A Course in

HETEROGENEOUS CATALYSIS

SOL W. WELLER
State University of New York at Buffalo
Buffalo, New York, 14214

HETEROGENEOUS CATALYSIS, once the darling of avant-garde physical chemists, has been largely disavowed by chemistry departments. During the past decade it has been increasingly taken up and nourished by chemical engineering departments—partly by necessity, since the applications of heterogeneous catalysis are of such vast industrial importance that we cannot allow the subject to go untaught and uninvestigated. The situation has not been totally satisfactory. Chemical engineering students, who often know too little chemistry (especially organic) to appreciate the complexities of real reactions, tend to concentrate excessively on transport phenomena (which they know relatively well), and to hold to an innocent belief that reaction mechanisms can be rigorously deduced from computerized curve-fitting of kinetic data.

We have adopted a compromise solution to this problem. A one-semester, introductory graduate course in heterogeneous kinetics is offered that is intended to provide the bare bones of a field whose literature is now enormous. The course is normally offered in late afternoon; it is open to full-time graduate students, to seniors who have already had an undergraduate course in applied kinetics, and to qualified part-time graduate students who are employed in local industry. Since there is substantial industrial activity in catalysis in the Buffalo area, experience indicates that 1/3 to 1/2 of a typical class is made up of such part-time students.

The course is intended to walk a middle road between theory and practice. One semester is inadequate to present, even in elementary fashion, all the topics one would like to cover: theories of adsorption, catalyst preparation, catalyst characterization, heterogeneous kinetics, limitations by physical factors, mechanistic studies, theories of catalysis, nature of surface complexes, and a survey of industrially important catalytic reactions.

A few comments on text and references may be useful. As with most graduate courses, the lectures are best based on one's accumulated experience and eclectic notes. A one-volume text, suitable for retention by the student as a reference, is nevertheless a convenience. After some experimentation we have found Thomas and Thomas, *Introduction to the Principles of Heterogeneous Catalysis*, to be quite useful for this purpose. A number of recent books provide an excellent supplement in specialized areas: Anderson's *Experimental Methods in Catalytic Research*, Thomas' *Catalytic Processes and Proven Catalysts*, Bond's *Catalysis by Metals*, Krylov's *Catalysis by Nonmetals*, Satterfield's *Mass Transfer in Heterogeneous Catalysis*, and Linsen's *Physical and Chemical Aspects of Adsorbents and Catalysts*. By way of multivolume references, there is the unending series of *Advances in Catalysis*; Emmett's *Catalysis*, now somewhat dated but still very useful; and the *Encyclopedia of Chemical Technology*, which contains some of the best descriptions of industrial catalytic processes.

The lectures attempt to touch on the topics listed in the following course outline:

Sol Weller did his undergraduate work at Wayne and obtained his Ph.D., from the University of Chicago in 1941, under the Nobel Prize winner in physics, James Franck. After serving in the N.D.R.C. and the Manhattan Project during W.W. II, he conducted research at the Bureau of Mines from 1945 to 1950 on synthetic liquid fuels processes and gas separations by fractional permeation. He was head of fundamental research at Houdry Process Corp. from 1950 to 1958. In 1958 he joined the Aeronutronic Division of Ford(later Philco-Ford) where, after a stint as Manager of Propulsion Research(he became Director of the Chemistry Laboratory and Acting Director of the Materials Laboratory of Philco. He came to SUNY/Buffalo in 1965 as professor of chemical engineering; there he has since contentedly pursued research in kinetics and catalysis, except for interludes as visiting professor at Berkeley and acting chairman at Buffalo. He is presently on leave, on a one-year U.N. appointment at the Centre for Industrial Research in Haifa.

I. Adsorption
   A. Physical adsorption and chemisorption
   B. Isotherm equations
   C. Kinetics of adsorption
II. Catalyst Preparation
   A. Clean surfaces
   B. "Practical" catalysts
III. Catalyst Characterization
   A. Measurement of adsorption isotherms
   B. Total surface area from physical adsorption isotherms
   C. Selective chemisorption techniques
   D. Average particle size
   E. Physical techniques (x-ray, magnetic, electron)
   F. Surface heterogeneity (heat of adsorption, temperature-programmed desorption isotherms)
   G. Entropy of adsorption
   H. Density (bulk, particle, true), pore volume
   I. Pore size distribution (adsorption, porosimetry)
   J. Diffusion in pores
IV. Reaction Rates in Porous Catalysts
   A. Historical
   B. Effectiveness factor in isothermal, simple reactions
   C. Poisoning and effectiveness factor
   D. Temperature gradients: intraparticle, boundary layer, interparticle
   E. Diagnostic criteria and diagnostic tests
   F. Effectiveness factor in complex reactions; selectivity
V. Kinetics of Surface-Catalyzed Reactions
   A. General principles
   B. Langmuir-Hinshelwood kinetics
   C. Alternate approaches
   D. Catalyst deactivation
VI. Theories of Catalysis
   A. Correlations of activity data for metals
   B. Theories: geometric, electronic
   C. Semiconductor compounds: Sabatier principle, "volcano" curves, surface chemistry
   D. Acid catalysis
   E. Relations to homogeneous catalysis
VII. Reaction Mechanisms
   A. Tracer studies
   B. Stereochemistry
   C. Surface species

Clearly the distribution of emphasis among these many topics will not be uniform. A few remarks will indicate the author's approach to this matter:

1. Adsorption is treated in some detail for two reasons. First, it provides a basic tool for catalyst characterization: physical adsorption for the analysis of catalyst texture (total area, pore eize distribution, etc.); and selective chemisorption, including variants such as "gas titration" techniques and isotopic exchange, for determination of specific surface area of a supported active component. Second, all rational treatments of catalytic kinetics require some assumptions about adsorption isotherms.

2. Methods of catalyst characterization are also emphasized because of their utility in understanding catalyst comparisons and time-dependent behavior of catalytic systems.

3. In the treatment of mass transfer limitations on Reaction rates, we have found it convenient to use Wheeler's development. It is exceptionally lucid, easy for the student to grasp and use without extensive experience, and effective in giving correct semi-quantitative answers in most practical situations. (Zeolites are a notable exception.)

4. Langmuir-Hinshelwood kinetics, particularly as extended and systematized by Hougen, Watson, and Yang, is developed in detail because of its elegance and intellectual attractiveness. However, the author's bias leads him to alert students to questions about the validity of the basic premises, and to caution them about drawing mechistic conclusions from kinetic measurements.

5. The problems of establishing reaction mechanism are illustrated by specific examples of non-kinetic methods that have been developed to attack this most difficult question. We have found it necessary to guard against over-selling one's personal enthusiasms here. For example, it was belatedly discovered that one early class almost unanimously concluded that IR studies of surface species provided a cure-all for catalytic problems.

OUR COURSE IS probably as well-characterized by what is left out, or at least de-emphasized, as by what is included. Several important topics are relatively slighted in the lectures. A few of these should be mentioned. (1) Theories of catalysis, and particularly electronic theories. It is the author's observation that after two decades of intensive effort by many people, such theories have proved of comparatively little predictive use in practice; and it is his feeling that *ex post facto* rationalization can be left by chemical engineers to others. (2) Detailed discussions of industrial catalysis. We feel that the fundamental tools provided to the student by the lectures should permit him to explore with understanding any specific catalytic process in which he becomes interested. Moreover, the individual student is required to make in depth a "case study" of some industrially important catalytic reaction as a term paper. (3) Contemporary developments in chemical kinetics, examples of which are the elegant treatment of complex reaction schemes by Wei and Prater, and Horiuti's concept of stoichiometric number and reaction rates near equilibrium. Such topics are not limited in scope to heterogeneous catalysis, and they are normally covered here in a separate graduate course in applied chemical kinetics. (4) Catalytic reactions over clean surfaces. The emphasis in the course is on "practical" catalysts.