ChE classroom

FUNDAMENTALS OF CHEMICAL PROCESSES

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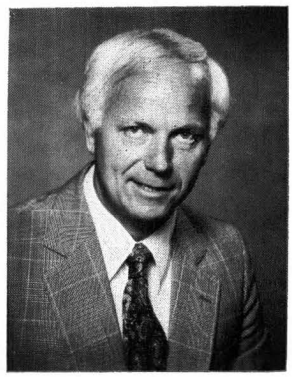

William R. Moser has been a professor in the chemical engineering department at Worcester Polytechnic Institute since 1981. Since earning his graduate degree in 1964 at MIT he has been active in the area of chemical processing at CIBA, Exxon, and Badger. His research interests are in mechanistic studies of heterogeneous and homogeneous catalyzed reactions using kinetic and in situ spectroscopic techniques. He has several publications and patents and holds membership in a number of professional societies.

THIS COURSE TEACHES the fundamental scientific principles controlling most chemical, petrochemical, and refining processes. The student population consists mainly of junior and senior chemical engineers, but the information is of equal value to advanced chemistry majors. A few mechanical engineers interested in plant construction also take the course. The objective of the course is to provide the student with a fundamental understanding of the chemical, catalytic and engineering sciences relating to the chemical reactions taking place in a variety of reactors of different configurations. Although many major commercial processes are discussed in the course, the emphasis is not on an enumeration of all of the major processes, but the direction is placed on understanding how and why the chemical transformations occur. This science is then merged with the technology of the two dozen or so reactors of radically different designs and configurations currently used commercially. Thus, the student gains an understanding not only of the process fundamentals but also of the devices used to successfully perform the processes. The course is kept current each year by introducing new processes which are in commercial development. Synthesis gas generation and utilization are discussed to address a long range technological need of engineering and science students. For the chemical engineering students the course serves the specific function of allowing them to become more conversant with chemical phenomenon. This is purposely done in response to the criticism from both industrial and academic scientists who feel that the current U.S. training of chemical engineers is deficient in chemistry. This course has a chemical orientation but it is placed in the context of learning all of the fundamental sciences which govern the major commercial processes which they will deal with in the future. The student should gain enough fundamental understanding of the chemical phenomena occurring inside of reactors of different designs so that in their future work they will be able to execute superior process designs and controls for these or other new processes.

COURSE DESCRIPTION

The prior requirements for the course are a fundamental organic chemistry course, an introductory inorganic chemistry course (usually included in the freshman chemistry series), and a keen interest in chemical engineering and chemical processes. Since the course is descriptive and qualitative, prior chemical engineering courses involving quantitative engineering calculations are not required.

A successful presentation of the technology described by this course requires the application of several principles of chemical engineering, organic, inorganic and physical chemistry, thermodynamics, kinetics and mechanical engineering. Thus, the instructor must make a careful choice as to the degree of review of these subjects which is adequate for the understanding of the chemical process technology. The approach currently used at WPI is to provide a concise review of just those principles which are required to master the chemi-

cal process concepts presented in the lecture of the day.

LECTURES

The technology presented in the course is accomplished in 24 lectures of 50 minute duration. In addition to outside reading from a list of 89 references taken from the original technical literature, three term papers are required on topics which are not discussed in the classroom lectures. Three one-hour, closed note and closed book exams are usually given during the duration of the course. The textbook currently used for the course is *Chemistry of Catalytic Processes* by Gates, Katzer and Schuit (McGraw Hill, 1979).

The course is divided into the following eight major topics:

1. **Survey of Major Chemical and Refining Processes**
2. **Homogeneous Catalytic Process Fundamentals**
3. **Heterogeneous Catalytic Process Fundamentals**
4. **Survey of Modern Commercial Reactor Configurations**
5. **Synthesis Gas Generation**
6. **Synthesis Gas Processes for Fuels and Chemicals**
7. **Technology of Major Advanced Chemical Processes**
8. **Major Refining Processes**

The division of lecture time committed to each topic may be seen in Table 1. The timing of exams and due dates for term papers is also shown. A

TABLE 1
Chemical Technology: Course Schedule

Lecture Number	Subject
1	Survey Major Chemical Processes
2	Homogeneous Metal Catalysis (A) Major Processes
3	Homogeneous Metal Catalysis (B) Co-ordination Chemistry (C) Bonding (D) Reactivity
4	Homogeneous Metal Catalysis (E) Metals (F) Stereochemistry (G) Key Intermediates
5	Homogeneous Metal Catalysis (H) Key Transformations
6	Homogeneous Metal Catalysis (I) Ligand Effects on Reactivity (J) Classification of Reactions
7	Heterogeneous Catalysis (A) Major Processes EXAM—HOMOGENEOUS CATALYSIS FUNDAMENTALS
8	Heterogeneous Catalysis (B) Surface Adsorption (C) Surface Kinetics
9	Heterogeneous Catalysis (D) Surface Chemistry Problem Set #1 Due—Ziegler-Natta Catalysis
10	Heterogeneous Catalysis (E) Types of Catalysts
11	Heterogeneous Catalysis (F) Zeolites and Their Structures
12	Heterogeneous Catalysis (G) Zeolites and Their Catalysis
13	Reactor Configurations for Major Processes
14	Synthesis Gas Catalysis and Synthetic Fuels
15	Synthesis Gas Production Processes (A) Reforming EXAM—HETEROGENEOUS CATALYSIS FUNDAMENTALS
16	Synthesis Gas Production Processes (B) Gasification (C) Downstream Processing
17	Synthesis Gas for Chemicals and Fuels (A) Methanol Synthesis Problem Set #2 Due—Catalytic Cracking
18	Synthesis Gas for Chemicals and Fuels (B) Methanol to Aromatic Gasoline (C) ZSM-5 Catalysis
19	Synthesis Gas for Chemicals and Fuels (D) Fischer-Tropsch Catalysis
20	Synthesis Gas for Chemicals and Fuels (E) New Syngas Processes for Ethanol, Vinyl acetate, and acetic anhydride Problem Set #3 Due—Heterogeneous Partial Oxidation
21	Synthesis Gas for Chemicals and Fuels (F) New Syngas Processes for Ethylene Glycol, Styrene, Xylenes
22	Advanced Technology for Chemical Intermediates (A) Acetic Acid EXAM—SYNTHESIS GAS TECHNOLOGY
23	Mature Technology for Chemicals (A) Wacker Process (B) Butane Oxidation (C) Hydroformylation
24	Refining Processes (A) Hydrodesulfurization (B) Reforming

brief description of the topics treated in the lectures for the eight major areas listed above follows.

1. Survey of Major Chemical and Refining Processes

The topic is introduced with a definition of the four principal types of reactions utilized in commercial reactors, *e.g.* heterogeneous catalyzed, homogeneous catalyzed, gas phase catalytic and non-catalytic, stoichiometric reactions in solution with their individual variations. Examples are given for each class. Also terms like conversion, selectivity, yield, etc., are defined.

2. Homogeneous Catalytic Process Fundamentals

Examples are given of the top fifteen commercial processes using homogeneous catalysts. The student would be expected to know the reactants, products, catalysts, and approximate reaction conditions for each process. Several new processes which are currently being considered for commercialization are also listed.

The objective of the course is to provide the student with a fundamental understanding of the chemical, catalytic and engineering sciences relating to the chemical reactions taking place in a variety of reactors of different configurations.

This section includes the important fundamental information on homogeneous catalysis. Thus, the key coordination chemistry principles required to understand the homogeneous catalyzed process (to be described later on) are tightly reviewed and discussed. A few of the concepts discussed are: elements of crystal field-molecular orbital theory; metal d-orbitals; d-electron activation of coordinated ligands; coordination stereochemistries of transition metal complexes; counting d-electrons; eighteen electron rule; key intermediates in homogeneous catalysis like metal carbonyls, hydrides, alkyls, etc.; key transformations in homogeneous catalysis like oxidative addition, insertion, electron transfer, etc.; ligand electronic and steric effects such as pi-acceptors, sigma-donors, cone angles, etc. Then the basic sub-classification of homogeneous metal catalyzed reactions like main group and transition metal catalysis, biocatalysis, phase transfer catalysis, polymer supported catalysis, etc., are briefly described. The typical kinetic treatments and methods for spectroscopic analysis are also illustrated.

3. Heterogeneous Catalytic Process Fundamentals

Fifteen examples are given of major commercial processes in terms of reactants, products, catalysts, and conditions, along with a brief discussion of a dozen other processes.

The fundamental aspects of heterogeneous catalyzed processes are discussed by reviewing principles of the chemistry and physics of surfaces and surface adsorption, *e.g.* macro- and micropores, Knudsen diffusion, chemisorption and physical adsorption; Langmuir-Hinshelwood and Rideal-Eley surfaces kinetic models, competitive chemisorption and catalyst poisoning; surface intermediates and surface chemistry.

This section also discusses the major subcategories of heterogeneous catalysts like supported and unsupported reduced metals, solid state inorganic catalysts, carbon catalysts, clays and zeolite catalysts. Several examples are given for each class.

A detailed discussion is devoted to the structure, physical and chemical properties, and catalytic properties of zeolites. Some of the topics discussed are X- and Y-type zeolites and ZSM-5 structures, modifications and molecular build up; pore openings and crystal structure; super acidity and super basicity; and a four component model for rationalizing the unusual activity of zeolite catalysts. The student is also introduced at this point to the relationship of shape selectivity and constraint index to the crystal and catalytic properties of zeolites. An assortment of several classes of zeolite structures is illustrated with 35 mm slides and three dimensional molecular models. Support materials used in heterogeneous catalyzed processes and their criteria for selection are briefly discussed.

4. Survey of Modern Commercial Reactor Configurations

Drawings of fourteen of the reactor configurations used commercially in both heterogeneous and homogeneous catalyzed processes are supplied to the student, and an example is given of a commercial product produced using each configuration. Within the discussion of these reactor configurations, the various thermodynamic, heat transfer, kinetic, reactor stability, mixing and other factors giving rise to the selection of a specific configuration, are examined. Specific examples of reactor configurations (process applications) are as follows: tube and shell (Lurgi methanol and ethylene oxide process); tray re-

actor with interstage cooling (ICI methanol synthesis) ; riser tube (catalytic cracking) ; fluidized bed (SOHIO acrylonitrile) ; slurry tank (polypropylene) ; radial bed (styrene synthesis) ; and others.

5. Synthesis Gas Generation

The major processes used in the production of synthesis gas are discussed along with their feedstocks and gaseous product compositions. The thermochemistry of each process is related to thermal and pressure effects on the syngas product ratios and to its consequence on the reactor design. Drawings for several process reactors such as methane reforming, partial oxidation, Lurgi non-slagging gasifier, Koppers-Totzek gasifiers and the Bi-Gas slagging gasifier are provided to the student along with a discussion of each. A survey of next generation gasifiers is given.

Post gasifier processing of raw syngas through water gas shift, bulk and trace sulfur removal processes, CO_2 removal and CO separation from H_2 is discussed. The chemistry of a Claus plant and Stretford plant is summarized.

6. Synthesis Gas Processes for Fuels and Chemicals

A survey of all commercial and potential fuels and chemicals processes using a syngas feedstock is given with reactants, products, catalysts, and reaction conditions. Details of the thermochemistry of methanol synthesis and its consequence on the evolution of the ICI, Lurgi and Chem Systems reactor and process configurations are discussed. The student is introduced to conventions used in process stream notations. The low pressure catalyst structure and syngas to methanol surface reaction mechanism are presented.

A detailed discussion is given to the conversion of methanol by the Mobil M process to aromatic fuels. The details of the ZSM-5 catalyst structure,

TABLE 2

Exam: Heterogeneous Catalysis Fundamentals and Commercial Reactor Configurations

Part 1. Describe the following commercial processes using structural formulae of starting materials, major products and heterogeneous catalysts required in the process

(A) Sohio Ammoxidation
(B) Styrene Process (Two Steps)
(C) Maleic Anhydride Process
(D) Catalytic Hydrodesulfurization Process
(C) Fischer-Tropsch Process
(D) Mobil M Process

Part 2. A. Describe the following adsorption processes for gaseous molecules on catalytic solid surfaces. Give examples of each.

1. Physical Adsorption
2. Chemisorption
3. Competitive Chemisorption

B. Briefly describe how a Langmuir-Hinshelwood surface kinetic mechanism differs from a Rideal-Eley mechanism. Give an example of each.

Part 3. Draw the structural formulae of the following heterogeneous catalytic surface intermediates

(A) Surface alkyl
(B) Selective surface oxidant
(C) Non-selective surface oxidant
(D) Surface hydroxy Carbene
(E) Bronsted acid surface site

Part 4. Discuss the following properties of zeolites

(A) Compare the 3A, 4A and 5A molecular sieves in terms of
(1) ions used to modify these zeolites
(2) size of pore opening for each
(3) example of molecules absorbed by each

(B) Briefly compare the structures and differences in composition of the X- and Y-type zeolites.

(C) Describe the "Supercage" in a commercial catalytic cracking catalyst in terms of (1) its geometric form and number of sides (2) size of its largest pore opening and (3) internal cage size.

(D) Why are zeolite catalysts as much as 10,000 times more reactive than amorphous aluminosilicates in catalytic cracking?

Part 5. (A) Sketch the reactor section for a commercial radial bed reactor showing the inlet reactant and product effluent locations and catalyst bed configuration.

(B) Why would one use such a complex reactor configuration in a commercial process?

(C) Sketch the reactor configuration for a typical trickle bed reactor used in catalytic hydrosulfurization in a refinery.

(D) What essential task does the trickle bed reactor perform which other designs do not accomplish.

(E) What is a typical contact time in a riser tube reactor and which of the following catalysts would a refiner use in this reactor for catalytic cracking: (a) ZSM-5, (b) X-type zeolite, (c) Ca-Y-type or (d) rare earth-Y-type?

acidity, and shape selectivity are merged with a detailed evaluation of an intercrystalline surface mechanism to understand the product distribution and catalyst stability.

A thorough discussion is devoted to the ARGE fixed bed and fluidized bed SASOL processes for the direct conversion of syngas to fuels. Catalysts, reactor configurations, slides of the Sasol II Plant, surface reaction mechanistic models, Schulz-Flory kinetics and thermochemistry of syngas conversion to various products are parts of these lectures.

The lectures on the conversion of synthesis gas to chemicals is less oriented toward reactors and total processes; rather, they concentrate more on the detailed reaction mechanisms, using the pertinent coordination chemistry intermediates, to rationalize the conversion of syngas to various products. This is the first opportunity that the student has in the course to apply the fundamentals learned earlier to homogeneous and heterogeneous catalyzed processes. Some of the processes discussed are: acetic anhydride, acetic acid, ethylene glycol, vinyl acetate, and ethanol.

7. Technology of Major Advanced Chemical Processes

This section also concentrates on reaction mechanisms for both homogeneous and heterogeneous catalyzed processes. Aromatic side chain oxidation and butane oxidation to acetic acid are described by listing each of the proposed individual, elementary reactions required to form products. The coordination chemistry of the Wacker process, Carbide and Shell oxo-processes, Halcon propylene oxide process and others are illustrated. Likewise, the proposed surface mechanisms for the super basic zeolite catalyzed conversion of toluene and methanol to styrene and ZSM-5 zeolite catalysts for p-xylene production are explored along with several other.

8. Major Refining Processes

The principal processes utilized in a modern refinery are surveyed. A few of the processes like hydrodesulfurization are described in detail by way of an examination of the crystal chemistry of the catalyst, processing of various feedstocks, and reactor configuration. Most of the students' understanding of catalytic reforming, and catalytic cracking comes from assigned textbook reading. Several of the processes are viewed by 35 mm slides of various refinery units.

TERM PAPERS

Three term papers are assigned for the purpose of examining the details of several important areas of chemical and petroleum processing technology which are not covered in class. The emphasis in the papers is to provide a concise description of the major scientific and engineering aspects of the technology. In the past, Ziegler-Natta catalysis, catalytic cracking, and technology of heterogeneous, hydrocarbon partial oxidation were assigned.

EXAMS

Three one-hour exams are usually given which cover all material discussed in class. These exams are closed notes and books and are given soon after the subject matter is discussed in class. No comprehensive final has been given until now. Table 2 shows a typical exam, given in March of 1982. The high grade was 99, the low was 41, and the class average of 53 students was 70. □

JUNIOR YEAR LAB

Continued from page 127.

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