable infrared free-electron laser. In the past, it has been impossible to study the infrared spectroscopy of molecules like these because the density produced in the gas phase is too low to detect. Now, however, the intense infrared available from OPO's or free-electron lasers makes it possible to do either single-photon or multiphoton photodissociation spectroscopy. For example, Fe+-(CO2)x complexes absorb near the free CO2 asymmetric stretch near 2349 cm-1 but with an interesting size dependent variation in the resonances. Small clusters have blue-shifted resonances, while larger complexes have additional bands due to surface CO2 molecules not attached to the metal. Intracluster reactions are observed for complexes of nickel or cobalt that couple acetylene molecules to make pi-bonded cyclobutadiene. M+(benzene) and M+(benzene)2 ions (M=V, Ti, Fe) represent half-sandwich and sandwich species, whose spectra are measured near the free benzene modes. These new IR spectra and their assignments will be discussed as well as other new IR spectra for similar complexes.

PHYS **99 [667344]: Size-selected cluster models for nm-scale catalysts: Adsorption & reactions in an atmospheric-pressure flow reactor**
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Gas-phase clusters can offer benchmark-level understanding of many important gas-solid processes, including those implicated in operating catalysts. Reactions of selected clusters are measured mass-spectrometically over a range of size-, composition-, coverage- and charge-states. Molecular adsorbates are introduced in an atmospheric-pressure flow-reactor, such that thermal adsorption kinetics and equilibria are measured over the entire range of relevant temperature and coverage. Adsorption isotherms and kinetic parameters are related to catalytic activity and compared with predictions of high-level theory. In this paper, selected results will be presented on the following systems: gold-cluster air-purification catalysis; carbon clusters as model soot-catalysts for SO_2 oxidation; vanadium-oxide cluster redox reactions; and sodium-chloride cluster reactions relevant to atmospheric aerosol catalysis.

PHYS **100 [657790]: Infrared spectroscopy on size-selected gas-phase clusters and cluster adducts**

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There are a variety of methods to spectroscopically investigate molecules and clusters in the gas-phase. In the infrared (IR) spectral region, methods are often limited by the availability of bright and tunable light sources. We use pulsed radiation from the free-electron laser FELIX to measure vibrational spectra of size-selected gas-phase clusters. FELIX has a tuning range from 2000 to 40 wavenumbers. The light comes in 5-microsecond-long macropulses energies of up to 150 mJ. This makes FELIX the ideal tool to resonantly pump large amounts energy into gas-phase species. This absorbed energy can then cause secondary processes such as fragmentation or ionization to occur. Measuring their yield as a function of excitation wavelength gives an IR spectrum of the molecule or cluster. Here, we report on IR spectra of transition metal-oxide clusters, as well as spectra of the clusters complexed with small organic molecules.

PHYS **101 [643894]: Atomic-scale structure of RuS_2 nanoclusters from $Ru_3(CO)_{12}$ and S_2 precursors**

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RuS_2 has been shown to be the most active catalyst for hydrodesulfurization. Using XPS and STM, we studied the formation and the structure of RuS_2 nanoclusters supported on an Au(111) template, which are of interest as a model catalyst. The adsorption and decomposition of $Ru_3(CO)_{12}$ on Au(111) surface yields islands of non-coalescing 3D metallic Ru nanoclusters with narrow size distribution. After exposure to S_2 at room temperature, Ru/Au(111) reacts with sulfur, forming RuS_2 characterized by 1.6 eV shift in binding energy of Ru 3d core levels. In contrast, the Ru(0001) surface does not form sulfide under the identical conditions. The STM studies show that the morphology of metallic ruthenium cluster-islands is preserved after reaction with sulfur. Upon annealing, small part of sulfide is found as truncated triangular islands. Atomic-resolution STM images show that these clusters are one layer thick RuS_2 nanocrystllites with their (111) plane parallel to the Au(111) substrate.

PHYS **102 [643258]: Size-, packing density-, and shape-controlled nanocrystal-coated nanotube fabrication using molecular recognition and conformation control of sequenced peptides**

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With recent interest in seeking new biologically inspired, device fabrication methods for nanotechnology, we are developing a new biological approach to fabricate metal nanowires by using sequenced peptide nanotubes as templates. The sequenced peptide molecules were assembled as nanotubes and the biological recognition of the sequenced peptide toward metals lead to efficient metal nanocrystal coatings such as Au, Ag, Cu, Ni on the nanowires. Highly crystalline metal nanocrystals were uniformly coated on the peptide nanotubes with the high-density coverage. The conformations and the charge distributions of the sequenced peptide on surfaces, determined by pH and ion concentrations in the growth solutions, control the size and the packing density of nanocrystals. In the case of Ag nanocrystals, the shape of nanocrystals was also controlled. It should be noted that metallic nanocrystals in diameter around 6 nm are in the size domain to observe significant conductivity change by changing the packing density, and therefore this system may be developed to a conductivity-tunable building block. We believe this simple metal nanowire fabrication method can be applied to various metals and semiconductors with peptides whose sequences are known to mineralize specific ions.

PHYS **154 [644277]: CO adsorption on TiO_2-supported gold clusters**

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Gold nanoparticles on a TiO_2 support have been shown to be among the most efficient catalysts for carbon monoxide oxidation. Despite a large number of studies, there is no commonly opinion about the mechanisms of such a high activity. To get insight into some of the factors of this activity, we have used first principles density functional calculations to study the interaction of small Au clusters with the TiO_2 surface, the adsorption of CO on these clusters in comparison with adsorption on unsupported (gas-phase) clusters, as well as CO and O_2 adsorption and possible mechanisms of CO oxidation on the bare TiO_2 surface. The central role of the surface stoichiometry in this problem is discussed.

PHYS **155 [641561]: Inelastic neutron scattering study of the species formed in situ on reacting H_2 and O_2 over Au/TiO_2 supported catalysts**

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The discovery that highly dispersed, supported Au catalysts exhibit significant activity for CO oxidation, even at sub-ambient temperatures, and that such Au particles ranging in size from 1-6 nanometers have unusual catalytic properties for a number of catalytic reactions including the commercially important epoxidation of propylene to propylene oxide represents a significant advance in fundamental and applied catalysis. Propylene epoxidation is a very complex reaction and a complete understanding of the catalytic conversion mechanism requires detailed studies to understand the intermediate species formed on the catalyst surface. Vibrational spectroscopy by means of inelastic neutron scattering (INS) is a powerful technique that may be used to identify such intermediates and reaction products. Here we present the results of INS studies of the species formed from reactions of H_2 with O_2 as well as propylene with H_2 and O_2 over Au/TiO_2 . The former reaction is a significant first step in clarifying the mechanism for oxidation by supported Au catalysts as it addresses directly the formation of hydrogen peroxide from hydrogen and oxygen at the surface of a Au supported catalyst. There is currently no spectroscopic evidence in the literature for these species and we report for the first time evidence for the formation of key surface intermediates such as hydro-peroxy species on the dispersed Au catalysts. Epoxidation of propylene carried out under these conditions at different temperatures, however, produces complicated vibrational spectra indicative of a number of intermediate and reactant species. The identities of these species are expected to provide clues as to the nature of the reaction mechanism. This work has benefited from the use of facilities at the Manuel Lujan Jr. Neutron Scattering Center, a National User Facility funded as such by the Office of Science, U. S. Department of Energy.

PHYS **156 [664007]: Aspects of propylene epoxidation by gold clusters supported on titania**

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Propylene epoxidation by Au clusters supported on titania is a complex process. I will discuss the possibility that the reaction has a peroxo intermediate. Our suggestions are based on density functional calculations and some experimental results.

PHYS **157 [657783]: Mechanistic aspects of carbon nanotube nucleation and growth by thermal and catalytic phenomena in condensed and uncondensed systems**

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The extraordinary properties of CNTs result in potential revolutionary applications. However, many applications will require better massive, selective syntheses. A more detailed account of the mechanism is necessary for these synthetic ambitions; however, the mechanism has puzzled investigators for 10 years. This research presents the first comprehensive solution to this mechanistic puzzle by using some older, simpler ideas and integrating with many new aspects. This mechanism is realized from nonclassical aspects, in particular the rehybridization mechanics of carbon atoms. This mechanism demonstrates thermally driven rehybridization in uncondensed plasma systems and catalytically driven rehybridization in condensed CVD systems. The catalytic effects of certain metals provide lower temperature pathways by electronic and spin density wave aspects for CNT formation. Multiple, modulated and interrelated catalytic functions allow more reversible mechanics during CVD growth. Furthermore, the nonclassical considerations of other important events result in new aspects leading to this 12 step comprehensive mechanism.

PHYS **158 [637479]: A density functional theory study of CO oxidation on Au-based catalysts**

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Gold-based catalysts have been regarded as a new generation of catalysts due to their unusually high reactivity for many reactions. As a result, they have attracted much attention recently. Aiming to provide insight into these systems, we have carried out extensive density functional theory calculations for CO oxidation on Au and Au/TiO_2. It has been found that (i) CO can react with atomic O with a barrier of 0.25 eV on Au steps; (ii) the barrier for CO reacting with molecular O_2 on Au steps is 0.46 eV; (iii) molecular O_2 adsorption is significantly increased on the Au/TiO_2 interface (about 1 eV); (iv) the barrier of $CO+O_2$ on the Au/TiO_2 interface is about 0.1 eV; and (v) the dissociation barrier of O_2 on the Au/TiO_2 interface is about 0.5 eV.

PHYS **159 [644320]: Density functional study of the selective epoxidation of propene on gold clusters supported on titania**
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Bulk gold is chemically inert but it is now well known that small gold nanoparticles are catalytically active when supported on a metallic oxide surface. The selective gas phase epoxidation of propene on Au nanoparticles supported on titania is one example. So far, we have looked at the adsorption of the reactant molecules on the various component of the catalyst. In this presentation, we will report our recent progress on the understanding of this reaction and the general rules that can be extracted from our calculations. Emphasis will be given to the adsorption of propene and to the binding mechanism that describes its interaction with Au nanoparticle and titania.

PHYS **184 [643550]: Model Ir and Pd catalysts by cluster ion deposition**
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Size-selected planar model catalysts have been prepared by deposition of mass- and energy-selected Ir and Pd cluster ions on TiO_2 and Al_2O_3 supports. Samples are characterized by a combination of X-ray photoelectron spectroscopy, low energy ion scattering, Auger electron spectroscopy, and temperature-programmed desorption/reaction. By controlling deposition impact energy, it is possible to influence the morphology of the supported metal, with results depending both on metal-support chemistry, and metal-support mass ratios. Both cluster size and morphology affect chemical properties and thermal stability of the deposited clusters. Results will be presented for CO desorption and oxidation, and for hydrazine decomposition.

PHYS **185 [634742]: DFT calculations on the formation of benzene from acetylene on small iron clusters**
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Large portions of the potential energy surfaces leading to the formation of benzene from acetylene on small (N=1-4)iron clusters have been examined using Density Functional calculations. We explain the variation of the rate constants for the successive adsorption of acetylene molecules on an iron cation and the experimental observations about the cyclodimerization reactions by referring to the spin conservation principle. The question of whether two acetylene molecules form a metallacycle or a cyclobutadiene molecule is elucidated. Some of the uncertainties associated with this type of calculation for complex reactions such as these will be discussed.

PHYS **186 [642608]: Nanoscale deposition of platinum on alumina**
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When a metal is deposited on an oxide, the interaction between metal and oxide significantly alters the metal surface chemistry, offering opportunities for the tailoring of surface properties.
We explore the chemistry of nanoscale supported metals, via a three-way comparison. We examine CO chemisorption on bulk platinum, to reveal the strengths and shortcomings of current density functional theory approaches, and to provide a basis for comparison. We model CO chemisorption on Pt layers epitaxially deposited on the alumina surface, to understand the evolution of surface chemistry with thickness. We also study Pt clusters deposited on alumina, highlighting the relationship between Pt cluster structure and CO binding.

This investigation offers insights into how nanoscale confinement in multiple dimensions affects chemistry, as probed by CO chemisorption. The complex structure of alumina offers additional opportunities for surface modification. The effects of alumina defects on Pt structure and chemistry will also be investigated.

PHYS **187 [655008]: First principles studies on nanoparticle gold catalysis**
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In the last 5 years a very large amount of studies have been devoted to study different aspects of the enhanced activity of supported Au particles. We will present first principles calculations showing the relevance of different aspects of the metal support interaction for these particles and analyze other elements related to the influence of the shape on the final activity of the nanoparticles.

PHYS **188 [644897]: Surface deposition of polymetallic clusters in helium droplets**
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Helium droplets, with 10^5 - 10^7 atoms, are used in a beam as hosts to assemble metal clusters for subsequent deposition on the surface of a catalytic support. This technique offers a straightforward experimental approach for the formation of clusters with sizes between N=2 and 1000 atoms, which may be applied to virtually any metal, combination of metals, or even composites of metals and molecules or reaction products. It also insures "soft landing" of the clusters via transfer of the collision energy to evaporating helium atoms. An obvious technological trade-off is a Poisson distribution of the formed metal clusters which will have a width of about $N^{1/2}$. Gold and gold-silver alloy clusters having about 20 atoms have been formed and subsequently deposited on a MgO(100) surface. The beam flux was about 1.2 10^{15} atoms/sterad cm^2 sec. Initial experiments on the catalytic activity of these so-formed clusters will be reported.

PHYS **189 [644095]: Characterization of supported nanoclusters at realistic reaction conditions**
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Polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) and scanning tunneling microscopy (STM) have been used to study catalytic surfaces under realistic conditions. For STM an experimental approach has been developed that allows a pre-selected area of the surface to be targeted and individual supported nanoparticles imaged over a reactive pressure range spanning twelve orders of magnitude. With PM-IRAS, the CO + NO reaction over Pd(111) and Pd clusters supported on a planar SiO2 surface has been investigated within the pressure range 10-6 – 240 mbar and between 300 and 625 K. The surface species under reaction conditions and the kinetics of the formation of the reaction products have been addressed and will be discussed.

PHYS **211 [642037]: Sequential oxidation of metal clusters**
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Using photoelectron spectroscopy and calculations based on density functional theory, we have systematically investigated the electronic structure of W and Au clusters interacting with atomic and molecular oxygen. The studies are aimed not only at understanding the effect of sequential oxidation on the properties of metal clusters but also on shedding light on the evolution of bulk properties as metal-oxide clusters grow. We show that the onset of oxide-like behavior of W4Om- (0<=6) clusters occurs at m=5, well below the bulk stoichiometric composition (W4O12). The signature of this onset is established from a systematic study of the vertical detachment energies (VDE), adiabatic electron affinities (AEA), and the energy gaps between highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO). An anomalous increase in the VDE, AEA, and HOMO-LUMO gap at m=5, accompanied by the cleavage of 50% of the W-W bonds and localization of electron charge density bear testimony for a transition from metal-like to oxide-like behavior. Similar studies also show that, contrary to the conventional understanding that atomic clusters usually differ in properties and structure from the bulk constituents of which they are comprised, a small cluster containing only 4 tungsten and 12 oxygen atoms bears all the hallmarks of crystalline tungsten oxide,

WO3. This observation based on a synergistic approach involving mass distributions under quasi-steady state conditions, photo-electron spectroscopy, and first principles calculations illustrates the existence of a class of materials whose embryonic forms are tiny clusters. We will also discuss the oxidation of gold clusters with atomic and molecular oxygen where an oxygen molecule is found to bind to a single Au anion dissociatively while it binds molecularly to larger Au anionic clusters as well as to all neutral Au clusters including a single Au atom. The relevance of these studies to a fundamental understanding of catalysis will be discussed.

PHYS **212 [634267]: Investigating stored metal clusters**
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Atomic clusters may be captured in ion traps for extended storage. While trapped they can be treated repeatedly by various interactions and their reaction can be monitored for extended periods of time. The use of Penning (ICR) traps adds mass spectrometric methods for the isolation of the particular cluster species of interest (e.g. size or charge state selection) as well as for analysis of the reaction products. Thus an apparatus like the Cluster Trap [1] provides the means for various interesting investigations. In several series of experiments metal clusters have been probed with respect to their physical properties (dissociation energies, fragmentation pathways, etc.). In addition, they have been subjected to chemical reactions and the resulting products have been further investigated. One particular example is the gold-cluster methanol system, where laser dissociation techniques have been applied to characterize the nature of the binding. Recent investigations aim at precision measurements of separation energies and the extension of previous studies to multiply charged clusters. [1] L. Schweikhard, S. Krückeberg, K. Lützenkirchen, C. Walther, Eur. Phys. J. D 9, 15 (1999); L. Schweikhard, A. Herlert, M. Vogel, in E.E.B. Campbell and M. Larsson (eds.): "The Physics and Chemistry of Clusters", World Scientific, Singapore, 2001, p. 267; L. Schweikhard, K. Hansen, A. Herlert, G. Marx, M. Vogel, Eur. Phys. J. D, in print.

PHYS **213 [667354]: Size effects in the temperature-dependent magnetization of iron clusters**
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Abstract text not available.

PHYS **214 [644502]: Nano-faceted Re surface: Probe for size and structural effects in catalytic chemistry**
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We report on the controlled fabrication, characterization, and reactivity of nano-faceted Re(12-31) as a probe for size and structural effects in alcohol oxidation reactions. Re(12-31) is an atomically-rough, morphologically-unstable planar surface. Room temperature adsorption of oxygen on this surface leads to a disordered chemisorbed oxygen overlayer with a rich distribution of chemical binding states. In contrast, when the O-precovered surface is annealed to temperatures above 700 K, drastic restructuring of the surface occurs to form nanosized facets with a ridged “hill-and-valley” morphology. The facet planes are identified as (01-10) and (11-21). By varying oxygen coverage, different oxygen coordination sites on the Re facet planes can be selectively populated and identified by distinct chemical shifts to higher binding energies in the Re 4f core levels. The formation of stable nanoscale Re facets with control over specific types of adsorbed oxygen species provides a model catalyst surface to study both size and structural effects, and the nature of catalytically active oxygen, in the decomposition and oxidation of methanol.

PHYS **215 [644524]: Probing of surface states with non-linear optical techniques**
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Recent experiments on deposited gold clusters have shown that Au_8 is almost inert in the oxidation of CO when the cluster is deposited on a perfect MgO (100) film, but if the substrate is defect rich the cluster is highly active [A. Sanchez *et al.*, J. Phys. Chem. A 103 (1999) 9573]. This is quite understandable since a non-stoichiometric surface has a number of color centers which introduce metallic-like states in the band gap of the insulator as shown experimentally on surfaces of BaF_2 using multiphoton-induced desorption and second harmonic generation, SHG [E. Matthias *et al.*, J. Vac. Sci. Technol. B 5 (1987) 11415, J. Reif *et al.*, Physica Scripta 35 (1987) 532]. These non-linear optical techniques are quite general and it will be discussed how they can be applied for the characterization of surfaces of insulators such as catalyst supports.