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CORRELATIONS BETWEEN SURFACE STRUCTURE AND

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PROGRESS REPORT

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**CORRELATIONS BETWEEN SURFACE STRUCTURE AND
CATALYTIC ACTIVITY/SELECTIVITY**

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APPENDIX: PREPRINTS/REPRINTS

I. PROJECT SUMMARY

The primary focus of this research is to address those issues which are keys to understanding the relationship between surface properties and catalytic activity/selectivity. These issues also impact the understanding of the origins of the enhanced catalytic properties of mixed-metal catalysts. The experimental approach utilizes a microcatalytic reactor contiguous to a surface analysis system, an arrangement which allows in vacuo transfer of the catalyst from one chamber to the other. Surface techniques being used include Auger (AES), ultraviolet and X-ray photoemission spectroscopy (UPS and XPS), temperature programmed desorption (TPD), low energy electron diffraction (LEED), high resolution electron energy loss spectroscopy (HREELS), infrared reflection absorption spectroscopy (IRAS), and scanning tunneling and atomic force microscopy (STM and AFM).

Our research program builds upon our previous experience relating the results of single crystal kinetic measurements with the results obtained with supported analogs. As well we are exploiting our recent work on the preparation, the characterization, and the determination of the catalytic properties of ultra-thin metal and metal oxide films. Specifically, the program is proceeding toward three goals: (1) the study of the unique catalytic properties of ultrathin metal films; (2) the investigation of the critical ensemble size requirements for principal catalytic reaction types; and (3) the modelling of supported catalysts using ultra-thin planar oxide surfaces.

II. INTRODUCTION

For the last several years at Texas A&M University (since 1988) we have been engaged in a DOE-BES Chemical Sciences sponsored research program directed toward the correlation of surface science studies on single crystal surfaces with the corresponding measurements on supported metal catalysts.¹⁻¹⁴⁸ This research has addressed the nature of "structure sensitivity" for hydrogenolysis reactions or reactions involving the breaking of carbon-carbon bonds.¹⁵⁻²⁴ Different crystal planes have been shown to exhibit variations in reactivity toward breaking this molecular bond type. These variations in catalytic activity have shown that the particle morphology of supported metals is responsible for the absolute activity of high area catalysts.

Another aspect of our research has been to address the nature of poisoning and promotion of transition metal catalysts.²⁵⁻³⁵ Atoms of varying electronegativity have been added systematically to the surfaces of metal single crystals and the submonolayer coverages of these impurities determined quantitatively by low-energy electron diffraction and Auger techniques. The carefully characterized catalysts have been used to study methanation, ethylene hydrogenation, and cyclopropane ring opening reactions. These studies have provided quantitative information regarding impurity poisoning and promotion effects in catalysis.

We have also investigated the fundamental mechanisms associated with the catalytic reactions between carbon monoxide and oxygen or nitric oxide,³⁶⁻⁴⁸ key reactions of automotive exhaust upgrading. These studies have shown an impressive correlation between the model catalysts and the corresponding supported materials and have led to a more complete understanding of these surface catalyzed reactions.

Recent work has addressed the mechanism by which bimetallic catalysts demonstrate improved catalytic properties over single component metal catalysts.⁴⁹⁻¹⁰⁹ Recent studies have shown that monolayer metal films supported on a second metal generally are electronically perturbed, and that this perturbation can dramatically alter the chemical and catalytic properties of the overlayer metal. In many cases, the metal overlayer exhibits chemisorptive and reactivity properties that are significantly different from those seen for the pure metal. For monolayers of Ni, Cu and Pd supported on Ta, W, Re, Ru, Rh, and Pt, a correlation has been found between the shifts in surface core-level binding energies measured by XPS and the modified peak desorption temperatures observed for CO from the metal adlayers by TPD. These observed trends have led to a clearer understanding of the nature of the metal-metal bonding in these mixed metal systems.

Additional studies⁹⁰⁻¹⁰⁹ using IRAS and HREELS have addressed the special properties of monolayer metal films regarding the chemisorption and reaction of various probe molecules, including CO and methanol. This work offers clues to the fundamental

nature of the altered properties of bimetallic catalysts.

We are also presently investigating the preparation of well-characterized supported metal catalysts using ultra-thin oxide surfaces.¹¹⁰⁻¹⁴⁸ The ultimate goal is the ability to generate supported particles with one to several metallic centers with highly specific size distributions. The specific target is the precise definition of the required ensemble size necessary for the onset of molecular synthesis, reactivity, and/or rearrangement, particularly for small alkane molecules. Recently ex situ STM and AFM studies have demonstrated atomically resolved images of 1-2 nm copper clusters on thin film silica.¹⁴⁵ In situ capabilities are planned for the near future to pursue this exciting development.

This experimental program currently utilizes ten surface analytical systems, all having a microcatalytic reactor contiguous to a surface analysis system.¹⁻¹⁴ 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, and XPS, 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. STM and AFM capability are also available for ex situ probing of the surface morphology.

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IV. SELECTED RECENT ACCOMPLISHMENTS: 1994

1. IRAS Study of CO Adsorption on S-Modified Mo(100) Surfaces

Infrared reflection absorption spectroscopy (IRAS) was used to study the adsorption of CO on a S modified Mo(110) surface. As the surface S coverage is increased up to 0.5 ML, the sulfur overlayer structure changes from p(2x2) to c(2x2). These changes can be observed in the IRAS spectra of adsorbed CO (see Fig. 1). In addition, it was noted that in the p(2x2)S overlayer, sulfur acted mainly as a site blocker; whereas in the c(2x2)S overlayer, electron withdrawing effects became apparent. Finally, the dissociative adsorption of CO was seen to occur on both clean Mo(110) and p(2x2)S/Mo(110) but not on c(2x2)S/Mo(110).

IRAS was also used to study the adsorption of carbon monoxide on mixed S and Co overlayers on a Mo(110) surface see Fig. 2). The results of this study indicate that there is a migration/segregation of the adatoms into 2-D and 3-D islands and that the different domains are distinguishable by the stretching frequency of the adsorbed CO. Clean Mo(110) as well as sulfided Co, (8x2)Co, p(2x2)S and C(2x2)S domains on the Mo(110) surface are all observable. In addition, sulfur was seen to act as both a site blocker and electron withdrawing agent on these surfaces. Finally, data obtained in this study suggest that the active adsorption site in a Co-MoS₂ catalyst could be a Co promoted Mo-S site.

Fig. 1. IR spectra of CO on a Mo(100) surface at 90K with the indicated sulfur coverages.

Fig. 2. IR spectra of CO adsorbed on S/CO/MO(100) at 90K with varying S coverages.

Publications Nos. 9 and 10 in DOE-BES Publication List (Section III)

2. Adsorption Isobars for CO on Pd/Ta(110) at Elevated Pressures and Temperatures Using Infrared Reflection-Adsorption Spectroscopy

IRAS has been used to study the adsorption of carbon monoxide on a Pd/Ta(110) surface. IRAS spectra were collected at pressures from 1×10^{-9} to 1.0 Torr and at temperatures from 90 to 500K. Adsorption isobars (see Fig. 3) were constructed from the IRAS spectra that allowed the determination of isosteric heats (see Fig. 4) of adsorption as a function of CO coverage. The heats of adsorption (ΔH) for CO on Pd/Ta(110) were determined to be ~ 15 kcal/mole lower than for CO adsorbed on a Pd(111) surface while the differential surface entropies (S_s) were comparable. The high coverage adsorption isosteres have a pronounced break that indicates that at high CO coverages and low substrate temperatures, the CO surface structures are not fully equilibrated.

Fig. 3 Adsorption isobars for CO on Pd/Ta(110)

Fig. 4 Plot of the isosteric heats of adsorption as a function of coverage for CO on Pd/Ta(110). The heats of adsorption for CO on Pd(111) and Pd/W(100) are shown for comparison.

Publications No. 6 in DOE-BES Publication List (Section III)

3. Preparation of Mixed $\text{Al}_2\text{O}_3/\text{SiO}_2$ Thin Films Supported on Mo(110)

Deposition of metallic Al onto a SiO_2 thin film, supported on a Mo(100) substrate, at 100K, followed by annealing to 1200K, leads to the formation of a homogeneous $\text{Al}_2\text{O}_3/\text{SiO}_2$ film (see AES of Fig. 5). In the temperature regime from 100K to 800K, Al is completely oxidized and metallic Si is formed. The important step for the formation of Si-O-Al bonds is the concerted diffusion of aluminum oxide into the bulk of the SiO_2 film with

the concomitant desorption of volatile silicon monoxide as a result of the solid state reaction of Si and SiO₂ in the temperature range from 800K to 1200K. XPS core level shifts indicate that the electronic structure of these films is very similar to that of bulk aluminosilicates.

Fig. 5 AES spectra of a Al(3 ML)/SiO₂/Mo(100) film as a function of annealing temperature.

Publications No. 17 in DOE-BES Publication List (Section III)

4. An Infrared Study of CO on NiO(100)

The nature of the interaction of CO with NiO(100) thin films (~20-50 Å) grown on a Mo(100) substrate has been investigated with IRAS. Isosteric heats of adsorption were measured for CO in a pressure range of 1×10^{-8} to 1 Torr and over a temperature range of 93 to 280K (see Figs. 6 & 7). The average heat of adsorption was found to be approximately 10.4 kcal/mol, with the heat of adsorption decreasing slightly with increasing CO coverage. This value for the heat of adsorption agrees very well with that measured for CO on MgO(100). The CO stretching frequency was found to decrease with an increase in the CO coverage. At constant coverage, the CO stretching frequency as well as the full width at half maximum were found to increase with increasing temperature.

Fig. 6 Isobaric plots (10^{-7} to 0.1 Torr) for CO on NiO(100).

Fig. 7 Claussius-Clapeyron plots for CO adsorption on a ~ 20 Å NiO(100) film supported on a Mo(100) substrate. CO coverages: A) $\theta = 0.2$, $E_A = 12.5$ kcal/mol; B) $\theta = 0.4$, $E_A = 9.2$ kcal/mol; C) $\theta = 0.6$, $E_A = 9.3$ kcal/mol.

Publications No. 21 in DOE-BES Publication List (Section III)

5. Structural and Catalytic Properties of Model Silica-Supported Palladium Catalysts: A Comparison to Single Crystal Surfaces

The structural and catalytic properties of model silica-supported palladium catalysts have been investigated with temperature-programmed desorption, infrared reflection-absorption spectroscopy of adsorbed CO, scanning tunneling and atomic force microscopies (STM and AFM), and catalytic CO oxidation at both low pressure and elevated pressure conditions. The CO oxidation reactions on Pd(111), Pd(110) and Pd(100) have also been investigated. By evaporating palladium onto silica thin films (100 Å), followed by an anneal to 900K, the size of the palladium particles can be controlled in a range of 30-500 Å. The surface of the palladium particles consists mainly of (111) and (100) facets (see Fig. 8), and exhibit catalytic activity similar to palladium single crystals for CO oxidation at both low pressure (10^{-8} - 10^{-6} Torr) and high pressure (15 Torr) conditions (see Fig. 9). At low pressures, the rate of CO oxidation increases with temperature, reaches a maximum at 500-600K, and then declines. At high pressures, the activation energy and turnover frequency for the CO oxidation reaction on the model catalysts compare favorable with analogous results from single crystal and high-surface-area catalysts (see Fig. 9). Thus, this system of metal particles supported on a silica thin film provides an excellent model to bridge between single crystal and high-surface-area

catalysts. The CO oxidation reactions on Pd(111), Pd(110) and Pd(100) have similar, but distinctive activation energies (28.1 ± 0.4 , 30.7 ± 0.5 and 29.4 ± 0.3 kcal/mol, respectively) and turnover frequencies, indicating a subtle structure-sensitivity for CO oxidation on different crystal planes of palladium.

Fig. 8 Infrared reflection-absorption spectra for CO on Pd(100), Pd(111) and model silica-supported palladium catalysts. The palladium coverages were 1, 7 and 15 monolayers. The model catalysts were annealed to 900K. All spectra were collected at 100K and in 10^{-6} Torr CO background.

Fig. 9 Arrhenius plot of the rate of CO oxidation on palladium (111), (110), (100) and silica-supported palladium catalysts. See text for details.

Publications Nos. 2, 3, 4, 5, 7, 16 in DOE-BES Publication List (Section III)

6. Particulate Cu on Ordered Al_2O_3 : Reactions with Nitric Oxide and Carbon Monoxide

The growth of small Cu particles, prepared by vacuum vapor deposition, on Al_2O_3 films on Mo(100) has been studied in the 80-800K substrate temperature range with Auger electron spectroscopy (AES) and temperature programmed desorption (TPD) (see Fig. 10). A model based on Auger measurements has been utilized to examine the number density and the average size of the Cu particles on Al_2O_3 . Nitric oxide decomposition on the Cu particles has been further investigated using TPD and high resolution electron energy loss spectroscopy (HREELS). TPD and HREELS data (see Fig. 11) clearly show that a fraction of the NO molecules reacts with the Cu particles to produce gaseous N_2 and N_2O in the 90-250K temperature range. The formation of N_2 at 770K is also evident and is due to the recombination of adsorbed N atoms from NO dissociation. The effects of retained oxygen, adsorption

temperature and particle size on the production of high-temperature N_2 have been examined. The reaction between nitric oxide and carbon monoxide has also been studied. The results show that besides the N_2 and N_2O products arising from NO decomposition, a small quantity of CO_2 is produced by the reaction between adsorbed CO and adsorbed oxygen.

Fig. 10 A family of TPD spectra of Cu deposited at $T_s = 600$ K as a function of equivalent monolayers, θ_{Cu} : (a) 0.16; (b) 0.33; (c) 0.50; (d) 0.67; (e) 0.98; (f) 1.25; (g) 1.55; (h) 2.09. The insert shows the heat of sublimation, derived from the leading edge analysis of the spectra, as a function of Cu coverage in equivalent monolayers. A linear heating rate of 10 K/s was used.

Fig. 11 HREELS spectra of (a) a clean Al_2O_3 film, $d_{Al_2O_3} = 8$ Å and (b) Cu/Al_2O_3 , $d_{Al_2O_3} = 8$ Å, $\theta_{Cu} = 2.7$, following a saturation exposure of ^{15}NO at 80K. The spectra were acquired using an electron beam with a primary energy of $E_p = 42$ eV and at the specularly reflected beam direction.

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

7. Structural and Catalytic Properties of Model Supported Nickel Catalysts

The surface structure and catalytic properties of model silica-supported nickel catalysts have been investigated with infrared reflection-absorption spectroscopy (IRAS) and reaction kinetics of ethane hydrogenolysis and carbon monoxide methanation. Nickel particles in the range of 15-80 Å were vacuum deposited onto silica thin films using established preparation procedures. Specific rates and activation energies for ethane hydrogenolysis and carbon monoxide methanation over the model catalysts are remarkably similar to the corresponding values for both traditional silica-supported nickel catalysts and nickel single crystals. The turnover frequency for CO methanation is independent of particle size for the dimensions studied. The ethane hydrogenolysis rate, however, increases with particle size to a maximum at ~25 Å, then decreases. This

reactivity trend is found to parallel a change in the percentage of bridging CO on the nickel particles as determined by IRAS.

Fig. 12 IRAS spectra of CO annealed to 300K for increasing nickel coverage.

Fig. 13 Correlation of the TOF for ethane hydrogenolysis (reaction conditions same as in Fig. 4, 600K) and the percentage of total bridge bound CO from the IRAS spectra of Fig. 3.

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

8. Adsorption and Reaction of $[\text{Re}_2(\text{CO})_{10}]$ on Ultrathin MgO Films Grown on a Mo (110) Surface: Characterization by Infrared Reflection-Absorption Spectroscopy and Temperature-Programmed Desorption*

The decarbonylation of $[\text{Re}_2(\text{CO})_{10}]$ on ultrathin MgO(111) films (~ 50 Å) grown on a Mo(110) substrate was investigated with infrared reflection-absorption spectroscopy and temperature-programmed desorption/decomposition. When $[\text{Re}_2(\text{CO})_{10}]$ was adsorbed at 320 K, it reacted with the MgO(111) surface, forming a rhenium subcarbonyl, $[\text{Re}(\text{CO})_4\{\text{OMg}\}]_2$, where $\{\text{OMg}\}$ represents oxygen on the MgO(111) surface. Upon heating to temperatures > 400 K, $[\text{Re}(\text{CO})_4\{\text{OMg}\}]_2$ was decarbonylated, forming $[\text{Re}(\text{CO})_3\{\text{OMg}\}]_3$. Further heating to temperatures > 600 K induced the formation of rhenium metal clusters. When it was adsorbed at 110 K, $[\text{Re}_2(\text{CO})_{10}]$ condensed on MgO(111), with a fraction of the first layer decomposing to form $[\text{Re}(\text{CO})_4\{\text{OMg}\}]_2$. In temperature-

programmed desorption experiments, $[\text{Re}_2(\text{CO})_{10}]$ multilayers desorbed at 295 K. An unidentified rhenium carbonyl species, probably rhenium pentacarbonyl, desorbed at 350 K. The CO stretching frequencies of the rhenium subcarbonyls were dependent on the coadsorption of water. The infrared spectra show that the symmetry of the surface-bound rhenium tricarbonyls is C_{3v} . The results are among the first characterizing the adsorption of metal complexes on well-defined metal oxide surfaces, and they demonstrate the value of structurally characterized supports for elucidation of the nature of the metal-support interface.

Fig. 14 Fourier transform infrared reflection-absorption spectra for $[\text{Re}_2(\text{CO})_{10}]$ on $\text{MgO}/\text{Mo}(110)$. The spectra were recorded after the surface had been briefly heated to the indicated temperature. $[\text{Re}_2(\text{CO})_{10}]$ was adsorbed at 320 K with an exposure time corresponding to 5 monolayers.

Fig. 15 (A) Fourier transform infrared reflection-absorption spectra for 2-monolayer $[\text{Re}_2(\text{CO})_{10}]$ on $\text{MgO}/\text{Mo}(110)$ heated to 500 K, (B) sample incorporating subsequently adsorbed 2-monolayer water at 110 K, (C) heated to 250 K after treatment of (B), and (D) heated to 300 K after treatment of (C).

* This work was carried out in collaboration with S. K. Purnell and Prof. B. C. Gates of the University of California, Davis.

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