

A Survey Course in

CATALYSIS

J. M. SKAATES

Michigan Technological University
Houghton, MI 49931

ATEN WEEK SURVEY COURSE in catalysis was designed to meet the needs of both chemistry and chemical engineering graduate students in Michigan Tech's Department of Chemistry and Chemical Engineering. The aim of the course is to show how modern chemistry and chemical engineering interact in the ongoing development of industrial catalysts. As the course developed, it attracted the attention of graduate students in metallurgy who were grappling with chemical phenomena in their research in physical and extractive metallurgy.

The course outline is given in Table 1. The appearance of Gates, Katzer, and Schuit's *Chemistry of Catalytic Processes*, McGraw-Hill, New York (1979) provided an organizational framework. This text is incisive, mercifully slender, and contains challenging homework problems at the end of each chapter. To maintain the pace shown in Table 1, a series of sixty-five transparencies showing chemical structures and reaction mechanisms were prepared for use with an overhead projector. At the beginning of the course each student is given photocopies of all sixty-five transparencies. Constant reference is made to a wall-hung periodic table, and to a well-known organic chemistry text (Morrison and Boyd) which most students own.

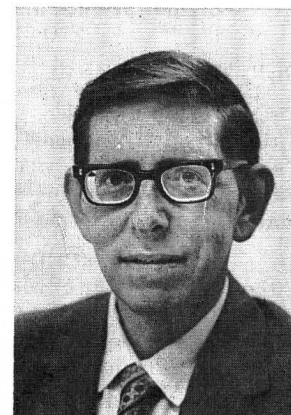
At the beginning of the course the students are asked to read two articles [1] which contrast industrial processes with textbook organic chemistry. Then a quick review of the active site theory and the Langmuir-Hinshelwood formalism is given for the benefit of students who have not taken the undergraduate chemical engineering kinetics course. Modern surface analysis techniques are described in a series of notes.

The discussion of thermal cracking is extended to cover computer modeling of ethylene manu-

facture [2] and recent research on high-severity pyrolysis [3]. The catalytic effect of the tube wall is demonstrated [4]. A set of notes entitled "Physical properties of coal-derived liquids as affecting their chemical processing" summarizes the work of Ubbelohde on melts of polynuclear aromatics and of Marsh on formation of semi-cokes from aromatic liquids. A seminal paper by Virk [5] provides a framework for understanding chemical processing of aromatic liquids.

Acid-catalyzed cracking of hydrocarbons is covered next, and the textbook treatment is supplemented by a study of the Socony-Mobil methanol-to-gasoline process over shape-selective zeolites. This provides an opportunity for examination of various processes for obtaining liquid fuels from coal. The advantages of the coal - synthesis gas - methanol - gasoline route are emphasized.

An historical approach is taken to solid-catalyzed reactions, with the search for the "active site" being the main theme. For the benefit of metallurgy students the enhanced reactivity at emergent dislocations is discussed on the basis of an excellent review article [6]. Three lectures are



J. M. Skaates received his B.Sc. (1957) at Case Institute of Technology and M.S. (1958) and Ph.D. (1961) at Ohio State University in chemical engineering. He worked at California Research Corporation for three years before joining the faculty of Michigan Tech. His teaching duties have included undergraduate and graduate courses in thermodynamics and kinetics, an undergraduate course in process control, and graduate courses in catalysis and in process optimization. He has been involved in research in catalysis, biomass pyrolysis, and wet oxidation.

The ninth week is devoted to a discussion of proposed mechanisms for five important industrial reactions. It is emphasized that mechanisms are never finally "proven," but are working hypotheses reflecting present knowledge.

devoted to the work of Somorjai on clean metal surfaces, with special attention to his parallel studies on iridium, platinum, and gold [7], and the linking of the unique catalytic activity of platinum to the high density of states at the Fermi level. Surface reconstruction on platinum-rhodium screens during the oxidation of ammonia is used to illustrate that interaction of surface metal atoms with adsorbates profoundly affects the metal-metal bonds. The geometric and electronic theories of catalysis by metals are represented as reflecting primitive ideas of metal surface morphology and bonding in metals.

The synthesis and catalytic properties of metal cluster compounds is presented as a third approach (after transition metal ions in solution and clean metal surfaces) for studying bonding of metal

atoms. Bonding of ligands to the metal clusters is compared with chemisorption of gases on bulk metal surfaces.

The ninth week is devoted to a discussion of proposed mechanisms for five important industrial reactions (Table 1). It is emphasized that mechanisms are never finally "proven," but are working hypotheses reflecting present knowledge. As an illustration, the electronic theory of catalysis, as applied to semiconducting metal oxides, fails to explain the baffling Schwab-Parravano discrepancy.

Oxidation of hydrocarbons by oxygen supplied from an inorganic oxide lattice illustrates that a novel idea, tested with simple apparatus [8], can have a big economic payoff. On the other hand, millions of dollars of research failed to uncover a

TABLE 1
Course Outline

WEEK	TOPICS COVERED
1.	Theory of active sites Langmuir-Hinshelwood mechanisms and rate equations
2.	Survey of modern surface analysis techniques. Thermal cracking of hydrocarbons: Free-radical mechanisms Cracking of aromatics Recent trends in thermal cracking
3.	Acid-catalyzed cracking of hydrocarbons: Carbonium ion formation on solid surfaces Carbonium ion mechanisms Silica-alumina catalysts Zeolite catalysts Socony-Mobil methanol-to-gasoline process
4.	Chemistry of transition metal ions Zeiss' salt Wacker Process for acetaldehyde from ethylene Oxo Process Designing liquid-phase homogeneous catalyst reactors.
5.	Types of defects on solid surfaces Emergent dislocations as active sites Surface morphology H-H, C-H, and C-C bond breaking on steps and kinks of metal surfaces Surface reconstruction during catalytic reactions
6.	Geometric theory of catalysis on metals Electronic theory of catalysis on metals Surface compound theory of catalysis on metals Metal alloy catalysts
7.	Supported metal catalysts Experimental techniques for characterizing supported metal catalysts Reforming of hydrocarbons Octane and cetane numbers Modeling catalytic reforming reactors
8.	Properties of small metal crystallites Interaction between metal crystallites and the support Metal cluster compounds Metal-metal bonding Bonding of carbonyl groups Bonding of hydrogen
9.	Ammonia synthesis mechanism Hydrocarbon synthesis by CO reduction Proposed mechanisms for Fischer-Tropsch Synthesis Proposed mechanisms for the methanation reaction Design of methanation reactors
10.	Mechanisms involving electron transfer between adsorbate and metal oxides Catalysis on semiconductors Electronic Theory of Catalysis as applied to semiconducting metal oxides Oxygen transfer from the solid oxide lattice Synthesis of acrolein and acrylonitrile from propylene Complex oxide catalysts Perovskite structures Scheelite structures Automobile exhaust converter catalysts

TABLE 2

Articles Assigned for Outside Reading and Evaluation

1. Witcoff, H., "How It's Really Done," *CHEMTECH*, December 1977, p. 753 *CHEMTECH*, April 1978, p. 229.
2. Riggs, W. M., and Beimer, R. G., "How ESCA Pays Its Way" *CHEMTECH*, November 1975, p. 652.
3. Kearns, J. D., Milks, D., and Kamm, G. R., "Development of Scaling Methods for a Crude Oil Cracking Reactor Using Short Duration Test Techniques," paper presented to the Division of Petroleum Chemistry, 175th National Meeting of the American Chemical Society, Anaheim (1978).
4. Hall, James W., and Rase, Howard F., "Relation Between Dislocation Density and Catalytic Activity and Effects of Physical Treatment" *I and EC Fundamentals*, 3, 158 (1964).
5. Johnson, O., "Classification of Metal Catalysts Based on Surface d-Electrons," *J. Catal.*, 28, 503 (1973).
6. Callahan, J. L., Grasselli, Robert K., Milberger, E. C., and Strecker, H. Arthur, "Oxidation and Ammoxidation of Propylene Over Bismuth Molybdate Catalyst," *I and EC Prod. Res. Rev.*, 9, 134 (1970).

satisfactory metal oxide replacement for platinum in the oxidation of unburned hydrocarbons in automobile exhaust.

Student evaluation of this course has been favorable, and their comments indicate that the excitement of catalyst research is "catching." The limitations of current chemical theories are evident in trying to understand many catalysts. Playing a "hunch," or serendipity, often lead to valuable catalysts and also to new chemistry for the theorist to interpret. □

REFERENCES

1. Witcoff, H., "How It's Really Done," *CHEMTECH*, December 1977, p. 753, *CHEMTECH*, April 1978, p. 229.
2. Shah, M. J., "Computer Control of Ethylene Production," *Ind. Eng. Chem.*, 59, 70 (1967).
3. Ennis, Boyd, and Orris, "Olefin Manufacture by Millisecond Pyrolysis," *CHEMTECH*, November 1975, p. 693.
4. Dunkleman and Albright, "Pyrolysis of Propane in Tubular Flow Reactors Constructed of Different Materials" *ACS Symposium Series*, No. 32, p. 261 (1976).
5. Virk, Chambers, and Woebecke, "Thermal Hydrogasification of Aromatic Compounds," *ACS Advances in Chemistry Series*, No. 131 (1974).
6. Thomas, J. M., "Enhanced Reactivity at Dislocations in Solids," *Advances in Chemistry*, 19, 293 (1969).
7. Somorjai, G. A., "Active Sites in Heterogeneous Catalysis," *Advances in Catalysis*, 26, 2 (1977).
8. Callahan, J. L. *et. al.*, "Oxidation and Ammoxidation of Propylene Over Bismuth Molybdate Catalyst" *I and EC Prod. Res. Dev.*, 9, 134 (1970).

POLYMER RESEARCH

Continued from page 177.

compatible. In summary, our objective is to provide the student with an understanding of molecular and continuum approaches and an understanding of the behavior of polymeric systems. We try to emphasize the need of understanding both the chemistry of these macromolecular systems and their engineering properties.

All students receive a similar background in coursework. Along with the courses mentioned above, 11 other polymer courses (including such topics as polymer synthesis, physical chemistry of polymers and surface analysis) are available in the four other departments participating in the interdisciplinary group. Because of the large number of graduate students now in our program, even the advanced courses are offered on a routine basis.

As a final note concerning educational aspects extending from chemical engineering in the polymer science area, we might point out that there are several industrially oriented polymer short courses offered at Virginia Tech each year. These courses are taught jointly through the polymer oriented chemical engineering faculty as well as other faculty members of the PMIL group. In short, we now offer the most extensive continuing education program in polymer science through a short course format than any other university in the nation.

SUMMARY

In this article we have attempted to outline the new growth in the polymer area at Virginia Tech, with emphasis being placed on the role of the Department of Chemical Engineering. The overall polymer science effort, as indicated, extends beyond a single department, encompassing five departments across two colleges. The growth of this program has been enormous in the last three years as a result of cooperative efforts of a truly interdisciplinary nature. The overall program, part of which is focused in chemical engineering, has become a highlight of the Virginia Tech campus and one which we anticipate will become even stronger in the future. It has achieved considerable outside funding and has developed modern research facilities necessary for graduate research. Inquiries concerning information about Chemical Engineering and the Polymer Materials and Interfaces Laboratory can be directed to either of the authors of this article. □