

HETEROGENEOUS CATALYSIS

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HETEROGENEOUS catalysis is a key technology in the chemical industry, and it has produced dramatic developments, but these developments have often gone unnoticed or are little understood by the public, including people who are technically educated. For example, few university graduates know what a zeolite is, and even fewer perceive the relationship between healthy air, unleaded gasoline, and catalysts. In contrast, the public is well aware of sophisticated materials, such as superconductors, and relationships such as communications and optical fibers.

In response to employment opportunities, and closely following popular perception, the glamour of catalysis among chemistry-oriented engineering students has declined in favor of more exciting and more visible technologies. Our once-popular yearly catalysis course is now a bi-yearly course attended by about ten graduate students from engineering and chemistry. This drop in attendance prompted us to change the perspectives of the course to make it more palatable to the incoming graduate student. The new catalysis course has elements of materials processing embedded in the classical format of catalytic mechanisms and surface chemistry. This approach opens up avenues for those beginning graduate students who are interested in a general understanding of surface technology, while still preparing those students whose main research objectives are in catalysis. This approach is necessary at this university, where



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it is the only course that exposes students to surface technologies.

The course outline shown in Table 1 clearly responds to the multidisciplinary character and breadth of catalysis. The instructors must attain the proper depth into each topic, realizing that it is not trivial to find in a one-semester course the synergic combination of solid state, surface science, organic chemistry, and catalysis practice needed to initiate the student of catalysis. The students interested solely in catalysis may have ambivalent feelings about this outline since the time dedicated to topics of catalysis is reduced to allow for general topics of materials science. On the other hand, however, the broader knowledge acquired about the solid state may actually benefit their research careers.

The first seven topics contain traditional material of catalysis, and the last four topics contain elements of solid state and surface chemistry, and of materials processing such as dopant diffusion, CVD, and sol-gel technology. In practice the topics are never covered sequentially. Our practice has been to dedicate two days every week to topics one through seven, and one day every week to topics eight through eleven. Each of the topics is covered in two to five class periods.

The fifteen-week three-credit course is based on current textbooks and journal publications, as listed in the references. The graduation requirements include two literature review papers, a midterm, and a final exam. The literature review papers are of seminal importance to the preparation of the students, who grade this activity as the most valuable of the course. It lets them acquire depth in at least two topics, and it also gives them the chance to improve their writing ability. The first paper allows them to polish both their writing and their literature searching skills. Two separate drafts are read by the instructor before the

final version is graded, giving the student a chance to focus the emphasis in response to the instructor's reactions. The second paper must be on a different topic, to avoid specialization in a narrow subject area and to force the student into a new literature search. The degree of quality improvement from the first to the second paper is generally large, justifying the double paper requirement. Several students have later stated that they used the second paper, without changes, as a chapter in their theses. Some even claim to have attached the papers to their resumes to show their communication skills!

Examples of recent topics in catalysis chosen by students are listed in Table 2, which may serve as a guide to new instructors who are implementing this

course. Balance between detail and generality must be provided by the instructor, especially for the first paper, which tends to be either a collected summary of a large number of publications or an organic chemistry approach to catalysis with little insight into the catalyst itself. In this course, much of the emphasis is placed on the description of structural, surface, and electronic transformations undergone by the solid catalyst and the adsorbed reactants, to the extent of current knowledge. Papers on an instrumental technique and interpretation of data from case studies using such techniques are also accepted. Peer student evaluation of the papers is required according to the form shown in Table 3 and is enforced by including in the final exam some conceptual questions related to

TABLE 1
Course Outline

Prerequisites: Elementary steps, rate determining step, Langmuir adsorption, heterogeneous reaction kinetics, mass and heat transport in porous catalysts, physical characterization techniques: BET surface area, mercury porosimetry and densitometry, experimental techniques and reactors. (These are part of the contents of the required graduate reaction engineering course and are not duplicated in the catalysis course.)

TOPICS

1. Introduction. Heterogeneous catalysis in industry. Economic importance. Definition of catalysis. Activity, selectivity and life. Classification of catalysts. Materials science aspects of catalysis. Overview of other materials sciences and their degree of development relative to catalysis. Role of surface science in catalysis. (Refs. 1-5; 6, Ch. 1; 7, Ch.1; 8, Ch. 1; 9-11)

2. Adsorption of Gases on Solids. Ideal (Langmuir) and non-ideal adsorption on solids. Chemisorption. Application of statistical and quantum mechanics to adsorption and desorption. General results on metals and non-metals. Agreement with theory. (Refs. 6, Ch. 2; 7, Ch. 2; 12-18)

3. Selected Instrumental Analysis Techniques. Bulk analysis: x-ray diffraction, infrared spectroscopy, electron spin resonance. Surface analysis: x-ray photoelectron, Auger, secondary ion mass spectrometry. Electron microscopy. Selective chemisorption. (Refs. 6, Ch. 5; 19-28; 29, Ch. 2; 30)

4. Kinetics. Collision theory, transition state theory, and steady state approximation, applied to catalytic kinetics. Temkin's formalism for uniform and nonuniform surfaces. Examples: Ammonia synthesis kinetics. Chemical vapor deposition of SiO₂. (Refs. 7, Ch. 3 and 4; 31, Ch. 4 and 7; 32, Ch. 8)

5. Major Chemical Processes. Their chemistry and catalysts. Catalytic cracking, Reforming. Partial oxidation of hydrocarbons, Hydrotreatment and demetalation. Steam re-

forming. Hydrocarbon synthesis. Catalytic conversion of auto exhaust gases. (Refs. 33, Ch. 1 and 3-5; 6, Ch. 10; 34; 35)

6. Early Generalizations in Catalysis. Polanyi and Bronsted relations. Compensation effect. Sabatier's principle in metals and nonmetals. Geometric factor. Balandin's multiplets, Kobosev's ensembles. Electronic factor. Band theory. Valence bond theory. (Refs. 7; 12; 33, Ch. 3; 36; 37; 50; 51)

7. Modern Generalizations in Catalysis. Surface acidity. Surface compounds. The surface states. Quantum mechanical approximation methods. Metal alloying. Mono and bimetallic clusters. Structure sensitivity. Metal and non-metal support interactions. Practical examples. (Refs. 7; 12; 33; 38-41; 43; 50)

8. Solid State Chemistry. Metals. Interstitial, ionic, layer compounds. Alloys. Oxides, single and mixed. Sulfides. Semi and Superconductors. Structures, some electronic features, general crystallization techniques, and phase diagrams. Amorphous solids. (Refs. 42; 37; 44-45)

9. Sol-Gel Chemistry. General principles. Detailed application to synthesis and modification of silica, alumina, silica-alumina. Catalyst supports. High-purity fused silica materials. Applications to optical materials. Hydrothermal synthesis. Zeolites. Catalyst synthesis by impregnation or precipitation. (Refs. 46; 47)

10. Defect Structure. Reversible and irreversible defects. Defect clusters. Shear structures. Diffusion and conduction in the solid state. Coordinatively unsaturated sites. (Ref. 48)

11. Surface Structures. Relaxation and reconstruction. Adsorbate-induced reconstructions. Modification of surface electronic properties by adsorption. Catalytic promoters. Deactivation and regeneration of catalytic sites. Doping and carrier density. Dopant-induced reconstruction. Thin-film generation. CVD, vapor-phase epitaxy, molecular and ion beam epitaxy. (Refs. 29; 32; 49)

TABLE 2
Examples of Recent Review Papers

- Catalytically Promising Structures of Ternary and Quaternary Compounds
- Scheelite-Structured Catalysts
- Properties of Small Metal Clusters
- Thin Film Model Catalysts
- Immobilization of Transition-Metal Complexes
- Asymmetric Syntheses on Heterogeneous Catalysts
- Shape-Selective Catalysis
- XRD of Zeolite Materials
- Preparation of Metal Clusters in Zeolites
- Synthesis of Gasoline-Range Hydrocarbons over Zeolites
- Designing Hydrodesulfurization Catalysts
- Hydrodenitrogenation Catalysis
- Catalysis by Single Crystals of Mo Chalcogenides
- The Active Phase in Hydrodesulfurization Catalysts
- Sintering of Supported Metal Catalysts
- Catalyst Poisoning by S Compounds
- Coking of Zeolites
- Oxidative Decarboxylation Catalysts
- Nitrobenzene Hydrogenation
- Methanation Catalysis
- Benzaldehyde Hydrogenation
- Catalysts of Coal-Char Gasification
- Methanol Synthesis
- Promotion by Potassium
- Temperature-Programmed Desorption and Reaction
- Electrocatalysis
- Photocatalytic Solids
- Auger Electron Spectroscopy
- Low Energy Electron Diffraction
- Infrared Spectroscopy of Adsorbates
- X-Ray Photoelectron Spectroscopy

the papers written by the class. Students become implacable judges of a classmate's writing when they must answer questions on it in a final exam.

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TABLE 3
Manuscript Evaluation Form

Title: _____ Author: _____

Assign a grade on a scale of 0 to 25 in each of the following four categories, and briefly explain your grading criteria in the space provided.

Points

1. Scientific Relevance. Author Understanding of the Topic. Does the author express clearly the importance of the topic? Could another aspect of it have been more important? Does the author understand the topic?
(Space)

2. Depth of Treatment. Was a reasonable amount of work put into the paper? Is the paper unclear because not enough, or too much, information was considered?
(Space)

3. Bibliography. Is the number of reference articles enough to treat the topic in sufficient detail? Are the references current?
(Space)

4. Style. Are the objectives, body of the paper, and conclusions clearly exposed? Is the paper easy to read? Is the paper sufficiently divided into sections? Is each section completely developed before the next section? Is the grammar or spelling poor? Is the writing succinct?
(Space)

Total Points: _____ /100

Confidential: Reviewer's Signature _____

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EXPERIMENTAL ERROR

Continued from page 94.

the complexity of the experiment by one dimension.

Next, it is evident that because of the variability in the gas absorption experiments, a single laboratory session generates too few data for a meaningful error

analysis. One way out of this difficulty is to pool the data obtained in several sessions before allowing the various student groups to analyze it. Also, they should attempt to get the largest range of L possible with the equipment and concentrate on replication. At each session, a student group will carry out duplicate experiments, for example, at just three values of L: highest, lowest, and at the mid-point to permit a test of the linearity of the correlation. After three or four groups have completed their experiments, the data can be pooled and analyzed. Students who have taken statistics courses that teach experimental design might wish to plan a single factorial experiment to include several student groups. In any event, the between-group variation can be analyzed to see if this is a contributing factor to the error.

3) Students should be encouraged to go directly to the original literature data and examine the actual measurements without citing a correlation for the least-squares fit of the data or some other deterministic model. They should be asked to note the scatter in the data through a variance or coefficient of variation or some other measure of variability.

4) Because our educational system pays high rewards for explaining phenomena, there is a great temptation for students to try to explain "everything." Without the restraint learned from error analysis, some students will try to explain random error, given the opportunity, and of course, the opportunity seems very tempting when the data are so few that the scatter is not obvious. Thus, the notion of caution and even of reluctance to explain can be one of the important by-products of error analysis.

CONCLUSIONS

While we do pay lip service to teaching mathematical statistics, its use in experimental design is often neglected. Therefore, student engineers, faced with experiments with large variability in the measurements, do not understand experimental error. They tend either to despair or to explain too much. Statistical analysis of error plus good experimental design can help students account for error and become informed about the relationship between theory and practice.

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