MOLECULAR LEVEL MEASUREMENTS IN CHEMICAL ENGINEERING

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For quality control of a complex polymerization, or tracing the cause of poor paint adhesion, or understanding substandard performance of a catalyst batch, and for a host of other challenges, practicing chemical engineers may well find the greatest benefit by using a molecular level approach to the problem. While it is likely that the engineer will have to call on an expert to bring the full power of a given technique to bear on a given problem, it is important that he or she be sufficiently aware of the molecular-level tools available to begin asking the right questions.

At Purdue, an elective course, called "Molecular Level Measurements in Chemical Engineering," for juniors, seniors, and graduate students, was designed to fill this need by sensitizing students to a variety of microscopic and spectroscopic characterization tools. Most students who graduate with a BS degree in chemical engineering have had only limited exposure to the characterization tools that will be available to them as professionals in industry or academia. Undergraduate engineering laboratory courses tend to focus on traditional chemical engineering equipment, and when chemistry laboratory courses use modern spectroscopic methods, they rarely make a connection to an engineering context. In our course, a brief discussion of the basic theory, instrument design, and sample requirements establishes the basic physics of the particular technique and the type of information it can give. Applications drawn from the literature illustrate the utility of the method in addressing engineering problems.

COURSE PHILOSOPHY

The course grew out of a conviction that chemical engineers can best extend their technical longevity through an understanding of the molecular basis of the properties and behavior of engineering materials and processes. To use this understanding, one must be able to make measurements on the molecular level.

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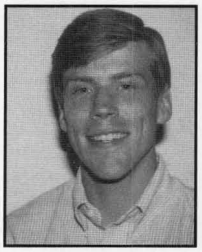

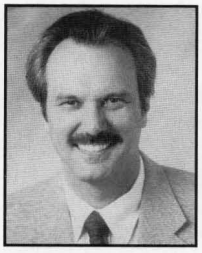

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The primary objective of the course is to introduce students to various tools that will extend their ability to solve problems. It is important to note that we stress that the course only *introduces* the various techniques and is not meant to make the students experts in a particular field. We have chosen breadth over depth to give students a wide scope of applications, but we try to include sufficient detail of some techniques to foster an appreciation of the care it takes to get the most information available.

The first of two secondary objectives of the course is the effective reading of technical papers. Our reliance on primary source material gives us an opportunity to emphasize critical evaluation of journal articles. Problem sets designed around current articles ask students to challenge and justify statements they read, to derive equations and discuss assumptions in the paper, and to consider what new or corroborating evidence might be obtained from alternative experimental approaches. For some students, these exercises provide the first recognition of the fallibility of the printed word and are, thus,

important steps in learning the winnowing process that is central to self-education.

Finally, we have incorporated laboratory exercises into the course that will at least *introduce* students to the hardware associated with advanced instrumentation. Each class day spent on an instrument limits the breadth of topics the course can cover, but the students confirm that *talking* about an experiment does not have the same impact as *doing* it. This past spring we included three lab periods to cover X-ray photoelectron spectroscopy, electron microscopy, and infrared and nuclear magnetic resonance spectroscopies.

COURSE DESCRIPTION

Table 1 gives the course outline. It begins with a brief overview of the techniques that will be covered in the class. Starting with the Propst diagram (see Figure 1) and the energy spectrum, we discuss the different ways of perturbing a sample with fields, photons, ions, neutrals, and electrons, and point out the types of information one might hope to learn.[1] Emphasis on applications shows where the course is heading and is intended to justify the need for the two-week review of background material that follows. Discussion of deBroglie's equation, the uncertainty principle, and Schrödinger's equation, together with derivations for a particle in a box and simple harmonic motion, and review of atomic and molecular orbital theory as well as some simple symmetry concepts provide the foundation on which all the molecular level techniques rest.

We begin quantitative surface analysis with a detailed discussion of X-ray photoelectron spectroscopy

TABLE 1
Outline of Major Topics

1. Introduction and Background (2 weeks)
- Propst Diagram
- Classical and quantum mechanics
- Symmetry

2. Quantitative Surface Analysis (4 weeks)
- X-ray photoelectron spectroscopy (XPS)
- Ion scattering spectrometry (ISS)
- Secondary ion mass spectrometry (SIMS)

3. Bulk and Surface Structural Analysis (4 weeks)
- Diffraction (XRD, LEED)
- Electron microscopy (TEM, SEM, AEM)
- Scanning probe microscopies (STM, SFM)

4. Chemical Characterization (4 weeks)
- Infrared spectroscopy (IR)
- Raman spectroscopy
- Nuclear magnetic resonance spectroscopy (NMR)
- Mass spectrometry (MS)

5. Case Studies (1 week)

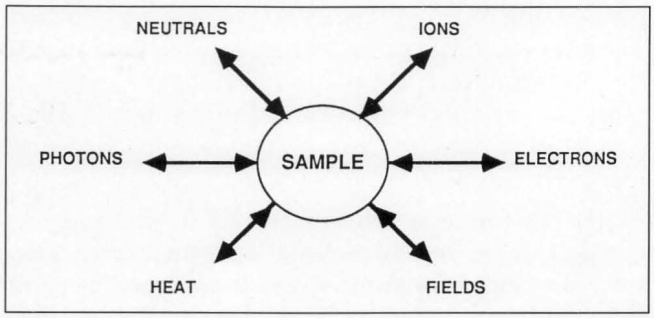

Figure 1. *The Propst Diagram. Arrows pointed inward represent various probes used to perturb the sample. Different responses to perturbation, indicated by the outgoing arrows, provide information about the sample.*

(XPS), including important features such as surface sensitivity, elemental and chemical state analysis, and quantitative capabilities. Detailed lectures focus on spectral interpretation by analysis of peak position, area, shape, and splitting.

In order to illustrate the potential of XPS, we spend several lectures discussing spectra from papers in the literature. One example of XPS analysis of the interactions between metal and metal oxide films shows students that surface properties are often much different from bulk properties, and that these differences directly affect the quality of the finished product.[2] These discussions are often the first time students are asked to extract information from spectra. Not surprisingly, they are initially reluctant to volunteer opinions, but we find that giving them the papers in advance and providing them with a few key questions to consider stimulates discussion.

After a relatively detailed presentation of XPS, we study Auger electron spectroscopy (AES), ion scattering spectroscopy (ISS), and secondary ion mass spectrometry (SIMS). Because much of the instrumentation and principles of XPS also apply to this next group of techniques, we move quickly through this part of the course to focus on applications of these tools.

The next section is on examination of bulk and surface structure by diffraction and microscopy. We begin this part of the course with a discussion of crystal structure and X-ray diffraction (XRD), electron diffraction, and low energy electron diffraction (LEED). Lectures are designed to compare and contrast the instrumentation as well as the information provided by each technique.

Scanning and transmission electron microscopies are introduced next. One class period is a laboratory demonstration of the potential of SEM and TEM for studying biological and structural materials. Before the laboratory session, we devote a lecture to

contrasting the two types of microscopes and explaining the differences in resolving power, instrument design, and sample requirements. Analytical tools such as energy dispersive X-ray analysis (EDX) and electron energy loss spectroscopy (EELS) are also introduced.

The last topic is scanning probe techniques, including scanning tunneling and scanning force microscopies. The students read a paper by Hoffman which reviews many of the scanning probe microscopies and applies them to characterization of carbon fiber materials.[3] In one problem set, students are asked to compare the types of information obtained by STM/SFM on carbon fibers with the information learned from SEM and TEM, and to explain the advantages and disadvantages of each technique.

The last group of techniques we discuss includes mass spectrometry and infrared, Raman, and nuclear magnetic resonance spectroscopies, and focuses on chemical characterization. At this point in the course, students have become familiar with the pattern of the presentation and can apply many of the concepts they learned earlier to this last set of tools. Thus, introducing each technique requires less time and we are able to shift the lecture content to more complex problems requiring multi-technique approaches. FTIR and solid-state NMR exercises examine different polymer systems and demonstrate the powerful analytical capabilities of these two instruments.

With one week of classes left in the semester at this point, we introduce a case study that involves trouble-shooting a process restart. The problem statement, (developed for us from plant experience by Dr. George Swan, Exxon Research and Development, Baton Rouge, Louisiana) includes a description of the reforming process and the catalyst changeover procedure, along with a flow sheet. Gas chromatographic analysis of the product stream and discussion of some of the attempts to find the cause of the low octane rating are also presented and are read by the students before the class discussion. In class, the students seek the solution by suggesting causes and analyzing consequences. When they suggest that new data be gathered, the wisdom of such a move is analyzed for its utility, cost, and time required. The instructor's role is to keep the students on track with a minimum of direction and to supply additional data if it is asked for and available. The twist in this problem is that the chromatography data are incomplete. Mass spectrometry is needed to discover a heat-exchanger leak that allows some of the feed to bypass the reactor. Even though this problem is relatively simple from an instrumentation point of view, the thought processes stimulated by the discussion are valuable for the students. We hope to develop additional case studies using real plant situations as the course evolves.

COURSE REQUIREMENTS

The course work includes three exams, a term paper, and ten problem sets. Exams focus on applying the principles learned. For example, one question on the first exam asks students to formulate a series of experiments to differentiate between three proposed reaction mechanisms, given a laboratory equipped with an XPS, ISS, SIMS, and a full range of isotopes. Other types of questions ask students to interpret spectra or to draw and label a schematic of an instrument.

The objective of the term paper is to get students to go into more depth for a particular technique. We give students the option to discuss a specific molecular measurement application of a technique introduced in class, or to discuss a new technique. They must submit paragraphs (which include three references from the literature) presenting their topics a month before the paper due-date so we can make suggestions and be assured they have started the assignment. Students normally choose topics that are too broad in scope and they need help focusing their ideas. A sampling of term-paper topics is given in Table 2.

Finally, we use problem sets to follow students' progress and to demonstrate application of techniques to engineering problems. We find that students respond most favorably to recent articles because they recognize the importance of these techniques in solving existing problems. In one problem set we ask students to read a recent paper, "High-Temperature in Situ Magic Angle Spinning NMR Studies of Chemical Reactions on Catalysts."[4] Although we do not expect the students to grasp all the details of solid-state NMR, we find they can understand how the

TABLE 2
Sample Term Paper Projects

- Positron emission tomography
- Scanning thermal microscopy
- Using TEM to determine inhomogeneity of highly cross-linked polymers
- Solid state NMR investigation of polymer morphology by multiple pulse spin diffusion experiments
- Chain branching studies of polymers using ^{13}C NMR
- X-ray diffraction for measuring residual stress in materials

technique is applied and what is learned, and they can also answer questions about sample preparation and suggest additional measurements which support the authors' overall conclusions.

We find it helpful, after handing back graded problem sets, to review questions which the students find difficult. These discussions, in addition to explaining the specific problem, generate additional questions. Oftentimes a student can be guided to answer his or her own question, and in many cases, help also comes from fellow classmates. Although these lectures break from the traditional lecture format, they are valuable for both the students and the instructor because they foster a more relaxed environment for learning, encourage questions, and give a measure of the students' understanding of the material.

RESOURCE MATERIALS

Because of the number of tools we cover and the broad nature of the material, we do not use one specific textbook. Instead, we use a compilation of review articles, book chapters, and papers in the literature. A chapter, "Catalytic Surfaces and Catalyst Characterization Methods," in *Chemical Industries Series*[5] serves to introduce many of the topics we cover. Since it focuses on catalytic systems, we use lectures and problem sets to challenge students to apply the techniques to other fields, including composites, polymers, and semiconductors. Papers in the literature are an excellent resource because they can be chosen to demonstrate a particular principle and to tailor the course to the interests of the students. The list of papers used (see Table 3) shows a balance of classics and the newest applications.

TABLE 3
Additional References Used

Books

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Finally, we recommend the students dust off their physical chemistry books when we review the background material at the beginning of the semester.

ON TEACHING TEACHERS

We would be remiss in closing this presentation without commenting on the special circumstances that brought Randy Smiley into this educational partnership. Essentially all chemical engineering lectures are given by faculty at Purdue, but we were encouraged to try this experiment through a Du Pont Fellowship granted to Randy. The success of the experiment is probably best illustrated by his own words:

> *I feel fortunate to have had the opportunity to teach a course during my graduate studies at Purdue. I was amazed at how markedly my lecture preparation and teaching style changed as the semester progressed. I became more efficient in preparing for lectures and much more relaxed in front of the students, which gave me confidence and made the students more responsive in class. The classes in which we discussed journal articles were clearly the most unpredictable and the most fun to teach. I also enjoyed developing the laboratory exercises used in the course. The period we spent at the Electron Microscopy Center gave students a view of the complexities of the equipment and sample preparation which would have been impossible to achieve in a classroom.*
>
> *Professor Delgass came to class during the first few weeks of the semester and gave me immediate feedback on my teaching style. In addition, we typically met once a week to discuss the class progress. Initially, this time was spent discussing course content, but later in the semester we talked about the other responsibilities facing a professor, including starting up a research group and writing proposals. In addition to my discussions with Professor Delgass, I found the book* Teaching Engineering[6] *helpful. It has hints about teaching skills, and discussions about tests, homework, and grading that are insightful. Overall, teaching in this supportive environment was a rewarding experience which I strongly recommend to any student who has any desire to pursue a career in academia.*

SUMMARY AND CONCLUSIONS

Understanding what tools are available and the type of information each technique gives is critical for engineers to be successful problem solvers. This course gives students the foundation of many characterization tools that will be available to them and should help bring a molecular point of view to their problem-solving skills. Exam questions and problem sets are designed to expose students to the practical potential of these tools and to hone their ability to critically evaluate the technical literature. Laboratory exercises familiarize students with instrumentation and sample requirements and demonstrate the principles taught during the lectures. Finally, case studies show students how techniques are applied directly to problems facing practicing engineers.

ACKNOWLEDGMENTS

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REVIEW: Elements of CRE

Continued from page 161.

- *Basic definitions (and the necessary un-definition that rate must not be defined as dC/dt, despite what students have usually learned in physical chemistry courses)*
- *Power-law and Langmuir-Hinshelwood-Hougan-Watson kinetics*
- *Design of ideal reactors, both isothermal and nonisothermal*
- *Using data to obtain rate expressions*
- *Product selectivity*
- *Mass transport in reaction engineering, including porous solids, slurry reactors, and mixing in nonideal flows*

Parallel to the technical exposition are difficulty-ranked problem sets and "Thoughts on Problem Solving" that are several-page end-segments of twelve chapters which discuss such formal approaches to problems as Kepner-Tregoe situation analysis.

The most striking additions woven into this edition are 1) treatments of chemical vapor deposition, biotechnology, and polymerization, and 2) emphasis on using packages for solving differential equations.

The first addition serves the obvious purpose of introducing these areas into the core curriculum, but even more subtly it also teaches how these "emerging technologies" are treatable by the classical techniques of reaction engineering. For example, I find the best way to introduce development of catalytic rate expression for heterogeneous catalysis is to