Teaching Materials that Matter: An Interactive, Multi-media Module on Zeolites in General Chemistry

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Abstract: This paper describes a two-week teaching module, based on the structure, properties, and applications of zeolites, that was taught in a general chemistry course. We chose to focus this module on zeolite science because of the beauty and versatility of zeolites as well as their many existing and potential uses in the chemical industry. The curriculum was centered around an interactive educational computer program about zeolites that we developed specifically for the module, entitled "Zeolite Explorer." The module also involved class lectures by faculty, a guest lecture from an industry leader, homework problems, handouts, overheads, and demonstrations. The class outline, lecture notes, handouts, overheads, homework, and "Zeolite Explorer" software are included with this article. We believe that this interactive, multimedia approach to teaching zeolite science generated more student interest in chemistry and learning an extremely important subject.

Introduction

Students often perceive general chemistry to be a list of obtuse principles to memorize, and which hold no importance outside the classroom. Too infrequently does this class offer students a clear picture of what real chemists do, what the science of chemistry is, or how it relates to everyday life [1-3]. In an attempt to engage students in the process of learning and to make their chemistry studies relevant to the world they inhabit, we developed a two-week module based on the structure, properties, and applications of zeolites [4-6]. We taught this module in the lecture portion of the course, toward the end of the 1997-1998 academic year. We felt that at that point the students had sufficient grounding in general chemistry. Our hope was that this module would simultaneously teach new material to the students and tie together chemical principles learned earlier in the semester. The subject of zeolite science is ideal for this purpose because of the beauty and versatility of zeolites as well as their many existing and potential uses in the chemical industry.

We developed an interactive, multimedia curriculum that illustrates chemical principles with a set of concrete and meaningful examples, connecting chemistry on the molecular level with important phenomena on the macroscopic scale. The curriculum was based on an interactive educational computer program about zeolites, called the "Zeolite Explorer," which we wrote specifically for the module. The curriculum also involved class lectures by faculty, a guest lecture from an industry leader, homework sets, handouts, overheads, and demonstrations, all geared toward generating more student interest in chemistry and a greater degree of student involvement in the act of learning [4, 7–10].

In the remainder of this article, we introduce the field of zeolite science, discuss the contents of the module, and describe the use of our novel software, "Zeolite Explorer."

Zeolites. Zeolite is a Greek word that means "boiling stone," because naturally occurring zeolites are minerals that absorb water that subsequently boils when heated. Zeolites are microporous, crystalline aluminosilicates consisting of three components: framework tetrahedra, cations, and adsorbed molecules. Depending upon the framework and cations, the adsorbed phase feels a local electrostatic environment ranging from nonpolar to extremely polar. Three important zeolite framework topologies are shown in Figures 1-3.

The technological importance of these materials cannot be overstated. For example, it is estimated that the monetary value of zeolitic catalysis to petroleum cracking over the past several decades is in excess of 100 billion dollars [11]. Zeolites are also used as molecular sieves for separating chemical mixtures, as ion exchangers and filters, as environmentally safe detergents, as desiccants for new coolant systems, and as hydrocarbon traps for new cold-start catalytic converters. Mesoporous sieves show promise for separating biomolecules and may be useful for making optical electronic materials with substantial quantum confinement.

The utility of zeolites arises from the number of distinct zeolite framework structures (over 100), and the fact that different materials with the same framework structure can exhibit widely different chemical properties. Zeolites thus provide a remarkably comprehensive platform for teaching the ideas and practices of chemistry.

Summary of the Module

A summary of the content of the zeolite module is given in the outline below:

I. Silicate bonding and structure

A. Lattice structures, unit cells, silicate structure including Si-O bonding, tetrahedral geometry, and effect of the oxygen-to-silicon ratio on oxygen atom bridging and structural complexity.

B. Zeolite structure including definitions of pore sizes, review of zeolite web sites. Building of various zeolite structures by different combinations of basic sodalite cages. Exploration of cage and channel zeolite structures. II. Modification of siliceous zeolite structures

A. Isomorphic substitution of Al for Si and introduction of charge into zeolite structures. Arrangement of charge compensating ions.

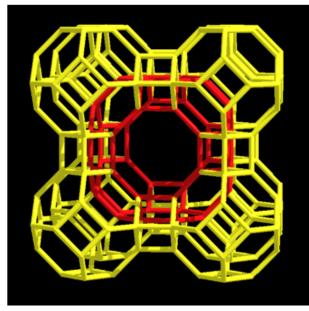


Figure 1. Zeolite structure type LTA (example: Zeolite A).

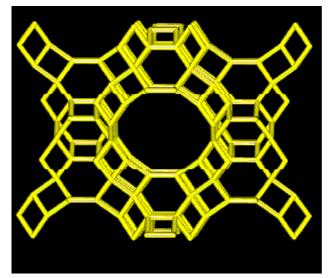


Figure 2. Zeolite structure type FAU (example: Zeolite Y).

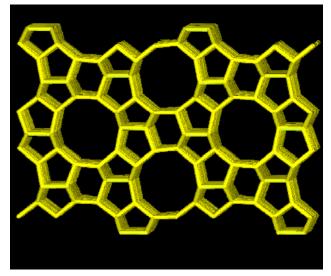


Figure 3. Zeolite structure type MFI (example: Zeolite ZSM-5).

III. Uses of zeolites

A. Industry executive guest lecturer to explain societal and economic importance of zeolites. Cost/benefit analysis of zeolite use in petroleum refining.

B. Student development of potential uses of zeolite microporosity and charge. Comparison of student-generated list with actual industrial uses.

C. Application of zeolite microporosity and charge in industrial synthesis of *p*-xylene. Relation to use of catalytic acid sites, steric constraints, and LeChatelier's principle.

Description of the Module

The instructor based his lessons on an outline presented to the students at the beginning of the module. Lectures involved the use of the blackboard, overheads, in-class student activities, handouts, and the zeolite software [10]. Some of the information in the software was not addressed in the classroom, but was left for students to discover on their own outside of class or in relation to a homework problem. Homework assignments were created to highlight the most important parts of the lessons and also to apply these new ideas to different situations. The questions required students to think through and reapply the principles they had learned earlier in the course, instead of just reiterating facts. For example, one of the questions read, "Predict which zeolite will have the greatest affinity for water: a zeolite with five Na⁺ ions per cage, one with five K^+ ions per cage, one with five Mg^{2+} ions per cage, or one with five Ca^{2+} ions per cage." The answer to this question was never stated in class or in the software, but was based on the underlying principles learned in class. The students were expected to infer a relationship that they could apply to this new example. In this way, the homework problems continue the interactive method of learning used in the classroom and in the software.

While the class module was centered on the software, other educational aides were developed to support the topic. In our teaching of zeolites, we provided students with a condensed outline of the material to be discussed and another outline upon which they could take notes. The note outline was designed, in part, in an effort to educate students about how to take and organize class notes during highly interactive class activities. One potential problem in general chemistry courses is that the students are new to college and many have not yet been taught the tools that will help them succeed in collegelevel courses, which are increasingly being taught using nontraditional methods. In this case, students spent a significant amount of class time discussing possible answers to questions generated by the instructor. They were asked to discover and predict properties of these materials, not simply to understand them. As such, the note outline provides headings under which students can write in their own notes, indicating to them that note-taking itself is necessary and also helping students to organize the large amount of descriptive material. Furthermore, the outline structure helps students prioritize the importance of different information, a task that can be difficult for first-year college students [12].

The lectures and software were synchronized throughout the module so that sometimes one enhanced the other, while at other times the lectures responded to student concerns outside the scope of the software. In general, however, the module was organized as follows. First, the structures of silicates,

Table 1. Zeolite Uses Suggested by Students

66	2
Applications: zeolite	Applications: zeolite charge
microporosity	
Storage of molecules	Water softening: removal of lead,
	salt, ions from water
Orienting molecules for a reaction	To hold a molecule in place for a reaction
Use of the pore size for size and	To ionize a substance
shape selectivity of reaction products and transition states	Desiccants and drying agents
Size separation of molecules	Increase density of adsorbed
	gases
Reation catalyst	To separate charged and
	uncharged molecules
	Redox Chemistry
	Acid–Based chemistry

aluminosilicates, and zeolites were analyzed at the molecular level in terms of structural building units; then, we discussed how these molecular structures determine the macroscopic properties of materials such as quartz and clay. The basics of lattice structure and unit cells were reviewed. Silicon-oxygen bonding structures were discussed, including the tetrahedral nature of the oxygen-silicon-oxygen bond angle. Lastly, the effect of the oxygen-to-silicon ratio on the structure of silicate networks was explored. Students learned that as the oxygen-tosilicon ratio decreases from four to two, the percentage of bridging oxygen atoms between silicon atoms increases and the silicate becomes more interlocked. The software was used to illustrate different silicate bonding patterns and zeolite structures and to show how the structure of a silicate changed when the ratio of its composite elements changed. In addition, the software was used to familiarize students with different molecular modeling representations such as stick, ball-andstick, space-filling, and tetrahedral connectivity.

Zeolites were defined and their special properties were briefly discussed. IUPAC definitions of microporous (pore size < 20 Å), mesoporous (20 Å < pore size < 500 Å) and macroporous (pore size > 500 Å) materials were given, and a web site containing the structures of all known zeolites was discussed (http://www.iza.ethz.ch/IZA). The primary, secondary, tertiary, and quaternary structural building units (SBUs) of zeolites were explored with the focus on relating the pore size and cage/channel structure of the zeolite with its quaternary structure.

The second section of the module proceeded with a more complicated analysis of the structures of zeolites. It then discussed the physical properties of zeolites based on their chemical structures. At this point student participation was required to analyze periodic trends, explaining why aluminosilicates are prevalent while other hypothetical silicates are not. The primary goal of this section was to help students learn to think like chemists; to look at physical data on the macroscopic scale and relate it to the chemical principles operating on the molecular level. This focused on comparing pure SiO₂ zeolites with aluminosilicates, in which the isomorphic substitution of aluminum introduces a negative charge into the zeolite framework. Periodic trends were invoked to explain why aluminum isomorphically substitutes silicon in zeolite structures. We addressed the arrangement and placement of charge compensating cations in aluminosilicate zeolites and examined how Coulomb's law controls these

structures. We further explored the consequences of this charge in regards to the hydrophilicity and physical properties of zeolites. As the silicon-to-aluminum ratio decreases, the number of water molecules absorbed by the zeolite, its hydrophilicity increases. For instance, although mica and talc are both clays, mica is hard and talc is soft. Why is that? The softness of talc, a neutral clay, is explained by the relatively weak intermolecular forces that hold it together in comparison with the strong ionic forces holding mica together, which create mica's hardness. Why are aluminosilicates much more hydrophilic than their silicate counterparts? The introduction of charged sites into the zeolite structure leads to strong iondipole forces between those sites and water molecules. Following student predictions of behavior, the software was useful in illustrating the effect on hydrophilicity of changes in the silicon-to-aluminum ratio, in visualizing the difference between two different clay molecular structures, and for seeing how changes in temperature and changes in the ionic strength of the zeolite affect the thermal motion of the molecules inside the zeolite. After the relationship between molecular structure and physical properties had been explored, the instructor could talk about the use of zeolites as desiccants, once more relating chemical principles to real-world situations, thus, creating a broader context and meaning for the classroom learning.

After the class was introduced to the structure of zeolites, a guest lecturer, the recently retired Vice Chairman and Chief Operating Officer for Witco Corporation, discussed with the students the economic relevance of zeolites. He spoke about the zeolite market, its producers, and some of the industrial uses of zeolites. He also performed a cost-benefit analysis of the use of zeolites in the fluid catalytic-cracking petroleum-refining industry, concluding that that in a typical refinery zeolites increased the net profit by more than \$300,000 per day.

By inviting a speaker from industry, the students were exposed to chemistry outside of the classroom that was based on the principles they were currently studying [13]. Based on an informal student survey, this connection did in fact increase student interest in the material and help bring it to life. This interest manifested itself in the next lecture when students were given the task of imagining how the charge and microporosity properties of zeolites could be used in other chemical processes.

The uses proposed by the students are listed in Table 1.

The final section of the zeolite module provided an example of how zeolites are used in the real world; this section both pulled together and built on the knowledge the students had already gained about zeolite structure and charge. Using the production of *p*-xylene as an example, a reaction important to the polyester industry, the software illustrates steric effects in shape-selective isomerization, the acid-base chemistry active in this process, and LeChatelier's principle as it affects the production of the desired isomer. The lecture focusing on these topics expanded on details and reaction mechanisms as necessary. As before, the students learned new material about the acid-base reaction occurring in the isomerization process and about the steric effects of a zeolite in a host-guest interaction, while still applying familiar concepts, such as equilibrium, to this new topic. All of the material was presented in the context of a chemical process relevant to our society, giving students one more example of what chemists do outside of the classroom or class-based laboratory. In taking chemistry out of the classroom, our hope is to interest more students in the discipline, in the general chemistry course itself, and to provide an engaging context for the principles they are learning.

Description of the Software

The software was designed with text, pictures, interactive exercises, and animated sequences to explain and illustrate the principles of zeolite structure and chemistry. Many of the static and dynamic images of zeolites were created using visualization software generously provided by Molecular Simulations, Inc [14]. In class, particular screens in the program could be shown to the students to illustrate zeolite chemistry on the molecular level or to stimulate class discussion. Instead of just dictating chemical relationships to students, an instructor can use this software to create an interactive learning environment where students are engaged in the process of thinking about the chemical principles at work [15–17].

The software, "Zeolite Explorer," is divided into three sections: "Structure," "Charge," and "Application." The first screens of the "Structure" section explain and illustrate the basic bonding rules of silicates and examine the effect of changing the oxygen-to-silicon ratio on the structure of the silicate. The text on the first screen explains why silicon atoms bond in a tetrahedral pattern with oxygen atoms. The next screen provides an interactive exercise where students can change the oxygen-to-silicon ratio of a silicate, with the program displaying the corresponding silicate bonding structure. The pictures show silicate rings, chains, sheets, and three-dimensional networks, all made of the same atoms, the structures distinguished only by their oxygen-to silicon ratio.

The second component of the "Structure" section examines the zeolites formed by silicate bonding. Text and pictures teach students that zeolites are crystalline inorganic solids with three-dimensional structures that contain a spacious cavity or channel, the shape of which changes depending on the particular zeolite. The next screens explore the construction of zeolites via attachment of structural building units. There is one series of animations that illustrates the construction of three distinct zeolites from one in the same tertiary building unit, the sodalite cage. These animations highlight three ways by which sodalite cages can bond, forming three different zeolites. The three-dimensional animations allow the viewer to visualize the distinct shapes and cavities of these zeolites, all formed from the same tertiary building unit, only with different connectivities. This visualization is an exciting educational tool that is not available in textbooks and that gives students a much deeper understanding of the structure, formation, and properties of zeolites. Another animation allows students to view several zeolites from different sides, with or without perspective, and using different model representations, enhancing their understanding of the difference between cage-type and channel-type zeolites. These animations help the students' visual perception of these complex structures.

The last component of the "Structure" section provides text about and pictures of the structure of clay, linking the previous chemistry to a real-world application. A molecular representation of the familiar clay talc illustrates layers of the previously discussed silicate structures combined into a new compound. The text here also explains how the layered structure of clays is beginning to make them very useful in the production of advanced, nanocomposite plastics, because clays can be "exfoliated" into melted plastic, hence increasing the rigidity of the plastic while keeping it lightweight.

In the second section of the software, "Charge," each screen continues the use of the subject of zeolites to investigate general chemistry topics. First, aluminosilicate zeolites are introduced, and students learn how the replacement of a silicon atom by aluminum adds a negative charge to the zeolite. The text reviews the principles of formal charge and Coulomb's law and explains that cations exist within certain zeolites to offset the negative charge brought in by the aluminum atoms. This screen also explains that the mobility of these cations in wet zeolites accounts for the ion-exchange properties of some aluminosilicate zeolites. Another interactive screen allows students to change the silicon-toaluminum ratio of the zeolite to observe the resulting changes in the number and placement of cations.

Next, a screen on aluminosilicate clays explains how the introduction of aluminum, and thus a site of negative charge, into the silicate layers affects the structure of the clay. This screen illustrates mica and compares its properties to that of talc, referring to the relative ionicity of the materials as reasons for each clay's relative hardness or softness. Also, hydrophilic and hydrophobic properties are introduced using the two clays as examples to connect a chemical property such as ionic strength, to a physical property such as hydrophilicity. This screen refers to and builds on the previous screen on silicate clays, methodically broadening the students' body of knowledge.

The next two components of the "Charge" section continue to explore how the negative charge in aluminosilicates gives those zeolites an affinity for water. The screens illustrate and explain the connection between the number of aluminum atoms and the hydrophilicity of a zeolite. One screen lets the student change the silicon-to-aluminum ratio and illustrates the relative number of water molecules absorbed at each ratio. The text explains how zeolites can thus be used as drying agents, emphasizing the importance of the principles of general chemistry outside the classroom.

In the last screens of this section, the thermal motion of zeolites is described and then explored in relation to the charge of aluminosilicates. Questions in the text challenge the student to apply the general principles they have previously learned about thermal motion to zeolites in particular. After the questions have been posed, animations on the next screen illustrate the thermal motion of benzene in a siliceous zeolite at three different temperatures and show the motion of benzene in an aluminosilicate zeolite. These movies clearly portray the effects of temperature and charge on the thermal motion of zeolites and molecules adsorbed therein, possibly confirming the relationships that the student has already thought through on her own.

The final section of the software, "Application," provides an example of how zeolites are used in the real world and builds on the knowledge the student has already gained about zeolite structure and charge. The first screen outlines the process by which *o*-xylene and *m*-xylene are isomerized to *p*-xylene, the raw material required for the production of polyesters. This and the following two screens depict how the shape of the particular zeolite used in this process controls the product

formed. The steric effect of the zeolite is described in the text and then further demonstrated by pictures of the three isomers of xylene within a channel zeolite, ZSM-5. These images provide a molecular explanation for shape selectivity that can be exploited on the macroscopic scale.

Two more screens apply the concepts of acid-base chemistry to zeolite activity. The text of the first screen explains that if an acidic zeolite is used, an acid-base reaction can occur between the zeolite and toluene (a reactant in this process) to produce the necessary intermediate for the production of p-xylene. Animated molecular graphics illustrate the reaction steps that generate the intermediate and explain the importance of the acidic nature of the zeolite in this process.

In the last screen, Le Chatelier's principle is applied to the whole process of the production of *p*-xylene, giving students the opportunity to apply chemical equilibria to a new situation, one that is economically and socially relevant. The molecular graphics shown here show that as *p*-xylene, produced by the acid-base reaction with an H^{+} donated by the zeolite and separated from the ortho and meta isomers by the shape of the zeolite, leaves the zeolite rapidly because of its streamlined shape, the isomeric equilibrium within the zeolite channel shifts. As a result, more ortho and meta forms will isomerize to *p*-xylene to re-establish the equilibrium to satisfy LeChatelier's principle. Thus, this last section of the software creates a context for all of the chemical principles learned earlier in the module and provides an example of how the concepts of general chemistry are applied outside the classroom, in industry, where many of our chemistry students may eventually be employed.

Conclusion

In this paper we have presented a detailed account of a twoweek module introducing students in general chemistry to an active area of solid-state materials-science research. The module made use of a variety of teaching techniques, including the traditional blackboard, sophisticated computer programs, and guest speakers from the commercial sector. It also made use of student-active learning techniques where the class is responsible for driving portions of the module context. It was our intent to show students, by way of a specific example, how the concepts learned in a traditional general chemistry course can relate to current chemical research and to advancing societal needs. The topic of zeolites served well in this role and also proved to have a surprising advantage in that the students were completely unaware of their existence prior to this introduction. This, we hope, helps alleviate a growing problem in the general chemistry curriculum: the students believe they have seen it all before.

Our goal in writing this account is to have other faculty make use of the materials, either as they are or following their own specific modifications. We include as ancillary materials all the materials related to the module including the "Zeolite Explorer" software, PDF files of lecture notes, student notetaking forms, overhead transparencies, and homework assignments and answers.

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