A Course in

HETEROGENEOUS CATALYSIS

Principles, Practice and Modern Experimental Techniques

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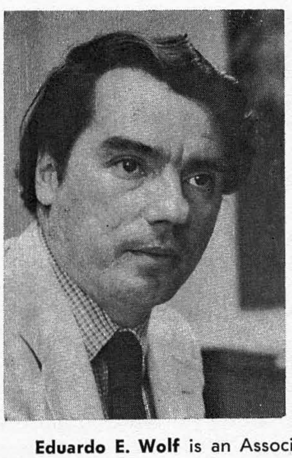
Catalysis is a multidisciplinary subject wherein collaboration among chemists, physicists, material scientists and engineers render the best results.

HETEROGENEOUS CATALYSIS PLAYS a key role in the chemical process industry as well as in energy conversion and pollution control processes. The development of new processes is often preceded by the discovery of a new catalyst. A case in point is, among many others, catalytic cracking in petroleum refining. The first cracking processes were non-catalytic, thermal processes designed to increase the fraction of petroleum that could be utilized as gasoline. The first catalytic cracking process used a treated clay as a catalyst which deactivated rapidly. Reactors were then developed to regenerate the coked catalyst by using cycling feeds, moving beds and fluidized beds. Synthetic silica alumina catalysts replaced the natural treated clays and these were superseded by catalysts containing zeolites dispersed on an amorphous silica alumina matrix. Optimum operation of the new zeolite cracking catalyst required short contact times and higher temperatures. This led to the replacement of the fluid bed reactor by the riser cracker or transport line reactor in which the vaporized feed is contacted and transported upward with regenerated catalyst in a vertical pipe. The strategic and economic implications of new catalysts development are evident when considering the history and present status of coal conversion processes. Such processes, first used in Germany during WW II, were briefly considered in the U. S. in the fifties, but finds its present full scale development and application in South Africa. Present efforts in synfuels development are a challenge open to future generations of scientists and engineers. The answers lie, in part, in our ability to develop new, more active and resistant catalysts which can withstand operation in the demanding environment of coal conversion processes. The task requires that we possess a better understanding of catalytic reactions and surfaces, as well as a command of the modern tools used for surface analysis and catalyst characterization.



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The advent of new spectroscopic tools for direct probing of surfaces requires an introduction to the methods of other disciplines not currently included in the traditional chemical engineering curriculum. Catalysis is a multidisciplinary subject wherein collaboration among chemists, physicists, material scientists and engineers render the best results. For this to occur, researchers in this area need to be equipped with the basic understanding of the complementary disciplines and tools, otherwise the dialog does not bear fruit. The course outline which follows has been organized in this multidisciplinary context comprising fundamental, practical, and experimental aspects of heterogeneous catalysis.

COURSE STRUCTURE AND DESCRIPTION

THE COURSE IS STRUCTURED so that lecture materials are combined with demonstration experiments dealing with the use of spectroscopic techniques for surface analysis. Table 1 presents an outline of the course in the form of a table of contents divided into three parts and subsections or chapters. Parts I and II comprise the lecture material whereas Part III consists of a brief description of the demonstration experiments. The experiments are also indicated in parenthesis in Part I to indicate the appropriate combination of lectures and experiments.

The list of experiments presented in Part III is incomplete since there are many other techniques for surface analysis and catalyst characterization. However, in practice, availability of equipment places a restriction on the types of experiments which can be conducted during the course. When I teach the course at Notre Dame, nine experiments are run for which I borrow the facilities of Chemistry (XPS), Materials Science (X-ray diffraction, SEM, TEM), our college (AES) and our own catalysis laboratories (FTIR, adsorption, kinetics). Fig. 1 shows some of the equipment used.

The demonstration experiments are presented to groups of three or four students. One lecture is conducted prior to the experiment to explain the basic characteristics and operation of the equipment and the type of data obtained. Emphasis is given to sample preparation and interpretation of results rather than to details concerning the apparatus hardware. The results obtained during the session are distributed among the students for their analyses, which are submitted later in the form of a short written report.

Part I is devoted to the principles and fundamentals of heterogeneous catalysis and related topics. Due to the diversity of the subjects treated (some of which could constitute a separate course) the scope of the treatment is limited to those aspects which are of import to catalysis.

The lecture material starts with an introduction to the solid state. It focuses on the nature of bonding in solids, structure of crystals and electronic structure of solids. The x-ray diffraction laboratory and transmission electron microscopy (TEM) laboratories are discussed and carried out concurrently with these lectures.

Following the introduction to the solid state there is an introduction to surface chemistry paralleling many of the concepts presented previously on geometrical and electronic structure of solids. Emphasis is given to electron emission and relaxation processes which are the basis of electron spectroscopy. The lecture material is demonstrated in the SEM x-ray dispersive analysis laboratory, x-ray photoelectron spectroscopy laboratory (XPS) and Auger electron spectroscopy laboratory (Scanning Auger, SAM).

Once the fundamentals of the solid-state and surfaces and the corresponding probing techniques are introduced, the more classical concepts of gas-surface interactions, such as physisorption, chemisorption and surface reactions are treated.

Experimental demonstrations of BET adsorption infrared spectroscopy and selective chemisorption of gases are presented concurrently with this material. A discussion of selected examples of catalyst preparation for laboratory testing closes Part I.

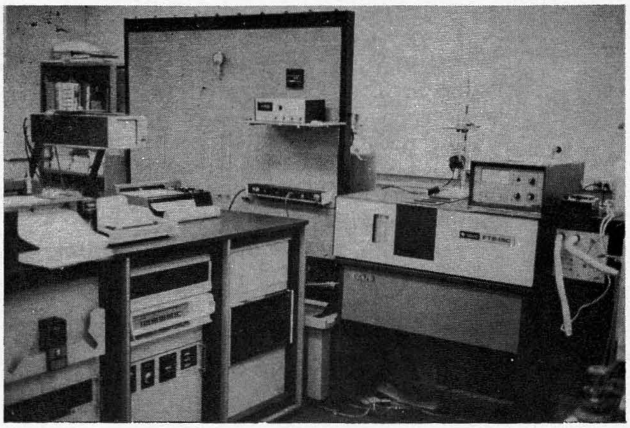

FIGURE 1. Fourier Transform Infrared Spectrometer (FTIR) in the author's laboratory, showing the data acquisition system, spectrometer and GC/IR interface.

Part II deals with the more empirical but no less significant subject of applied and industrial catalysis. Beginning with an introduction on the development and preparation of industrial catalysts, there follows a discussion of reaction engineering aspects of catalysts and catalytic reactors. Mass and heat transport limitations in catalysts pellets are analyzed in terms of observables. A short discussion of catalyst deactivation analyzes its different causes and remedies. The balance of the lecture material is devoted to a description of some of the major industrial catalytic processes grouped according to the chemical elements in-

TABLE 1

Principles, Practice and Modern Experimental Techniques in Heterogeneous Catalysts

PART I: INTRODUCTION TO THE PRINCIPLES OF HETEROGENEOUS CATALYSIS

1. Introduction
   - 1.1 Catalyst, Types and Physical Characteristics
   - 1.2 Catalysis, Catalytic Sequence, Energetics
2. Introduction to the Solid State
   - 2.1 Nature of Bonding in Solids
   - 2.3 Structure of Crystals (X-ray Diffraction Laboratory, Experiment No. 1, Section 13)
   - 2.4 Electronic Structure of Solids
   - 2.5 Imperfections in Solids (Transmission Electron Microscopy Laboratory, Experiment No. 2, Section 14)
   - 2.6 Structural Transformations in Solids
   - 2.7 Summary
3. Introduction to Surface Chemistry
   - 3.1 Structure and Description of Solid Surfaces (Low Energy Electron Diffraction (LEED) Laboratory, Section 16)
   - 3.2 Thermodynamics of Surfaces (Scanning Electron Microscopy-Energy Dispersive X-ray Analysis Laboratory, Experiment No. 3, Section 15)
   - 3.3 Emission and Relaxation Processes Involving Valence Electrons and Inner Electron Shells
   - 3.3 Principles of Electron Spectroscopy
Auger Electron Spectroscopy
X-ray Photoelectron Spectroscopy
(Scanning Auger Microprobe Laboratory, Experiment No. 4, Section 15)
Other Spectroscopic Techniques
(XPS Laboratory, Experiment No. 5, Section 15)
   - 3.4 Summary
4. Interaction of Gases with Surfaces
   - 4.1 Gas-Surface Interactions-Adsorption
   - 4.2 Physical Adsorption; Isotherms, Energetics (BET Laboratory, Experiment No. 7, Section 17)
   - 4.3 Chemisorption, Molecular Aspects, Isotherms, Heats of Chemisorption, Rates of Adsorption-Desorption
   - 4.4 The Surface Chemical Bond (Infrared Spectroscopy Laboratory, Experiment No. 6, Section 16)
   - 4.5 Kinetic of Catalytic Reactions, Site Balances
   - 4.6 Empirical Activity Patterns and Activity Correlations; Acidity, Geometric Correlations, Electronic Correlations (H_2 Chemisorption Laboratory, Experiment No. 8, Section 17)
   - 4.7 Preparation and Characterization of Catalysts for Laboratory Testing
   - 4.8 Summary (Catalytic Kinetic Laboratory, Experiment No. 9, Section 20)

PART II: INDUSTRIAL AND APPLIED CATALYSIS

5. Industrial Catalysts
   - 5.1 The Development of Industrial Catalysts and Catalytic Processes
   - 5.2 Preparation of Industrial Catalysts
   - 5.3 Mass and Heat-Transport Effects in Catalyst Design
   - 5.4 Reaction Engineering Considerations
   - 5.5 Catalyst Deactivation
   - 5.6 Summary

INDUSTRIAL CATALYTIC PROCESSES

6. Reactions of C-H
   - 6.1 Petroleum Refining-Overview
   - 6.2 Catalytic Cracking
   - 6.3 Catalytic Naphtha Reforming
   - 6.4 Hydrocracking
   - 6.5 Catalytic Alkylation
7. Reactions of C-O-H
   - 7.1 Steam Reforming
   - 7.2 Methanol Synthesis
   - 7.3 Fischer-Tropsch Synthesis
   - 7.4 Water Shift Reaction
   - 7.5 Methanation
   - 7.6 Partial Oxidation of Hydrocarbons
8. Reactions of N-H-O
   - 8.1 Ammonia Synthesis
   - 8.2 Ammonia Oxidation, Urea
   - 8.3 Acrilonitrile Production
9. Reactions of S-O, S-H
   - 9.1 S-Oxidation, Sulfuric Acid Manufacture
   - 9.2 S-Production, Claus Process
10. Complex Systems
    - 10.1 Automobile Pollution Control
    - 10.2 Coal Gasification-Liquefaction
    - 10.3 Hydroprocessing of Heavy Oils and Coal Liquids
    - 10.4 Demetallization of Heavy Oils
11. Other Catalytic Processes

PART III: MODERN EXPERIMENTAL TECHNIQUES FOR CATALYST CHARACTERIZATION

12. X-ray Diffraction
Experiment No. 1
13. Electron Microscopy
Experiment No. 2, Transmission Electron Microscopy
Experiment No. 3, SEM, X-ray Dispersive Analysis
14. Electron Spectroscopy
Experiment No. 4, Auger Electron Spectroscopy
Experiment No. 5, X-ray Photoelectron Spectroscopy
Other Spectroscopic Techniques
15. Low Energy Electron Diffraction
Introduction
16. Infrared Spectroscopy
Experiment No. 6, Fourier Transform IR, GC/IR
17. Gas Adsorption Techniques
Experiment No. 7, BET Adsorption
Experiment No. 8, H_2 Chemisorption
18. Catalytic Kinetic
Experiment No. 9, Fixed Bed, Differential and CSTCR Reactors
19. Other Experimental Techniques

volved in the main reactions (i.e., C-H, C-O, etc.). Each process is described in terms of the chemistry involved, thermodynamics, and kinetics aspects. Emphasis is given to the catalyst activity, selectivity and deactivation in relation to process operation and reaction engineering aspects. Cross reference is made to the fundamental aspects discussed in Part I whenever possible.

The typical enrollment in the course is ten to fifteen graduate students from chemical engineering and science. The material is presented in two, 75 minute lectures, and about one laboratory session per week. Grades are assigned on the basis of a written exam and a term paper. The latter consists of a written report and an oral presentation which provides stimulating discussion as well as fresh references and new ideas on specialized topics. The research papers focused on energy related catalytic processes with emphasis in fossil fuel and coal processing.

No text is available which covers all the material included in Table 1. Hence I prepared a set of notes based on more specialized books and papers dealing with specific subjects and techniques as well as information and experience accumulated in our own laboratory.

The combination of theory and experiments has a strong impact on the students, even though in some cases they do not directly operate the equipment due to its complexity and specialization. The majority of the engineering students have not been exposed to surface analysis and electron microscopy techniques, and thus feel that they acquired new knowledge in the course. The combination of principles, industrial application and experiments equips the students with a new perspective of catalysis and catalytic reaction engineering which enables them to face a larger variety of problems with a larger diversity of tools.

I enjoyed teaching the course because it provides an opportunity for interaction with colleagues from other disciplines, which enriched my own knowledge and perspective of the subject. □

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