

## CHEMISTRY OF CATALYTIC PROCESSES

B. C. GATES, J. R. KATZER,  
J. H. OLSON, and G. C. A. SCHUIT  
*University of Delaware*  
*Newark, Delaware 19711*

**M**OST INDUSTRIAL REACTIONS are catalytic, and many process improvements result from discovery of better chemical routes, usually involving new catalysts. Because catalysis plays a central role in chemical engineering practice, it is strongly represented in chemical engineering teaching and research at Delaware. A graduate course entitled "Chemistry of Catalytic Processes" is designed to present a cross section of applied catalysis within the framework of detailed consideration of important industrial processes. The course brings together the subjects of chemical bonding, organic reaction mechanism, solid-state inorganic chemistry, chemical kinetics, and reactor design and analysis. There is no stronger evidence of the value of integrating chemistry and chemical engineering than the industrial successes in catalytic processing.

Five classes of industrial processes are considered in sequence: catalytic cracking, catalysis by transition metal complexes, reforming, partial oxidation of hydrocarbons, and hydrodesulfurization. Each class is introduced with a description of the processes, which is followed by details of the catalytic chemistry and process analysis and reactor design.

To the extent that each subject allows, ties are drawn between the reaction chemistry and process design. For example, the new zeolite cracking catalysts are used primarily because they have high selectivity for gasoline production, but they also have such high activity compared to the earlier generation of silica-alumina catalysts that they must be used diluted in a silica-alumina matrix to prevent overcracking. Their application has required redesign of catalytic crackers to accommodate rapid reaction predominantly in the riser tube (located upstream of what was formerly the fluidized-bed reactor); redesign must also accommodate a changed energy balance resulting

from the reduced coke formation on zeolite catalysts and must promote more complete coke removal in regeneration. The reactor design may be based on a simplified series-parallel reaction network, on the assumption of a small deviations from piston flow in the riser, and on a balance between the energy required for the endothermic cracking reactions and the energy produced in coke burn-off from catalyst particles in the regenerator.

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The processes are introduced in an order leading roughly from the simplest to the most complex chemical concepts and from the best understood to the least well understood catalytic chemistry (Table 1). Cracking is the first subject presented because the zeolite catalysts have known crystalline structures and relatively well defined acid centers; the cracking reactions proceed via carbonium ion intermediates, giving well characterized product distributions. The second subject, catalysis by transition metal complexes, also involves well defined species and is unified by the idea of the cis-insertion mechanism, which is discussed on the basis of ligand field theory and exemplified in detail by Ziegler-Natta polymerization.

Reforming introduces metal catalysis, the concept of bifunctional reaction mechanism and ties with acid catalysis. Theory of metal catalysis is incomplete although solid-state theory and molecular orbital calculations on small metal clusters provide insight; a tie still remains to be drawn between catalysis by metal complexes and catalysis by clusters of metal atoms. The concluding topics of partial oxidation and hydrodesulfurization involve solid state and surface chemistry of transition metal oxide and sulfide catalysts; there is a thorough understanding of a few oxidation catalysts (for example, bismuth molybdate catalyzing ammoxidation of propylene) but for the most part the chemistry is not

well understood, and the ties between the chemistry and the process design cannot be well developed.

### COHERENCE VIA CHEMICAL CONCEPTS

**T**HE COHERENCE of the course is provided by the chemical rather than by the engineering concepts, and the latter are interwoven as dictated by their practical value to the various processes. For example, interphase mass transfer is considered in analysis and design of the gas-liquid reactors used in the oxo, Wacker, and vinyl acetate processes, which involve homogeneous catalysis by transition metal complexes. Mass transport in catalyst pores is important in hydrodesulfurization (affecting rates of the desired reactions and rates of reactions giving pore-blocking deposits); the unique phenomena of mass transport in the molecular-scale intracrystalline pores of zeolites are introduced with catalytic cracking and form the basis for an introduction to shape-selective catalysis. Analysis of reactor and catalyst particle stability is central to the discussion of catalytic oxidation processes, for which catalysts are selected and reactors designed to give high yields of valuable partial oxidation products and low yields of CO<sub>2</sub>.

Instrumental methods of analysis essential to catalyst characterization are introduced as they are appropriate to the process, giving a representation of the breadth of their usefulness. For example, chemisorption measurements, electron microscopy and x-ray line broadening to determine metal surface areas and crystallite sizes are introduced in discussion of catalytic reforming, which involves supported-metal bifunctional catalysts. Infrared spectroscopy is useful for probing the detailed structures of transition metal complexes (for example, the rhodium complexes used as oxo catalysts) and for indicating the structures of acidic centers on zeolite surfaces. Electron spin resonance and magnetization studies have provided essential information about oxidation and hydrodesulfurization catalysts containing transition metal ions.

The course is an attempted synthesis of chemistry and chemical engineering; the synthesis is traditional in practice, but not in teaching, and there is a lack of appropriate secondary literature sources. Consequently we have prepared a thorough set of typewritten notes (portions of which have been published as review articles

(1, 2)). The notes are based largely on primary literature, and since the literature of industrial processes does not give a good representation of current practice, the interpretations may sometimes be out-of-date and erroneous.

Many improvements in the course have resulted from criticisms given by practitioners, and we have attempted to include students from industry in classes with first-and-second-year graduate students. The course has been offered in the 4:30 to 6:00 P.M. time period, which is convenient to many potential students who are employed nearby. Response has been favorable enough that the course is also offered yearly as a one-week short course. Those attending have been predominantly industrial chemical engineers and chemists (in about equal numbers), some traveling from as far as the west coast and Europe. □

### REFERENCES

1. Schuit, G. C. A., "Catalytic Oxidation over Inorganic Oxides as Catalysts," *Memoires de la Societe Royale des Sciences de Liege, Sixieme Serie, Tom I*, 227, 1971.
2. Schuit, G. C. A., and Gates, B. C., "Chemistry and Engineering of Catalytic Hydrodesulfurization," *AICHE Journal* 19, 417 (1973).

**TABLE 1**  
**Course Outline**

- I. ZEOLITE-CATALYZED CRACKING AND RELATED PROCESSES
  - A. Processes
    1. Catalytic Cracking
      - a. Process Conditions
      - b. Reactor Operation
      - c. Regenerator Operation
    2. Hydrocracking and Isomerization
  - B. Reactions and Chemistry
    1. Chemical Bond Theory
      - a. Atomic Orbitals and Energy Levels
      - b. Molecular Orbitals
        - i. Linear Combinations of Atomic Orbitals
        - ii. Symmetry Aspects
        - iii. The Secular Determinant
      - c. Multiple Atom Systems
        - i. Hybridization Theory
        - ii. Electron-Deficient, Delocalized Molecular Bonds
    2. Carbonium Ions
      - a. Electron Deficiency Properties
      - b. Classical and Non-Classical Carbonium Ions
      - c. Reactivity and Characteristic Reactions
    3. Cracking Reactions
      - a. Thermal Cracking
      - b. Acid-Catalyzed Cracking
  - C. Catalysts
    1. Amorphous Catalysts
      - a. Preparation
      - b. Structure and Surface Chemistry
      - c. Acidity: Measurement and Correlation

George Schuit received his Ph.D. from Leiden and worked at the Royal Dutch Shell Laboratory in Amsterdam before becoming Professor of Inorganic Chemistry at the University of Technology, Eindhoven, The Netherlands. His research interests are primarily in solid state inorganic chemistry and catalysis, and his recent publications are concerned with hydrodesulfurization and selective oxidation of hydrocarbons. He has been on organizing committees for the Roermond Conferences and the Third International Congress on Catalysis, is a member of the Royal Dutch Academy of Sciences and is on the editorial board of the *Journal of Catalysis*. In 1972 he was National Lecturer of the Catalysis Society and Unidel Distinguished Visiting Professor at the University of Delaware; he now holds joint appointments at Eindhoven and Delaware.

Jon Olson obtained a Doctor of Engineering degree at Yale and worked for E. I. duPont de Nemours and Company before joining the faculty at Delaware. With wide ranging interests in

chemical engineering, he has recently done research concerning analysis of fixed-bed catalytic reactors, fouling of chromia/alumina catalysts, partial oxidation, and automotive emissions control.

Jim Katzer received a Ph.D. in Chemical Engineering from MIT and has been at Delaware since 1969. His primary research interests are catalytic chemistry and mass transport in catalysts. His recent work has emphasized applications of catalysis to pollution abatement, particularly catalytic reduction of nitrogen oxides, supported metal catalysis, catalyst poisoning mechanisms, and transport and reaction in zeolites.

Bruce Gates received his Ph.D. from the University of Washington. He did postdoctoral research with a Fulbright grant at the University of Munich and worked for Chevron Research Company before joining the Delaware faculty in 1969. His current research concerns hydrodesulfurization, catalysis by transition metal complexes and design and evaluation of synthetic polymer catalysts.

2. Crystalline (Zeolite) Catalysts
  - a. Structure and Surface Chemistry
    - i. Primary and Secondary Structural Units
    - ii. Type Y Zeolite
    - iii. Mordenite
  - b. Acidity
    - i. Chemical Probes
    - ii. Instrumental Probes
    - iii. Explanation from Structural Considerations
    - iv. Active Sites and Activity Correlations
- D. Reaction Mechanisms
  1. Reaction Chemistry Related to Surface Structure
    - a. Amorphous Catalysts
    - b. Zeolite Catalysts
  2. Hydrogen-Transfer Activity of Zeolites
  3. Activity and Selectivity Comparison of Zeolites and Amorphous Catalysts
  4. Reaction Network and Deactivation: Quantitative Models
- E. Influence of Catalytic Chemistry and Mass Transport on Choice of Processing Conditions
  1. Superactivity of Zeolites
  2. Mass Transport Effects in Zeolites; Shape-Selective Catalysis
  3. Effect of Zeolite Cracking Chemistry on Reactor and Regenerator Design
- F. Quantitative Reactor Design
  1. Riser-Tube Cracker Design
  2. Regenerator Design
- II. CATALYSIS BY TRANSITION METAL COMPLEXES
  - A. Processes
    1. Wacker Process
      - a. Reactions, Product Distribution, and Kinetics
      - b. Processing Conditions
      - c. Reactor Design
    2. Vinyl Acetate Synthesis
    3. Oxo Process (Hydroformylation)
    4. Methanol Carbonylation to Acetic Acid
    5. Ziegler-Natta Polymerization: Transition from Homogeneous to Heterogeneous Catalysis
  - B. Chemical Bond Theory
    1. Ligand Field Theory
    2.  $\sigma$  and  $\pi$ -Bonding in Complexes
  - C. Catalysts
    1. Wacker—Pd Chloride
    2. Hydroformylation—Co and Rh Carbonyls
    3. Carbonylation—Rh-Phosphine Complexes
    4. Ziegler-Natta Polymerization—Transition Metal Chlorides and Metal Alkyls
  - D. Reaction Mechanisms
    1. The General Cis-Insertion Mechanism
      - a. Experimental Evidence
      - b. Molecular Orbital Explanation
    2. Detailed Mechanisms of Particular Reactions
      - a. Ethylene Oxidation
      - b. Hydroformylation
      - c. Carbonylation
      - d. Stereospecific Polymerization
  - E. Quantitative Process Design
    1. Design of Gas-Liquid Reactors; Mass Transfer Influence
    2. Preparation and Characterization of Solid Catalysts
      - a. Transition Metal Complexes Bound to Inorganic Surfaces
      - b. Complexes Bound to Organic Matrices
- III. CATALYTIC REFORMING
  - A. Process
    1. Principal Chemical Reactions
    2. Thermodynamics and Kinetics
    3. Supported Metal Catalysts
    4. Process Conditions and Reactor Design
  - B. Reactions and Chemistry
    1. Mechanisms of Metal Catalyzed Reactions
      - a. Hydrogenation-Dehydrogenation and H-D Exchange
      - b. Isomerization and Hydrogenolysis
      - c. Cyclization
      - d. Aromatization
    2. Chemical Bond Theory
      - a.  $\sigma$ - and  $\pi$ -Bonds
      - b. Delocalized Bonds
      - c. Bands in Metals
      - d. d-orbital Contribution to Transition Metal Bands
    3. Metal Catalysis
      - a. Electrons and Metal Bond Strength
      - b. Electrons and Adsorption on Metals

- c. Theoretical Calculations of Electronic Properties and Surface Bond Strength
  - d. Catalytic Activity: Surface Compound Correlations
  - e. Alloys
    - i. Miscibility Gaps and Surface Composition
    - ii. Catalytic Activity: Ligand and Geometric Effects
- C. Dual-Functional Supported-Metal Catalysts (Pt/Al<sub>2</sub>O<sub>3</sub>)
1. The Metal, Practical Considerations
    - a. Preparation and Characterization
    - b. Effects of Crystallite Size on Activity
    - c. Sintering and Poisoning
    - d. Alloys
  2. The Alumina Support
    - a. Preparation and Properties
    - b. Structure
    - c. Development and Control of Acidity
- D. Reaction Networks and Reaction Mechanisms
1. Dual-Functional Nature of Catalyst
    - a. Reaction Steps and Relation to Catalyst Functions
    - b. Studies with Physically Separated Functions, Mass Transport Considerations
    - c. Effect of Support Acidity on Reforming Reactions
    - d. Poisons and Poisoning Studies
  2. Cyclization Reaction Network and Reaction Mechanism
  3. Overall Network
- E. Relation of Processing to Catalytic Chemistry
1. Balancing the Strengths of the Catalyst Functions
  2. Mass Transport Effects on Selectivity
  3. Optimum Design of Dual-Functional Catalytic Systems
  4. Regeneration Procedures Related to Catalyst Structure and Stability
  5. Lumping in Fixed Bed Reactor Design for Many Reactions
- IV. SELECTIVE OXIDATION OF HYDROCARBONS CATALYZED BY METAL OXIDES
- A. Processes
1. Phthalic Anhydride
    - a. Reactions
    - b. Process Conditions
  2. Maleic Anhydride
  3. Acrolein and Acrylonitrile
  4. Ethylene Oxide
- B. Reactions and Chemistry
1. Chemical Bond Theory
    - a. Electrostatic Bonds in Solid Oxides
    - b. Changes in Cation Oxidation State
  2. Allylic Intermediates
  3. Mars-van Krevelen Mechanism
  4. Reaction Network for Naphthalene Oxidation
- C. Catalysts
1. Composition and Structure
    - a. V<sub>2</sub>O<sub>5</sub> and MoO<sub>3</sub>-V<sub>2</sub>O<sub>5</sub>
    - b. Bi<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub>
    - c. Fe<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub>
    - d. UO<sub>3</sub>-Sb<sub>2</sub>O<sub>3</sub>
    - e. Cu<sub>2</sub>O
  2. Oxidation Selectivity
    - a. Correlations
      - i. Oxygen Bond Strength
      - ii. Metal Oxide Structure
    - b. Oxygen Interchange with Metal Oxides
    - c. Microscopic Considerations, Active Sites
- D. Detailed Reaction Mechanisms involving Olefins—Examples Based on Solid and Intermediate Complex Structures
1. Solid Structures, Bismuth Molybdate and Uranium Antimony
  2. Surface Chemistry
  3. Reactant-Surface Interactions
  4. Reaction Mechanism
- E. Quantitative Reactor Design—The Hot Spot Problem
1. Influence of Catalytic Chemistry on Choice of Processing Conditions; the Need for Selective Catalysts
  2. Fluidized Bed Reactors
  3. Fixed Bed Reactors
  4. Heat and Mass Transfer in Catalyst Particles
  5. Catalyst Particle Stability
- V. HYDRODESULFURIZATION
- A. Processes
1. Sulfur-containing compounds in Petroleum and Coal-Derived Liquids with Hydrogen
  2. Compositions of Co/Mo and Ni/Mo Catalysts
  3. Processing Conditions
    - a. Petroleum Distillates
    - b. Petroleum Residua
    - c. Coal
  4. Reactor Design: Fixed and Fluidized Beds
- B. Reactions and Chemistry
1. Model Reactant Compounds
    - a. Desulfurization Reaction Networks of Thiophene and Benzothiophenes
    - b. Kinetics of Hydrodesulfurization of Thiophene and Benzothiophenes
  2. Petroleum Feed Stocks
    - a. Composition of Feed Stocks
    - b. Simplified kinetics for Petroleum Feed Stocks
- C. Catalysts
1. Structure of Cobalt Molybdate and Nickel Molybdate Catalysts
  2. Texture
  3. Interaction of Catalyst with the Support
  4. Effects of Promoters
  5. Catalytic Sites
    - a. Monolayer Model
    - b. Intercalation Model
- D. Reaction Mechanisms of Model Compounds
- E. Process Design
1. Relation of Process Design to Catalytic Chemistry of Hydrodesulfurization and Side Reactions
  2. Influence of Intraparticle Mass Transport on Catalyst Effectiveness
  3. Catalyst Aging: Pore Blocking and Interstitial Deposition
  4. Hot Spots and Reactor Stability; Analysis of Trickle Bed and Slurry Bed Reactors