

HETEROGENEOUS CATALYSIS

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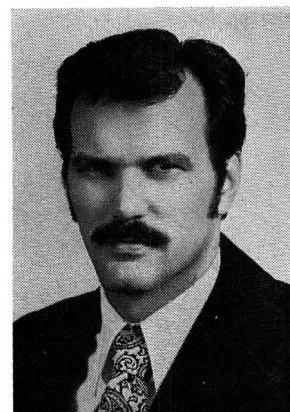
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AS THE BACKBONE of the chemical and petroleum industries and a key to the solution of current problems concerning energy and the environment, heterogeneous catalysis is firmly rooted in the domain of chemical engineering. The intersection of chemistry, physics, and engineering in catalysis provides a broad spectrum of intriguing fundamental and practical questions. The breadth and complexity of the subject, however, require a balance of survey versus depth in presentation of material in a one semester graduate course. The choice of organization and specific topics must be geared to the make-up of the class as well as to the prejudices of the instructor.

At Purdue a class of 25 students in this course may include chemists (~15%), chemical and non-chemical engineers bound for the Ph.D.,

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Master's and, in a few cases, B.S. degree. This diverse class background and the desire to make the course available at the graduate level without prerequisites necessitate inclusion of a review of chemical kinetics. The prejudice of the instructor has dictated organization of the course primarily in terms of theoretical concepts. No text with the orientation and emphasis outlined in Table 1 is available, but J. M. Thomas and W. J. Thomas, *Introduction to the Principles of Heterogeneous Catalysis*, Academic Press, New York (1967), supplemented by Alfred Clark's



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book *The Theory of Adsorption and Catalysis*, Academic Press, New York (1970), or J. J. Thompson and G. Webb, *Heterogeneous Catalysis*, John Wiley and Sons, Inc., New York (1968), represents a reasonable compromise. Additional sources of material and some key papers read by the students and discussed in class are also included in Table 1. Heavy reliance on original papers slows the pace but helps to achieve one of the course goals: familiarity with the literature and ability to read it critically.

PROVIDING ORIENTATION

DETAILS OF THE COURSE material are best discussed with reference to Table 1, which also indicates the approximate class time spent on each area. Section I was an experiment last year to provide orientation to the field and motivation for the array of topics that follows. Sinfelt's elegant investigation of ethane hydrogenolysis over supported metals proved to be a good vehicle for this purpose, in spite of difficulties the students had initially in dealing with terms and concepts that were not fully developed until later in the course.

Sections II, III and IV of the course outline represent a view of catalysis from the gas side of the gas-solid interface and also include details of physical characterization of catalysts. The emphasis in Sections III and IV is on establishing criteria for the validity and chemical significance of kinetic parameters. Simple expectations such as the exothermicity of adsorption or a rate of adsorption not exceeding the collision rate with the surface, for example, can help prevent a computer's propagating physical or chemical nonsense from a mathematical fit of kinetic data. Working knowledge in this area is stressed through homework problems and student reviews of recent papers presenting kinetic analyses. A more complete review of kinetics and quantitative discussion of design and heat, mass and momentum transfer in chemical reactors is the province of "Chemical Reactor Design," which, along with courses in thermodynamics, transport, and mathematics, makes up the graduate core curriculum in chemical engineering at Purdue.

Sections V and VI present a view of catalysis from the solid side of the gas-solid interface. These sections contain much new subject matter and are the most difficult for many students. The material is presented to help students establish a basis for the understanding and construction of chemical models for catalyst behavior and to provide them with criteria for comparing different catalysts. Unique explanations of the catalytic action are difficult to achieve, but concepts such as ensemble, or surface geometry, effects on catalytic selectivity and modification of the electronic properties of metal surfaces by alkali adsorption or semiconductor surfaces by contact with metals, for example, can contribute to progress in the field. Section VII reinforces some of these concepts, introduces others, and also provides discussion of industrial applications of catalysis. Many students choose deeper study of industrial reactions for their term papers.

EXPERIMENTAL TECHNIQUES

AN APPARENT OMISSION in the outline is a general section on experimental techniques. This area is covered in literature readings, a tour of the extensive catalysis research facilities in the School of Chemical Engineering, the term paper option, and a requirement that teams of two students prepare for distribution to the class a one page summary of a particular technique.

The summary includes the underlying principles, experimental requirements, information available, catalytic applications, and a few directive references. Though after several revisions a notebook of these descriptions of experimental techniques will become quite useful, future versions of the course will provide more direct discussion of this area through further integration of sections V, VI and VII. □

TABLE 1
Course Outline

- I) OVERVIEW (4 Lectures)—Discussion of "Catalytic Hydrogenolysis over Supported Metals," J. H. Sinfelt, *Catal. Rev.*, 3; 175 (1969)
Emphasis: The nature of catalysts and catalysis research.
- A) Relation of Hydrogenolysis to Petroleum Processing—Catalyst Selectivity
 - B) Nature of Catalysts
 - 1) Support
 - 2) Metal Dispersion and its Measurement
 - 3) Methods of Preparation
 - C) Kinetic Analysis
 - D) Comparison of Group VIII Metals
 - 1) Activity Pattern
 - 2) Correlation of Activity with Electronic Properties
 - 3) Crystallite Size Effects
 - 4) Support Effects
 - 5) Ru/Cu Bimetallic Clusters (J. H. Sinfelt, *J. Catal.*, 29, 308 (1973))
- II) CHEMICAL KINETICS (8 Lectures)—(M. Boudart, *Kinetics of Chemical Processes*, Prentice Hall, 1968)
Emphasis: The relation between sequences of elementary steps and the rate expression, recognition of valid kinetic parameters.
- A) Derivation of Rate Equations from Sequences of Elementary Steps
 - 1) Langmuir Adsorption
 - 2) Steady State Approximation
 - 3) Rate Determining Step Approximation
 - B) Rate Constants for Elementary Steps—Orders of Magnitude
 - 1) Transition State Theory
 - 2) Collision Theory
 - 3) Further Evaluation of Rate Parameters, (M. Boudart, D. E. Mears, and M. A. Vannice, *Ind. Chim. Belge.*, Special Issue 36, Part I, 281 (1967), and M. Boudart, *AIChE Journal*, 18, 465 (1972))
 - C) Correlation and Estimation of Kinetic Parameters
 - 1) Polanyi Relation
 - 2) Van Tiggelen Formula
 - 3) Principle of Sabatier
 - 4) Compensation Effect
 - D) Non-Uniform Surfaces
 - 1) Freundlich and Temkin Isotherms
 - 2) 2 Step Reactions

Experimental techniques are covered by requiring teams of two students to prepare for distribution to the class a one page summary of a popular technique . . . including the underlying principles, experimental requirements, information available, catalytic applications and a few directive references.

III) SURFACE AREA AND PORE STRUCTURE

(3 Lectures)

- A) Selective Chemisorption
- B) BET Theory—Approximations, Results and Applications
- C) Pore Size Distribution
 - 1) Kelvin Equation
 - 2) Hysteresis in BET Isotherm
 - 3) Mercury Porosimetry

IV) HEAT AND MASS TRANSFER INFLUENCE ON KINETIC PARAMETERS (4 Lectures)

(C. N. Satterfield, *Mass Transfer in Heterogeneous Catalysis*, MIT Press, (1970))

Emphasis: Qualitative behavior, diagnostics to insure true kinetics.

- A) Bulk or Film Diffusion
- B) Pore Diffusion
 - 1) Macropore
 - 2) Micropore
- C) Heat and Mass Transfer Diagnostics (P. B. Weisz and J. S. Hicks, *Ch.E. Science*, 17, 265 (1962))
- D) Diffusion Influence on Selectivity
- E) Poisoning

V) PROPERTIES OF SOLIDS (7 Lectures)

Emphasis: Development of important parameters and differences between classes of solids.

- A) Crystal Structure
 - 1) Crystal Lattices
 - 2) Miller Indices
 - 3) Geometry of Surface Planes
- B) Electronic Structure
 - 1) Review of Atomic and Molecular Orbitals
 - 2) Band Structure
 - a) Metals
 - b) Semiconductors—Intrinsic/Extrinsic
 - c) Insulators
 - d) Temperature Dependence of Conductivity
 - 3) Image Potential
 - 4) Work Function—Changes on Adsorption
 - 5) Collective vs. Localized Electron Picture

VI) THEORETICAL CONCEPTS IN ADSORPTION AND CATALYSIS (8 Lectures)

Emphasis: Examination of the degree to which simple theoretical approaches can describe catalytic phenomena.

- A) Metals
 - 1) Ionic Model for Adsorption
 - 2) Localized Covalent Model for Adsorption
 - 3) Summary of Current Theoretical Approaches to Metal-Adsorbate Bonding
 - 4) Ensemble vs. Ligand Effects (Y. Somorjai and W.M.H. Sachtler, *J. Catal.*, 32, 315 (1974))

- a) CO Adsorption—Bridged and Linear
- b) Alloy Surfaces
- c) Infrared Spectroscopy

B) Non-Metals

- 1) Boundary Layer Theory of Adsorption on Semiconductors
 - a) Depletive/Cumulative
 - b) N₂O Decomposition
- 2) Catalyst/Support Electronic Interaction
 - a) Metals on Semiconductors
 - b) Semiconductors on Metals
- 3) Thermochemical Approach—CO Oxidation Over NiO
 - a) Carbonate Intermediate
 - b) ¹⁸O Isotope Tracer
- 4) Ligand Field Approach

VII) CATALYTIC REACTIONS AND CATALYTIC CHEMISTRY (11 Lectures)

A) Oxidation

- 1) Summary of Industrial Processes and Catalysts
- 2) Ethylene to Ethylene Oxide
 - a) Unique Selectivity of Ag
 - b) O₂⁻ Intermediate (P. A. Kilty, N. C. Rol and W.M.H. Sachtler, in *Catalysis*, Vol. 2, J. W. Hightower ed., North Holland (1972) p. 929)
 - c) Radiation Induced Selectivity Change (J. J. Carberry, G. C. Kuczynski, and E. Martinez, *J. Catal.*, 26, 247 (1972))
 - i) Importance of Surface Ca Impurity
 - ii) X-ray Photoelectron Spectroscopy

B) Hydrogenation (R. J. Kokes, in *Catalysis*, Vol. 1, J. W. Hightower ed., North Holland (1972), p. A-1)

- 1) Comparison of Metals and Metal Oxides
- 2) Propylene on ZnO—Details of Catalytic Chemistry

C) Cracking

- 1) Summary of Industrial Processes
- 2) Carbonium Ion Reactions
- 3) Brønsted and Lewis Acid Sites on Silica/Alumina and Zeolites

D) Reforming

- 1) Dual Functional Catalysts
- 2) Dehydrocyclization on Clean Surfaces (G. A. Somorjai, *Catal. Rev.*, 7, 87 (1972))—Relation between Clean Surface Research and Catalysis

E) NO Reduction

- 1) Summary of Auto Exhaust Problems
- 2) Molecular Orbital Symmetry Rules— $2\text{NO} \rightleftharpoons \text{N}_2 + \text{O}_2$ as a Symmetry Forbidden Reaction