

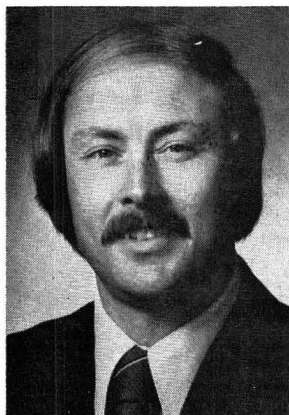
# A Course on

## HETEROGENEOUS CATALYSIS

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**H**ETEROGENEOUS CATALYSIS plays a dominant role in many of today's commercial processes, particularly in the petroleum and chemical industries. The recent emphasis on energy conversion and air and water pollution only serves to provide two more areas in which catalysis can have a significant impact. The field of heterogeneous catalysis draws heavily on the disciplines of chemistry, engineering, physics, surface science and materials science. It requires a major effort for a researcher to bring together knowledge from these diverse fields and to be cognizant of recent developments in these areas. This requirement to be knowledgeable about recent research presents one of the two major challenges in teaching a graduate course in catalysis; the other is the realization that no single text is available in print today which adequately covers all the aspects of heterogeneous catalysis. Therefore, one must



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gather material from a variety of sources such as: texts, review articles, and original papers, both past and current. However, this approach does have the advantage of familiarizing the students with the literature and emphasizing the role of research in the development of this field.

In the reference section, a list of textbooks is given which provides a nucleus of material for studying the principles and theories of catalysis. Unfortunately, some of these texts, designated by an asterisk, are out of print. Chapters from these texts which are particularly applicable to specific topics are noted in the course outline. Original papers from the literature which are especially pertinent to certain subjects are also listed in the reference section. This list is by no means complete, but it does provide at least one reference to introduce the student to each topic. Several recently published books have been included which, although not available for the original course, should be useful for the development of certain subjects.

At Penn State, the class of 28 students consisted of equal numbers from chemical engineering, chemistry, and materials science, plus a physicist. This diversity is typical in catalysis courses and forces one to maintain a balance between the breadth and depth of presentations of chemistry, solid state physics, and mathematical analysis. (I find that my own limitations tend to provide this balance automatically!) In lieu of a final exam, the students were asked to apply principles, correlations, and theories discussed in this course to a variety of topics which were obtained from the recent literature. This forced the student to study a particular area in depth, to understand the principles involved, and to assess their applicability to the problem. One such effort was significant enough to result in a publication in a refereed journal (reference 13).

A tremendous amount of time can be spent looking for papers and data from which to develop lectures and show examples of certain aspects of catalysis. It is hoped that the course de-

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scribed here, with the list of references, can save time for others. The course outline is presented in Table 1, and the appropriate references are listed in parentheses. A 10-week term at Penn State consists of ten 75-minute class periods per credit. Since this was a 3-credit course, the 30 lectures represent material for a 3-credit semester course.

Because adsorption is the initial step in heterogeneous catalysis, this topic (Section II) was discussed first. The traditional approaches to rates of adsorption and desorption were supplemented by recent results in surface science. Also, a new perspective on the Elovich equation was presented and discussed.

The topic of kinetics (Section III) was introduced by a discussion of the theories and approxi-

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mations which apply to homogeneous gas-phase reactions. Reactions catalyzed on solid surfaces were then discussed, and the consequence of assuming ideal surfaces was shown by the use of Hougen-Watson type rate equations. The limitations and simplifications involved in this approach were discussed in detail. With this background, various correlations in catalysis could then be introduced.

The development of the science of catalysis depends heavily on experimental research, and

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

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| <p><b>I. INTRODUCTION (1 Lecture)</b></p> <ul style="list-style-type: none"> <li>A. Brief history of catalysis</li> <li>B. Processes using heterogeneous catalysts (1)</li> <li>C. Definitions</li> </ul> <p><b>II. ADSORPTION (2-4) (4 Lectures)</b></p> <ul style="list-style-type: none"> <li>A. Rates of adsorption and desorption (5-7)</li> <li>B. Physical adsorption—BET eq.</li> <li>C. Chemisorption           <ul style="list-style-type: none"> <li>1. Ideal surfaces—Langmuir eq.</li> <li>2. Nonideal surfaces—Temkin eq., Freundlich eq.</li> <li>3. Heats of adsorption</li> <li>4. Activated adsorption—Elovich eq. (8)</li> </ul> </li> </ul> <p><b>III. CHEMICAL KINETICS (E) (11 Lectures)</b></p> <ul style="list-style-type: none"> <li>A. Homogeneous Reactions           <ul style="list-style-type: none"> <li>1. Collision theory</li> <li>2. Absolute rate theory</li> <li>3. Steady-state approximation</li> </ul> </li> <li>B. Heterogeneous reactions on ideal surfaces           <ul style="list-style-type: none"> <li>1. Derivation of rate equations—Langmuir isotherm (9)</li> <li>2. Simplifying assumptions—rate determining step, most abundant surface intermediate (B, 10)</li> <li>3. Estimation and evaluation of constants in rate eq. (10-13)</li> </ul> </li> <li>C. Correlations in kinetics and catalysis (B — Chap. 8, 14, 15—Chap. 7)           <ul style="list-style-type: none"> <li>1. Polanyi relation</li> <li>2. Brönsted relation</li> <li>3. Hammett relation</li> <li>4. Van Tiggelen formula</li> <li>5. Compensation effect (16-17)</li> <li>6. "Volcano" Plot—examples (18)</li> </ul> </li> <li>D. Catalysis on nonideal (nonuniform) surfaces (19)</li> </ul> <p><b>IV. HEAT AND MASS TRANSFER EFFECTS ON RATE EQUATIONS (20) (4 Lectures)</b></p> <ul style="list-style-type: none"> <li>A. Interphase transport</li> <li>B. Intraphase transport (pore diffusion)</li> </ul> | <ul style="list-style-type: none"> <li>C. Experimental tests for transport effects (21-23)</li> </ul> <p><b>V. CATALYST CHARACTERIZATION (2 Lectures)</b></p> <ul style="list-style-type: none"> <li>A. BET surface areas (D)</li> <li>B. Pore size distribution (24)           <ul style="list-style-type: none"> <li>1. Mercury porosimetry</li> <li>2. Nitrogen desorption method (Kelvin eq.)</li> </ul> </li> <li>C. Metal crystallite size           <ul style="list-style-type: none"> <li>1. Chemisorption (25, 26)</li> <li>2. X-ray diffraction</li> <li>3. Electron microscopy</li> <li>4. Other physical techniques (Mössbauer spectroscopy, magnetization, etc.)</li> </ul> </li> </ul> <p><b>VI. THEORETICAL CONCEPTS IN CATALYSIS (4 Lectures)</b></p> <ul style="list-style-type: none"> <li>A. Sabatier's Principle</li> <li>B. Geometric factor (27, 28)</li> <li>C. Ensemble theory—Kobosev</li> <li>D. Electronic factor           <ul style="list-style-type: none"> <li>1. Band theory (29)</li> <li>2. Pauling's % d-character (30)</li> </ul> </li> <li>E. Alloys (31-34)</li> <li>F. Structure sensitivity and insensitivity (35)</li> <li>G. Activity, specificity, selectivity (36)</li> </ul> <p><b>VII. CHEMISTRY AND KINETICS OF CATALYTIC PROCESSES (3+ Lectures)</b></p> <ul style="list-style-type: none"> <li>A. Catalytic cracking and hydrocracking—dual functional catalysts (37)           <ul style="list-style-type: none"> <li>1. Carbonium ion reactions</li> <li>2. Acid sites on solid surfaces</li> <li>3. Examples of activity and selectivity</li> </ul> </li> <li>B. Reforming—Hydrogenation, hydrogenolysis (37, 38)</li> <li>C. CO hydrogenation (39-40)           <ul style="list-style-type: none"> <li>1. Methanation</li> <li>2. Fischer-Tropsch synthesis</li> <li>3. Alcohol formation</li> </ul> </li> <li>D. Ammonia synthesis (41)</li> <li>E. Oxidation (ethylene oxide production) (42)</li> <li>F. Others (CO oxidation, NO reduction)</li> </ul> |
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the importance of obtaining kinetic data free from heat and mass transfer effects was stressed in Section IV. A number of tests were described which can be used to determine the absence of transport limitations.

Section V introduced the class to characterization techniques used for solid catalysts. Due to their wide use, supported metal catalyst systems were emphasized and chemisorption techniques to measure metal surface area were stressed.

In Section VI, a historical approach was used to introduce theoretical developments in heterogeneous catalysis. After this background, the present status of heterogeneous catalysis was considered by discussing alloy systems and addressing such topics as: differences between bulk and surface compositions, ligand *vs.* ensemble effects, and new models to describe the electronic behavior of metals and alloys. The work of Sinfelt and of Sachtler and coworkers was especially useful here to illustrate the potential benefits of alloy and bimetallic cluster systems in catalysis.

Finally, a presentation of various catalytic processes exposed the class to commercial reaction systems, allowed a discussion of the basic chemistry involved, and provided an opportunity to delve into fundamental studies which pertained to that particular process. □

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