Chemistry of Bimetallic and Alloy Surfaces
Continuation/Incremental Funding Application

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Progress Report for First Funding Period (June 1, 1990 - November 30, 1991)

In the first funding period (18 months), we continued our work on elucidating the underlying principles that govern chemical reactions occurring on bimetallic and alloy surfaces. Our goal is to aid in the atomic level explanation of the reactivity and selectivity of alloy and bimetallic cluster catalysts and to provide a fundamental basis for the design of new catalysts with improved performance. Our approach is to use a battery of surface science methods to obtain fundamental data on the thermochemistry and kinetics of the adsorption and reaction of molecules on extensively characterized, single-crystal bimetallic surfaces. We measure changes in chemisorption bond strengths, adsorption site distributions, and hydrocarbon fragment stability and reactivity and correlate these results with the geometric and electronic structure of the metal atoms on the surface. Often, our aim is to carefully design experiments that isolate the several factors (e.g., ensemble and ligand effects) that control surface chemistry and catalysis on bimetallic and alloy surfaces in order to better understand the importance of each contribution.

In the past 18 months, we have continued to study how alkali promoters strongly affect the reactions of hydrocarbons on Pt and Ni surfaces by altering the electronic structure and inducing significant site-blocking effects. We have shown that bismuth coadsorption provides benchmark data on ensemble sizes required for chemical reactions on Pt and Ni surfaces. Surface alloys of Sn/Pt are being used for detailed probing of ensemble sizes and also reactive site requirements.

Some of the highlights and noteworthy accomplishments made during the first period of this grant are given below:

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- A semi-empirical GVB method for estimating surface thermochemistry of adsorbed hydrocarbons was developed with Prof. Emily Carter of UCLA. I believe that this method will have an enormous impact on our ability to construct "zeroth order" potential energy diagrams for understanding surface reaction energetics. This method was applied to the unpromoted and K-promoted ethylene dehydrogenation reaction on Pt(111), and is currently being used in a number of other hydrocarbon reactions.
- Studies in collaboration with Prof. David Ramaker of George Washington Univ. have shown new insight into the nature of surface carbon on Ni(100). Adsorbed carbon has appreciable C-C bonding even in the "carbide" state, and presumably exists as C_n polymers to a large extent.
- The surface alloys that are formed from deposition of Sn on Pt(111) and Pt(100) have been characterized and studied concerning their chemisorption properties. Most importantly, a surface structural determination of Sn deposited on Pt(111) by Low Energy Alkali Ion Scattering (ALEISS) was carried out in collaboration with Dr. Steve Overbury of Oak Ridge National Laboratory and Dr. Mark Paffett of Los Alamos National Laboratory. Surface structures resulting from the deposition and annealing of Sn on Pt(111) and exhibiting p(2 x 2) and p($\sqrt{3} \times \sqrt{3}$)-R30° LEED patterns were studied. Azimuthal and polar incident angle dependencies were measured for 500 and 1000 eV Li⁺ ions scattered from the clean and Sn covered surfaces. Shadowing and blocking effects adequately describe the single scattering from the clean Pt surface. The data support a structural model in which the Sn is incorporated into the Pt surface rather than existing as an overlayer. Analysis of the Sn angle dependence indicates that the Sn is not co-planar with the Pt but is protruding 0.022 ± 0.05 nm above the surface. The results are critical for interpreting the chemistry of these surfaces and represent an important advance in our understanding of metal alloy surface structure in their own right.
- The influence of potassium adatoms on the adsorption and desorption kinetics of hydrogen on the Pt(111) single-crystal surface was studied. Dissociative H₂ sticking probabilities were

measured as a function of potassium coverages. Even small amounts of potassium drastically reduce the sticking probability for H₂ on Pt(111). For example, when $\Theta_K \geq 0.04$ the sticking probability of H₂ at 100 K has been reduced by more than a factor of 10. We also find that the role of an adsorbed precursor state in H₂ adsorption on Pt(111) is decreased by the presence of K, and the activation energy for dissociative adsorption of H₂ is increased. Hydrogen adatoms adsorbed on the K modified surface are thermally stabilized compared to Pt(111). The peaks observed during H₂ TPD occur with peak temperature up to 150 K higher for the K modified surface than for equivalent hydrogen coverages on Pt(111). We explain these observations by a simple Pt atoms, due to charge transfer from K to Pt. This has two effects, (i) to destabilize the bonding of H₂ to the surface and (ii) to stabilize the bonding of H_(a) to the surface. A decrease in the Pt-H_{2(a)} interaction caused by K lowers the initial sticking probability, inhibits the role of an adsorbed H₂ precursor in the adsorption kinetics, and causes an increase in the activation energy for dissociative adsorption H₂. These effects dominate over the possible effects of the increased Pt-H bond strength in enhancing the kinetics for H₂ adsorption.

- We have successfully installed and calibrated a collimated gas beam doser in one of our vacuum chambers. This will enable us to make the first accurate measurements of adsorption probabilities of hydrocarbons relevant to hydrocarbon conversion catalysis on Pt and bimetallic Pt surfaces. We have now measured the adsorption coefficient of CO on the Pt(111) surface as a function of temperature and CO coverage, and also the influence of coadsorbed K, O, and H.
- A small volume reaction cell (that can be evacuated to ultrahigh vacuum) was also designed, fabricated, and has recently been assembled. We can use this reactor to perform atmospheric pressure reaction kinetics studies of unsupported Pt and Pt alloy catalysts (i.e., low surface area polycrystalline metals) in our laboratory. We have received and installed a gas chromatograph (GC) and differentially-pumped mass spectrometer as analytical instrumentation for these studies. We have just received delivery of a reaction cell/transfer rod assembly that will

allow us to move the sample from the catalytic reaction chamber into the UHV surface analysis chamber for the most important experiments.

Publications supported by DOE

1. "Coadsorption of Ethylene and Potassium on Pt(111). 2. Influence of Potassium on the Decomposition of Ethylene", R. G. Windham and B. E. Koel, *J. Phys. Chem.*, **94**, 1489-1496 (1990).
2. "A Method for Estimating Surface Reaction Energetics: Application to the Mechanism of Ethylene Decomposition on Pt(111)", E. A. Carter and B. E. Koel, *Surface Sci.*, **226**, 339-357 (1990).
3. "Chemisorption of High Coverages of Atomic Oxygen on the Pt(111), Pd(111), and Au(111) Surfaces", D. H. Parker and B. E. Koel, *J. Vac. Sci. Technol.*, **A 8**, 2585-2590 (1990).
4. "Temperature Programmed Desorption of Bi on Ni(100)", M. E. Jones, J. M. Heitzinger, R. J. Smith, and B. E. Koel, *J. Vac. Sci. Technol.*, **A 8**, 2512-2516 (1990).
5. "Interaction of Dimethylamine with Clean and Partially Oxidized Copper Surfaces", J. A. Kelber, J. W. Rogers, Jr., B. A. Banse, and B. E. Koel, *Appl. Surface Sci.*, **44**, 193-204 (1990).
6. "Chemisorption of CO, H₂, and O₂ on Ordered Sn/Pt(111) Surface Alloys", M. T. Paffett, S. C. Gebhard, R. G. Windham, and B. E. Koel, *J. Phys. Chem.*, **94**, 6831-6839 (1990).
7. "Hydrogen-Induced Low Temperature CO Displacement from the Pt(111) Surface", D. H. Parker, D. A. Fischer, J. Colbert, B. E. Koel, and J. L. Gland, *Surface Sci.*, **236**, L372-L376 (1990).
8. "Methyl Chloride and Trichlorosilane Adsorption on Cu(110)", K. A. Magrini, S. Gebhard, B. E. Koel, and J. L. Falconer, *Surface Sci.*, **248**, 93-103 (1991).
9. "Spectroscopic Evidence for Carbon-Carbon Bonding in "Carbide" Layers on Metals", F. L. Hutson, D. E. Ramaker, and B. E. Koel, *Surface Sci.*, **248**, 104-118 (1991).
10. "Interpretation of the Carbon Auger Line Shapes for the Adsorption and Decomposition of Ethylene on Ni(100)", F. L. Hutson, D. E. Ramaker, B. E. Koel, and S. C. Gebhard, *Surface Sci.*, **248**, 119-133 (1991).
11. "Structure of Metal Overlayers by Low Energy Alkali Ion Scattering: Cu/Ru (0001) and Sn/Pt (111)", S. H. Overbury, D. R. Mullins, M. T. Paffett, and B. E. Koel, in Structure of Surfaces III, Springer Series in Surface Science, Proceed. of ICSOS III, Milwaukee, 1990, M. A. Van Hove and S. Y. Tong, (Eds.), (Springer-Verlag, New York), in press.
12. "A Multitechnique Surface Science Examination of Sn Deposition on Pt(100)", M. T. Paffett, A. D. Logan, R. J. Simonson, and B. E. Koel, *Surface Sci.*, in press.

13. "High Resolution Electron Energy Loss Spectroscopy (HREELS)", B. E. Koel, in Encyclopedia of Materials Characterization, Vol. on Instrumental Analytical Techniques for Surface and Micro Analysis, C. Evans, R. Brundle, and S. Wilson, Eds., (Butterworth, 1992), in press.
14. "Surface Structural Determination of Sn Deposited on Pt(111) by Low Energy Alkali Ion Scattering", S. H. Overbury, D. R. Mullins, M. T. Paffett, and B. E. Koel, *Surface Sci.*, **254**, 45-57 (1991).
15. "A Vibrational Study of Borazine Adsorbed on Pt(111) and Au(111) Surfaces", R. J. Simonson, M. T. Paffett, M. E. Jones, and B. E. Koel, *Surface Sci.*, **254**, 29-44 (1991).
16. "Hydrogen-Induced CO Displacement from the Pt(111) Surface: An Isothermal Kinetic Study", D. H. Parker, D. A. Fischer, J. Colbert, B. E. Koel, and J. L. Gland, *Surface Sci.*, in press.
17. "Hydrocarbon Coverage Effects on the Structure Sensitivity of Acetylene and Ethylene Dehydrogenation on Ni(100)", S. C. Gebhard, M. E. Bartram, B. E. Koel, and J. E. Houston, *Surface Sci.*, submitted.
18. "Extracting the Coverage Dependence of Kinetic Parameters in Temperature Programmed Desorption: Application to CO on Ni(100)", M. E. Jones, D. Parker, and B. E. Koel, *Surface Sci.*, submitted.
19. "Influence of Potassium on the Adsorption of H₂ on Pt(111)", S. C. Gebhard and B. E. Koel, *J. Phys. Chem.*, submitted.
20. "Low Energy Electron Induced Chemistry: CH₃Cl on Ag(111)", X.-L. Zhou, P. M. Blass, B. E. Koel, and J. M. White, *Surface Sci.*, submitted.
21. "Low Energy Electron Induced Chemistry: C₂H₅Cl on Ag(111)", X.-L. Zhou, P. M. Blass, B. E. Koel, and J. M. White, *Surface Sci.*, submitted.
22. "Effects of Surface Modifiers (K(a), O(a), and H(a)) on the Adsorption Kinetics of CO on Pt(111)", L. Q. Jiang, B. E. Koel, and J. L. Falconer, *Surface Sci.*, submitted.

Seminars on DOE-Sponsored Research

A. Invited Lectures

6/90	"Adsorption/Desorption on Alloy Surfaces",
DOE Surface Studies Conference, 16th, Golden
6/90	"Chemisorption and Reaction on Metal Alloy Surfaces",
Symposium on Frontiers of Surface Chemistry, Catalysis Research Center,
Hokkaido University, Sapporo, Japan
11/90	"Chemistry of Bimetallic and Alloy Surfaces"
University of California, Irvine, CA, Department of Chemistry

- 10/91 "Adsorption and Desorption Kinetics of Methylcyclohexane and Toluene on Potassium and Carbon Modified Pt(111) Surfaces"
18th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS)/13th Pacific Conference on Chemistry and Spectroscopy and 27th Western Regional ACS Meeting, Symposium on Reactions at Surfaces, Anaheim

B. Contributed Talks/Papers

- The Influence of Potassium on the Adsorption of Hydrogen on Pt(111)
S. C. Gebhard, R. G. Windham, and B. E. Koel,
16th DOE Surface Studies Conference, Golden, CO, June, 1990
- Vibrational Spectroscopy of Borazine Adsorption on Pt(111)
R. J. Simonsen, **M. T. Paffett**, and B. E. Koel,
16th DOE Surface Studies Conference, Golden, CO, June, 1990
- Structure of Metal Overlayers by Low Energy Alkali Ion Scattering: Cu/Ru (0001) and Sn/Pt (111)
S. H. Overbury, D. R. Mullins, M. T. Paffett, and B. E. Koel,
3rd International Conference on Structure at Surfaces (ICSOS III), Milwaukee, WI, 1990.
- CO Displacement and Repulsive Interactions on the Pt(111) Surface
D. H. Parker, D. A. Fischer, J. Colbert, B. E. Koel, and J. L. Gland,
Chemistry at Surfaces Meeting, Irvine, CA, October, 1990
- Growth Modes and Chemistry of Bismuth on Ni(100)
J. M. Heitzinger and B. E. Koel,
Chemistry at Surfaces Meeting, Irvine, CA, October, 1990
- Vibrational Spectroscopy of Borazine Adsorption on Pt(111)
R. J. Simonsen, M. T. Paffett, B. E. Koel, and M. Trenary,
37th National Symposium of the American Vacuum Society, Toronto, Canada, October 1990
- Influence of Potassium on the Adsorption of H₂ on Pt(111)
S. C. Gebhard, R. G. Windham, and B. E. Koel,
12th North American Meeting of the Catalysis Society, Lexington, KY, May, 1991
- Effects of Surface Modifiers (K(a), O(a), and H(a)) on the Adsorption Kinetics of CO on Pt(111)
L. Q. Jiang, B. E. Koel, and J. L. Falconer,
California Catalysis Society, Fall Meeting, Santa Barbara, CA, November, 1991

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Brief Description of Plans for Upcoming Year

We plan to continue our work on elucidating the underlying principles that govern chemical reactions occurring on bimetallic and alloy surfaces. Our goal is to aid in the atomic level explanation of the reactivity and selectivity of alloy and bimetallic cluster catalysts and to provide a fundamental basis for the design of new catalysts with improved performance. Our approach is to use a battery of surface science methods to obtain fundamental data on the thermochemistry and kinetics of the adsorption and reaction of molecules on extensively characterized, single-crystal bimetallic surfaces. In addition, we plan to make increasing use in the future of data from atmospheric pressure reaction kinetics studies of unsupported Pt and Pt alloy catalysts in order to connect the observed catalytic rates with the details of surface composition and structure and the rates of elementary reaction steps measured in UHV. We are constructing now, using funds from other sources (including USC), two reaction cell/transfer rod assemblies that will allow us to move the sample from a catalytic reaction chamber into a UHV surface analysis chamber. One instrument will be optimized (small reactor volume) for kinetics measurements using a GC and one apparatus will have reflection-absorption FTIR (FT-RAIRS) capability for both UHV and higher pressure measurements.

Objectives for the next funding period of this grant are given below:

- Finish to some extent our studies of ethylene adsorption on Pt(111) and K-modified Pt(111). This involves evaluating further the site blocking effects in K coadsorption by detailed comparison to Bi data and modeling studies of Bi and ethylene coadsorption.
- Analyze data obtained in collaboration with Dr. Tom Taylor of Los Alamos National Laboratory on CO chemisorption on Ag/Cu(110) surfaces.

- We plan to extend our work using mainly TPD and HREELS to measure the influence of potassium on the bonding mode and strength of the chemisorption bond of hydrocarbons adsorbed on platinum and nickel surfaces. Particular attention will be given to the interaction of coadsorbed potassium with acetylene on Pt(111), and to the interaction of coadsorbed potassium and ethylene on Ni(100). An important goal is also to determine the influence of potassium on the decomposition kinetics of acetylene and ethylene and on the nature and stability of the hydrocarbon fragments formed.
- We plan to evaluate the use of coadsorbed bismuth to determine adsorption and reaction ensemble size requirements of hydrocarbons on nickel single crystal surfaces. This evaluation will require measurements of the structure and bonding of Bi adatoms on Ni surfaces. We have already made some progress in this regard. Ethylene and acetylene interactions will be studied first in order for us to also evaluate the role of site-blocking in describing the influence of potassium on adsorption and reaction of these molecules on Ni.
- An important goal for us is to study hydrocarbon chemistry on ordered Sn/Pt alloy surfaces that can be formed by vapor depositing Sn on Pt(100). These unique surfaces may allow us to probe the actual type and number of sites required for chemical reactions at surfaces, as opposed to simply the ensemble size or "areal" requirements, by comparison to similar studies on Sn/Pt(111).
- We plan to carry out surface chemistry studies of model HDS and HDN catalysts formed by vapor-depositing cobalt and/or nickel on molybdenum single crystal surfaces. These surfaces will be well-characterized, and our experience suggests that the composition and structure of these bimetallic surfaces can be controlled and varied in a planned manner to reveal the relative importance of the several factors that control the chemistry and catalysis of these surfaces. Particular attention will be given to hydrocarbon adsorption, especially heteroatom containing molecules, and to the role of sulfur in modifying the structure and chemistry of these surfaces.

ER F 4620 1
(7-85)U.S. Department of Energy
Grant Application Budget Period Summary
(See Reverse for Definitions and Instructions)OMB Approval
No. 1910-1400

Please Print or Type

Organization Department of Chemistry University of Southern California		Period Covering: From: 12/01/91 To: 11/30/92		FOR DOE USE ONLY Proposal No: Award No.:	
Principal Investigator (P.I.)/Project Director (P.D.): Bruce E. Koel		DOE Funded Person-Mos.		Funds Requested By Applicant	
A SENIOR PERSONNEL PUPD Co Pls. Faculty and Other Senior Associates (List each separately with title. A 6 show number in brackets. Attach separate sheet if required.)		Cal	Acad	Sum	\$
1 Bruce E. Koel				2	12,556
2					
3					
4					
5					
6 (1) TOTAL SENIOR PERSONNEL				2	12,556
B OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)					
1 () POST DOCTORAL ASSOCIATES					
2 () OTHER PROFESSIONALS (TECHNICIAN PROGRAMMER ETC.)					
3 (2) GRADUATE STUDENTS 50%		12			29,400
4 () UNDERGRADUATE STUDENTS					
5 () SECRETARIAL CLERICAL					
6 () OTHER					
TOTAL SALARIES AND WAGES (A + B)					41,956
C FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) (28%)					3,516
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)					45,472
D EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM)					
Turbomolecular pump					8,000
TOTAL EQUIPMENT					
E TRAVEL 1 DOMESTIC (INCL CANADA AND U.S. POSSESSIONS)					800
2 FOREIGN					
F OTHER DIRECT COSTS					
1 MATERIALS AND SUPPLIES					1,734
2 PUBLICATION COSTS/PAGE CHARGES					500
3 CONSULTANT SERVICES					
4 COMPUTER (ADPE) SERVICES					
5 CONTRACTS AND SUBGRANTS					
6 OTHER conference					2,500
TOTAL OTHER DIRECT COSTS					
G TOTAL DIRECT COSTS (A THROUGH F)					59,006
H INDIRECT COSTS (SPECIFY RATE AND BASE)					
TOTAL INDIRECT COSTS 60.5% MTDC					30,859
I TOTAL DIRECT AND INDIRECT COSTS (G & H)					
J APPLICANT'S COST SHARING (IF ANY)					
K TOTAL AMOUNT OF THIS REQUEST (ITEM I LESS ITEM J)					89,865
PUPD TYPED NAME & SIGNATURE Bruce E. Koel		DATE 10.18.91			
INST. REP. TYPED NAME & SIGNATURE Cornelius J. Pings		DATE 10/21/91			

ER F 4620.1
(7-85)U.S. Department of Energy
Grant Application Budget Period Summary
(See Reverse for Definitions and Instructions)OMB Approval
No 1910-1400

Please Print or Type

Organization: Department of Chemistry University of Southern California		Period Covering: From: 12/01/91 To: 11/30/92		FOR DOE USE ONLY Proposal No: Award No.:	
Principal Investigator (P.I.)/Project Director (P.D.): Bruce E. Koel		DOE Funded Person-Mos		Funds Requested By Applicant	
A SENIOR PERSONNEL PVPD Co PIs, Faculty and Other Senior Associates (List each separately with title. A 6 show number in brackets Attach separate sheet, if required)		Cal	Acad	Sum	\$
1 Bruce E. Koel				1	6,278
2					
3					
4					
5					
6 (1) TOTAL SENIOR PERSONNEL				1	6,278
B OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)					
1 () POST DOCTORAL ASSOCIATES					
2 () OTHER PROFESSIONALS (TECHNICIAN PROGRAMMER ETC)					
3 (2) GRADUATE STUDENTS 50%		12			29,400
4 () UNDERGRADUATE STUDENTS					
5 () SECRETARIAL CLERICAL					
6 () OTHER					
TOTAL SALARIES AND WAGES (A + B)					35,678
C FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) 28%					1,758
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)					37,436
D EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM)					
Turbomolecular pump					8,000
TOTAL EQUIPMENT					
E TRAVEL 1 DOMESTIC (INCL CANADA AND U S POSSESSIONS)					2,000
2 FOREIGN					
F OTHER DIRECT COSTS					
1 MATERIALS AND SUPPLIES					5,234
2 PUBLICATION COSTS/PAGE CHARGES					1,000
3 CONSULTANT SERVICES					
4 COMPUTER (AOPE) SERVICES					
5 CONTRACTS AND SUBGRANTS					
6 OTHER conference					2,500
TOTAL OTHER DIRECT COSTS					
G TOTAL DIRECT COSTS (A THROUGH F)					56,170
H INDIRECT COSTS (SPECIFY RATE AND BASE)					
TOTAL INDIRECT COSTS 60.5% MTDC					29,143
I TOTAL DIRECT AND INDIRECT COSTS (G + H)					
J APPLICANT'S COST SHARING (IF ANY)					
K TOTAL AMOUNT OF THIS REQUEST (ITEM I LESS ITEM J)					85,313
PVPD TYPED NAME & SIGNATURE Bruce E. Koel		DATE 10.18.91			
INST. REP. TYPED NAME & SIGNATURE Cornelius J. Pings		DATE 10/21/91			

END

**DATE
FILMED**

01 / 22 / 92