THE PHYSICAL AND CHEMICAL PROPERTIES OF NANOSTRUCTURED MIXED-METAL CATALYSTS

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Overall Research Goals and Specific Objectives for the period 1/1/11-12/31/11
The main targets of this study has been to synthesize well-defined nanoclusters of Ni, Co, Pt, Rh and Pd as well as mixed-metal nanoclusters on ultrathin oxide surfaces and to characterize their detailed morphology using scanning probe techniques. The focus of the research is an understanding of the effects of metal-substrate interactions and overall composition on the structure/stability of single metal and mixed-metal nanoclusters and their catalytic activity.

DOE Interest and Potential Impact:
New strategies for the synthesis of well-defined nanostructured catalysts that are highly stable toward reaction conditions and thermal-induced sintering are necessary for the development of highly dispersed, size-limited catalysts for new catalytic applications. The development of *in situ* methods for characterizing the morphology of nanocatalysts and the surface species formed during reaction are keys to the ultimate synthesis of practical commercial nanocatalysts. These key issues are central to the proposed work.

Accomplishments during the Period 1/1/11 – 12/31/2015:
Ni-Based Model Catalysts for Light Alkane Dehydrogenation
The structure reactivity, surface segregation, and hydrogen spillover were studied on supported Ni, Ni-Au and Ni-Cu model catalysts for light alkane dehydrogenantion and hydrogenolysis.

Ni-Au bimetallic model catalysts were prepared as thin films on Re(0 0 0 1) or Ru(0 0 0 1) single crystal substrates. Surface compositions and electronic structures of the Ni-Au thin films were characterized by low energy ion scattering spectroscopy and X-ray photoelectron spectroscopy, respectively. Surface alloys were prepared by annealing Ni-Au thin films from 500 to 800 K, resulting in substantial surface enrichment of Au. Annealing a Ni-Au thin film with a 1:1 bulk composition ratio at 700 K for 10 min resulted in a surface alloy with 84% (atomic concentration) of Au in the outermost surface layer. The surface atomic structure was investigated using CO as probe molecules, which exclusively adsorbs on the Ni atoms rather than on the Au atoms at room temperature. Polarization modulation infrared reflection

absorption spectroscopy of CO adsorption on Ni-Au surface alloys showed that CO adsorption on two-fold bridge sites decreased and finally disappeared with an increase of Au surface concentration. The absence of Ni bridge site CO adsorption indicated that Ni atoms were isolated by Au atoms on Ni-Au alloyed surface.[1]

It is of great importance to study the catalytic structures under real reaction conditions especially for the bimetallic catalysts, where facile surface restructure or surface segregation can be driven by adsorbate adsorption. Here, we report CO interaction with Cu-Ni/SiO2 bimetallic model catalysts studied by CO temperature programmed desorption (TPD) and in situ CO polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) under CO pressures varying from ultrahigh vacuum (UHV) to near ambient pressure. Under UHV conditions, Cu is enriched on the surface of Cu-Ni/SiO2 bimetallic catalysts. CO spillover from Cu to Ni on Cu-Ni/SiO2 bimetallic catalysts has been observed at about 200 K under UHV conditions. In situ CO PM-IRRAS shows surface segregation of Ni on the Cu-Ni/SiO2 bimetallic catalysts induced by CO adsorption at ambient pressure CO. The behavior of CO induced surface segregation can lead to severe errors in Ni active site measurements by the selective CO chemisorption on Cu-Ni/SiO2 bimetallic catalysts.[2]

The kinetics of cyclohexane dehydrogenation was studied under near atmospheric pressure (25 Torr) at 600 K on Ni/SiO2/Mo(110) model catalysts prepared under ultrahigh vacuum conditions. The supported Ni model catalysts were characterized by Auger electron spectroscopy, temperature programmed desorption (TPD) and polarization modulation infrared reflection absorption spectroscopy (PM-IRAS). The average Ni particle sizes and particle size distributions were acquired by scanning tunneling microscopy. The kinetics results show that, for Ni particles below 2.5 nm in diameter, the specific rates (turnover frequency of benzene or TOF) increase with a decrease in particle sizes, while for Ni particles larger than 2.5 nm, the TOF is particle size independent. H-2- and CO-TPD experiments as well as CO PM-IRAS spectroscopy confirm the change of Ni particles' surface structures as a function of particle size. The particle size effect on reaction kinetics is explained by the sharp increase in the fraction of low coordinated Ni atoms on the surface of particles below 2.5 nm in diameter.[3]

Inspired by previous studies on model systems, a series of silica-supported Au-Ni catalysts were prepared and tested for the conversion of propane in the presence of hydrogen. The Au-Ni/SiO2 catalysts were prepared by successive impregnation, i.e. Ni was deposited first followed by Au. TEM/EDX results confirmed the presence of bimetallic Au-Ni nanoparticles. The dehydrogenation of propane to propylene was observed on the Au-Ni bimetallic catalysts, whereas only hydrogenolysis products were observed on the monometallic Ni catalyst. The selectivity to propylene was found to increase monotonically with the Au loading. The results are in good agreement with the results on model catalysts.[4]

Hydrogenolysis and dehydrogenation of propane were studied over model nickel-gold catalysts. The supported model Ni-Au catalysts were prepared by depositing Ni and Au onto a planar silica film. Infrared reflection absorption spectroscopic data showed that isolated Ni sites appeared and became dominant on the surface with the addition of Au to Ni. For the conversion of propane in the presence of hydrogen, the dehydrogenation of propane to propylene was observed on the Ni-Au bimetallic catalysts, whereas only hydrogenolysis products were observed on the monometallic Ni catalyst. A correlation was found between the concentration of isolated Ni sites and the catalytic activity for propane dehydrogenation.[5]

The spillover of hydrogen from Ni to Cu was directly observed on bimetallic Ni-Cu thin films and nanoparticles by hydrogen temperature programmed desorption (TPD) via depositing Cu atoms onto Ni surfaces precovered with atomic hydrogen. The spillover of hydrogen between metals could result in over counting of active sites by hydrogen selective adsorption methods, and also provides a new concept for catalyst design.[6]

Propane hydrogenolysis has been investigated on Ni-Cu/SiO2 model catalysts under elevated pressure conditions. The surface Ni active sites on Ni-Cu/SiO2 were measured by selective hydrogen adsorption under ultrahigh vacuum (UHV) conditions. The specific activity of propane hydrogenolysis shows a slight increase and then decrease with increasing Cu coverages on Ni-Cu/SiO2 bimetallic catalysts, and varies within the 0.6 s(-1) to 2.0 s(-1) range. On the contrary, many previous studies show a three-to-five order decrease in the specific activity of ethane or propane hydrogenolysis over Ni-Cu bimetallic catalysts. The significant difference was explained by the possible over counting of active Ni sites in the selective hydrogen chemisorptions under atmospheric pressure conditions due to hydrogen spillover from Ni to Cu. New structure-activity relationships for Ni-Cu bimetallic catalysts in propane hydrogenolysis were established based on the present work. Furthermore, possible carbon deposits in this reaction were examined by post reaction Auger electron spectroscopy.[7]

Cobalt-Based Model Catalysts for F-T Synthesis
The structure sensitivity and surface reconstructing of Co and Co-noble metal model catalysts were studied for Fischer-Tropsch synthesis.

In order to study the intrinsic particle size effect of Co catalysts in Fischer-Tropsch synthesis, a series of Co/SiO_2 model catalysts with various metal coverages (0.25-6.0 ML), corresponding to sizes in the range of 1.4-10.5 nm were prepared in an ultrahigh vacuum chamber and tested at 513 K under atmospheric pressure in a batch reactor. The Co particle size distribution and the number of active sites were estimated from the TEM images. Kinetic data and post-reaction XPS spectra showed that for the small Co particles (1.4-2.5 nm), the Co surface was readily oxidized by water vapor, while for the relatively large Co particles (3.5-10.5 nm), such oxidation was not evident. The oxidation for the small Co particles leads to lower TOF and higher CH_4 selectivity, while both reactivity and selectivity were relatively constant for the relatively large Co particles. The lack of intrinsic particle size effect for the metallic Co particles in the range of 3.5-10.5 nm is consistent with structure insensitivity in FT synthesis.[8,9]

The effects of the addition of Ag, Au, or Rh to a 15 wt% Co/SiO_2 catalyst on the Fischer-Tropsch (FT) synthesis were studied. Both Au and Rh showed a promoting effect on the FT activity, whereas the addition of Ag decreased the activity. The addition of a small amount of Rh (0.1-0.5 wt%) increased the CO conversion by 50% without affecting the selectivity. It was found that Rh catalyzed the reduction of cobalt oxides, but it did not change the number of surface cobalt atoms. It is proposed that the higher activity of Rh-promoted catalysts is due to the hydrogen spillover from Rh to Co during FT synthesis.[10]

Co-Rh bimetallic model catalysts were prepared as thin films on a Mo(1 0 0) substrate and as dispersed clusters on a SiO_2 support under ultrahigh vacuum conditions. The surface composition and electronic structure of the Co-Rh thin films on the Mo(1 0 0) substrate were characterized with low energy ion scattering spectroscopy (LEIS) and X-ray photoelectron spectroscopy (XPS). The surface composition and morphology of the Co-Rh

dispersed clusters on the SiO(2) support were determined by LEIS, XPS and transmission electron microscopy (TEM) with energy dispersive X-ray spectroscopy (EDX).Co-Rh thin films form a stable alloy between 700 and 1000 K with substantial surface enrichment of Co. Annealing a 1:1 Co-Rh thin film at 700 K for 30 min yields an alloy with 79% (atomic concentration) of Co in the outmost surface layer. The Co and Rh atoms mixed to form bimetallic clusters between 700 and 800 K with Co segregated to the cluster surface. TEM images showed that the Co-Rh clusters were highly dispersed on the SiO_2 support and the average particle size of the bimetallic clusters increased monotonically with the total Co fraction.[11]

Model Catalysts of Supported Nobel Metals and Their Alloys
The structures of thin oxide film supported nanoparticles of Pt, Pd, Au, Rh and their alloys were characterized by UHV surface science technique and in-situ/operando techniques. The CO oxidation, n-heptane dehydrogenation, and Ethylene hydroformylation kinetics under near realistic conditions were studied on these model catalysts.[12-14]

Graphitic overlayers on metals have commonly been considered as inhibitors for surface reactions due to their chemical inertness and physical blockage of surface active sites. In this work, however, we find that surface reactions, for instance, CO adsorption/desorption and CO oxidation, can take place on Pt(111) surface covered by monolayer graphene sheets. Surface science measurements combined with density functional calculations show that the graphene overlayer weakens the strong interaction between CO and Pt and, consequently, facilitates the CO oxidation with lower apparent activation energy. These results suggest that interfaces between graphitic overlayers and metal surfaces act as 2D confined nano-reactors, in which catalytic reactions are promoted. The finding contrasts with the conventional knowledge that graphitic carbon poisons a catalyst surface but opens up an avenue to enhance catalytic performance through coating of metal catalysts with controlled graphitic covers.[14]

Temperature desorption spectroscopy (TDS) and infrared reflection absorption spectroscopy (IRAS) were used to study CO adsorption on the terrace and step sites of Pt nanoparticles grown in ultrahigh vacuum on SiO(2). The percentage of terrace sites obtained by TDS measurements from four average particle sizes (>4, 4.2, 3.3, 2.6, and 2.5 nm) are compared to a simple hard sphere counting model of a truncated cuboctahedron. It is demonstrated experimentally that when the average Pt particle size is reduced from 4.2 to 2.5 nm, the percentage of terrace sites decreases by similar to 50%, consistent with the hard sphere models. Pt particle morphology is further explored by blocking the terrace sites with ethylidyne (derived from ethylene). CO adsorption on the unoccupied sites of Pt nanoparticles precovered with ethylidyne demonstrates a continuous red-shift in IRAS with increasing particle size. Similarities and differences between Pt nanoparticles and high-index single crystals are discussed.[15]

The structure sensitivity of n-heptane dehydrocyclization has been evaluated on Pt nanoparticles as a function of Pt particle size. Pt particles were vapor-deposited onto a SiO_2 surface in ultrahigh vacuum (UHV) and then run under near-atmospheric pressures (195 Torr) by transferring the samples in situ to a batch reactor connected to the UHV system. The results demonstrate that the reaction rate increases as the particle size is decreased from 4 to 1.5 nm, consistent with results on high surface area technical catalysts. However, as

particle size is further decreased below 1.5 nm, the reaction rate decreases, thus providing evidence of an optimum particle size for the dehydrocyclization reaction under the experimental conditions. The reactions on the nanoparticles are also compared with results obtained on Pt(100) and Pt(110) single crystals, which were run in the same apparatus under identical conditions. The differences between supported and unsupported It demonstrate that nanoparticles deactivate at a slower rate than single crystals, which suggests participation from the underlying silica support.[16]

$C_2H_4/CO/H_2$ reaction is investigated on Rh/SiO_2 model catalyst surfaces. Kinetic reactivity and infrared spectroscopic measurements are investigated as a function of Rh particle size under near atmospheric reaction conditions. Results show that propionaldehyde turnover frequency (TOF) (CO insertion pathway) exhibits a maximum activity near $< d(p)> = 2.5$ nm. Polarization modulation infrared reflection absorption spectroscopy under CO and reaction ($C_2H_4/CO/H_2$) conditions indicate the presence of Rh carbonyl species ($Rh(CO)_2$, $Rh(CO)H$) on small Rh particles, whereas larger particles appear resistant to dispersion and carbonyl formation. Combined these observations suggest the observed particle size dependence for propionaldehyde production via CO insertion is driven by two factors: (i) an increase in propionaldehyde formation on undercoordinated Rh sites and (ii) creation of carbonyl hydride species ($Rh(CO)H$)) on smaller Rh particles, whose presence correlates with the lower activity for propionaldehyde formation for $< d(p)> < 2.5$ nm.[17]

Model catalyst surfaces, consisting of vapor-deposited metal nanoparticles supported on a planar oxide support, can help to link reactivity studies on well-defined single crystal surfaces with those conducted on high-surface area supported catalysts. When coupled with near atmospheric pressure kinetic and spectroscopic techniques, these well-defined model catalyst surfaces represent a useful approach to combine the power of surface analytical techniques with reactivity studies under relevant reaction conditions. Here, we review recent results of our investigations characterizing the physical and catalytic properties of Pt/SiO_2 and Rh/SiO_2 model catalyst surfaces. As will be discussed, the model catalyst approach can help simulate the complexities of catalytic reactions on supported catalysts, helping to provide insights into the role of particle size, particle morphology, and surface adsorbates in dictating the observed structure-sensitivity (activity and selectivity) during reactions at near atmospheric pressures.[18,19]

Pd-Au bimetallic model catalysts, synthesized either as thin films on Mo(110) or as nanoparticles on a TiO_2 thin film, were used in CO oxidation at both low (1 x 10(-7) Torr) and elevated (8-16 Torr) CO pressures' Alloying with Au forms isolated Pd sites that are incapable of dissociating O(2). This inability causes reactivity loss at low reactant pressures. Moreover, alloying also electronically modifies Surface sites and affects the reaction activation energy. At elevated pressures, I'd preferentially segregates to the surface to form contiguous Pd sites and CO oxidation reactivity is regained. Under stoichiometric conditions and relatively low temperatures, Pd-Au alloys Show superior reactivity compared with pure Pd due to more facile CO desorption (less CO inhibition). Under net oxidizing conditions, metallic Pd displays superior reactivity due to its higher capability of dissociating O_2. However, pure Pd oxidizes and loses reactivity more readily than do Pd-Au alloys.[20]

Polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) was used to investigate the effects of water on CO oxidation catalyzed by TiO_2 supported Au. The introduction of water into the reactant mixture caused two effects: (1) a decrease in the CO coverage; and (2) the appearance of a carbonate species. Since both effects inhibit CO oxidation, the promotional effects of water found by previous researchers can only be

rationalized by its effects on molecular oxygen adsorption and activation. Although this argument is not confirmed by the PM-IRAS data alone, this conclusion is consistent with previous studies. It is further inferred from this study that carbonate species first form on TiO_2 sites and then migrate to Au sites. Surface hydroxyl species may play the same promotional role as adsorbed water.[21]

Microscopic and spectroscopic techniques at near-atmospheric pressures have been used in recent years to investigate CO oxidation over Pt-group metals. New insights have been obtained that allow broadening of the understanding of this reaction beyond the ultrahigh vacuum regime where it is well-understood. However, new issues also have arisen that need clarification. In this paper, we review recent work in our laboratory, using polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) and reaction kinetics measurements from ultrahigh vacuum to near-atmospheric pressures. These studies reveal a continuity of this reaction with respect to pressure over Pt, Pd, and Rh; that is, Langmuir-Hinshelwood kinetics is exhibited over a wide pressure range with no apparent "pressure gap". The difference between Ru(0001) and other noble metals is well-understood with respect to higher oxygen binding energies and reduced CO inhibition. It is concluded that for all Pt-group metals the most active phase is one saturated with chemisorbed oxygen and with low CO coverages. The significance of oxide phases under most industrially relevant catalytic conditions suggested recently in the literature is not consistent with the experimental data.[22,23]

CO oxidation was carried out over Ru(0001) and $RuO_2(110)$ thin film grown on Ru(0001) at various O_2/CO ratios near atmospheric pressures. Reaction kinetics, coupled with in situ polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) and post-reaction Auger electron spectroscopy (AES) measurements, were used to identify the catalytically relevant phases under different reaction conditions. Under stoichiometric and reducing conditions at all reaction temperatures, as well as net-oxidizing reaction conditions below similar to 475 K, a reduced metallic phase with chemisorbed oxygen is the thermodynamically stable and catalytically active phase. On this surface CO oxidation occurs at surface defect sites, for example step edges. Only under net-oxidizing reaction conditions and above similar to 475 K is the RuO_2 thin film grown on metallic Ru stable and active. However, RuO_2 is not active itself without the existence of the metal substrate, suggesting the importance of a strong metal-substrate interaction (SMSI).[24]

Electrocatalysis
Structural, Compositional and Electrochemical Characterization of Pt-Co Oxygen-Reduction Catalysts.

Pt-Co thin-film electrocatalysts have been characterized using low-energy ion-scattering spectroscopy (LEISS), X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), temperature-programmed desorption (TPD) and electrochemistry (EC). For comparative purposes, LEISS and EC were also carried out on a bulk Pt_3Co (111) single crystal. The extensive experimental work resulted in the establishment of the surface phase diagram of the alloy film marked by a substantial divergence between the composition at the interface and that in the interior. When a dual-layer deposit of Pt and Co was annealed at high temperatures, alloy formation transpired in which the outermost layer became single-crystalline and enriched in Pt. The preferential surface segregation of Pt, however, was not sufficient to generate a platinum-only overlayer or "skin". Invariably, Co was found to co-

exist with Pt, independent of the substrate [Mo (110) or Ru (0001)] employed; Pt_3Co was the most favored composition. The same result, the absence of a Pt skin, was likewise indicated at the post-thermally-annealed surface of the bulk Pt_3Co (111) monocrystal. For alloy-film surfaces more enriched in Pt than Pt_3Co, the topmost layer was constituted primarily, but not exclusively, of Pt (111) domains. The proclivities of the alloys towards enhanced catalysis of the oxygen-reduction reaction were assessed in terms of their voltage efficiencies, as manifested by the open-circuit potential (OCP) in O_2-saturated sulfuric acid electrolyte. The Pt_3Co surface, whether from the thin film or the bulk single crystal, exhibited the highest OCP, a significant improvement over pure Pt but still appreciably lower than the thermodynamic limit. The degradation of the Pt_3Co thin-film surface was predominantly due to Co corrosion. A minimal amount was spontaneously dissolved upon simple immersion in solution; slightly higher dissolution occurred at potentials above the OCP. The fraction that was not immediately corroded proved to be stable even after prolonged periods at potentials more positive than the OCP.[25,26]

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