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Chemical Structure and Kinetics at Liquid/Solid Interfaces

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DESCRIPTION OF PROJECT

This program of research was to develop spectroscopic and kinetic methods for exploring chemical structure and molecular dynamics at interfaces between dielectric solids and liquids. The research was carried out using fluorescence and vibrational spectroscopy from probe molecules where spectral and temporal differences in emission, absorption, or scattering provide information about the surface onto which they are adsorbed or bound. Studies focused on the interfacial chemistry of insulating surfaces in contact with liquids. The spectral and temporal response of bound or adsorbed molecules were used to observe differences in the chemical environment at the liquid-solid interface. Time-resolution was also valuable in sorting out heterogeneous surface environments from differences in emission rate constants, adsorption rates, and reaction kinetics. The dynamics of transport, adsorption, desorption, and binding of molecules to solid surfaces are being measured using perturbation methods. Fluorescence, infrared, and Raman spectroscopy were adapted to observe perturbations of interfacial chemistry by concentration changes on time-scales of seconds to milliseconds, by temperature-jump perturbations in microseconds, and by laser photoexcitation on time-scales of nanoseconds.

SIGNIFICANT RESULTS

Fluorescence from aluminum ion complexed with silica-immobilized 8-hydroxyquinoline was measured in order to observe double-layer potential effects at insulators on chemical reactivity at liquid-solid interfaces. We also carried out the direct measurements of the rates of siloxane binding reactions to oxide surfaces using vibrational spectroscopy methods, including ATR-FTIR and Raman. These methods have been adapted to conductive interfaces leading to several collaborative studies and one independent investigation of anion adsorption to noble metals in the double layer region.

The structure of pyridine monolayers at silica surfaces was studied by Raman spectroscopy, where the proton transfer to the adsorbate was observed to vary with adsorbate coverage under the control of the surface potential. The spectral methods were adapted in a collaborative study to the structural forms of zirconia, and may be extended to surface site identification.

Solid-surface disorder in pyrogenic silicas was found to be a source of inhomogeneous kinetics in the fluorescence decay of surface-bound excited states. We have also developed analytical procedures for optimal extraction of reaction rates from inhomogeneous environments (typical of interfaces), and applied the method to nanosecond, multicomponent fluorescence lifetime data. We applied these methods to the study of measuring rates of interfacial fluorescence quenching to determine the rates of encounter near a solid surface; evidence for surface diffusion of adsorbates was found and rates of lateral diffusion were determined.

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A new form of interfacial kinetic measurement was developed: the Joule-discharge temperature-jump technique, which was applied to the study of adsorption/desorption kinetics at liquid/solid interfaces. Fluorescence thermometry was used to prove feasibility of conductive temperature-jump perturbations of porous silica samples and to investigate the influence of pore structure on connectivity and heating kinetics. The first observations of the effect of adsorption kinetics on equilibria for reversed-phase liquid chromatography were reported.

Perhaps our most significant breakthrough was the discovery of surface diffusion of covalently-bound (chemisorbed) species at insulating surfaces. In particular, we acquired evidence for diffusion of siloxane-bound species on silica surfaces from the appearance of excimer emission from immobilized 3-(1-pyrenyl)-propyl-dimethylmonochlorosilane (3PPS). The negligible excimer emission from sparingly derivatized silica, kept dry following derivatization, was compared with the strong excimer emission from the same sample stored in a humid atmosphere for 20 days. The observation suggested that the low concentration of surface-bound molecules were originally dispersed far apart upon binding (little excimer); exposure to water vapor could generate a small equilibrium concentration of hydrolyzed 3PPS species which could migrate by surface diffusion, rebind to the surface, and produce clustering of the bound ligands. We measured the time evolution of excimer emission following exposure to water, and found kinetic evidence for surface diffusion of chemisorbed 3PPS. The growth of excimer emission follows Smoluchowski kinetics for biomolecular collisions in two dimensions; two surface coverages were tested and could be fit to a single value for the surface diffusion coefficient (10^{-20} cm^2 sec^{-1}) and a reasonable value of the collision radius (10 A). The temperature dependence of the diffusion rate give an energy barrier to migration that was consistent with hydrolysis of the surface siloxane bond.

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2. "Temperature-jump Investigation of Sorption/Desorption Kinetics at Reversed Phase Chromatographic Silica/Solution Interfaces", S. W. Waite, D. B. Marshall, and J. M. Harris, Anal. Chem. (revised, back in review).

INVITED PRESENTATIONS AT MEETINGS OF SCIENTIFIC SOCIETIES

1. "Kinetics of Binding Silane Reagents to Silica Surfaces", Chemically Modified Surfaces Symposium, Midland, MI, June 28, 1989.

2. "Chemical Reaction Kinetics at Liquid/Solid Interfaces", 3rd International Symposium on Kinetics in Analytical Chemistry, Dubrovnik, Yugoslavia, September 26, 1989.

3. "Kinetics of Binding Silane Reagents to Silica Surfaces", Symposium on Materials for Sensors and Separations, Materials Reserach Society Meeting, San Francisco, April 16, 1990.

4. "Transport and Kinetics at Chromatographic Silica/Solution Interfaces", Symposium on Fundamentals Studies of Chromatographic Surfaces, 1991 Pittsburgh Conference, Chicago, March 7, 1991.

5. "Chemical Kinetics at Dielectric Liquid/Solid Interfaces", Fisher Award Symposium Honoring Royce Murray, 201st National ACS Meeting, Atlanta, April 16, 1991.

6. "Molecular Transport and Kinetics at Liquid/Solid Interfaces", Chemically Modified Surfaces Symposium, Chadds Ford, PA, July 31, 1991.

7. "Transport and Kinetics at Chromatographic Silica/Solution Interfaces", Symposium on Fundamenal Advances in Liquid Chromatography, 203rd National ACS Meeting, Washington, DC, August 24, 1992.

8. "Molecular Transport and Kinetics at Silica/Solution Interfaces", Symposium on Investigation of Chromatographic Surfaces, 19th Annual FACSS Meeting, Philidelphia, September 21, 1992.

9. "Multichannel Raman Spectroscopy for Investigation Chemical Reaction Kinetics", Symposium on Array Detectors in Spectroscopy, 1993 Pittsburgh Conference, Atlanta, March 10, 1993.

10. "Surface Binding, Heterogeneity, and Migration of Siloxane Ligands on Silica", Symposium on the Molecular Basis of Liquid Chromatography, 206th National ACS Meeting, Chicago, August 24, 1993.

CONTRIBUTED PRESENTATIONS AT MEETINGS OF SCIENTIFIC SOCIETIES

1. "Time-Resolved Fluorescence Studies of Molecular Transport at Liquid/Solid Interfaces", with A. L. Wong, Syposium on Solid-State Fluorescence Spectroscopy, 198th National ACS Meeting, Miami, September 14, 1989.

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3. "Raman Spectroscopy as a Probe of Interactions between Acetonitrile and Chromatographic Silica", with K. L. Rowlen and E. H. Ellison, 45th NW-10th Rocky Mountain ACS Regional Meeting, Salt Lake City, June 14, 1990.

4. "Measurements of Energy Dispersion at Liquid-Solid Interfaces: Fluorescence Quenching of Pyrene Bound to Fumed Silica", with A. L. Wong and D. B. Marshall, 45th NW-10th Rocky Mountain ACS Regional Meeting, Salt Lake City, June 15, 1990.

5. "Microsecond Fluorescence Thermometry of Porous Silica Heated by a Joule Discharge", with S. W. Waite, E. H. Ellison, and D. B. Marshall, 45th NW-10th Rocky Mountain ACS Regional Meeting, Salt Lake City, June 15, 1990.

6. "Raman Spectroscopic Study of Solvation Structure in Acetonitrile - Water Mixtures", with K. R. Rowlen, 1991 Pittsburgh Conference, Chicago, March 8, 1991.

7. "Fluorescence Study of Lateral Diffusion of Chemisorbed Siloxane Species at Silica Surfaces", H. Wang and J. M. Harris, 45th ACS Analytical Summer Symposium, Logan, UT, June 24, 1992.

8. "Direct Measurement of Sorption/Desorption Kinetics at a Reversed-Phase Chromatographic Silica Gel", S. W. Waite and J. M. Harris, 1993 Pittsburgh Conference, Atlanta, March 10, 1993.

9. "Temperature-jump Relaxation Kinetics at Liquid-Solid Interfaces: Joule Heating of Porous Silica and Direct Measurement of Sorption/Desorption Kinetics", S. W. Waite, J. M. Harris, and D. B. Marshall, 205th National ACS Meeting, Denver, April 1, 1993.

10. "Surface Binding and Migration of Siloxane Monolayers on Silica", H. Wang and J. M. Harris, XXth Annual FACSS Meeting, Detroit, October 21, 1993.

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