Chem. Educator **2002,** *7,* 33–36

First-Year Undergraduate Laboratory Experiments with Zeolites

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Received October 29, 2001. Accepted November 30, 2001

Abstract: The synthesis of Zeolite A or Linde Type A zeolite is described as an undergraduate laboratory geared for the first-year student in general chemistry. The procedure describes the synthesis, isolation, and various qualitative and quantitative characterization methods related to the material's water-softening ability.

Introduction

Zeolites are of considerable commercial importance in applications ranging from water softening to catalysis in the petrochemicals industry. In recent years, they have also become popular materials to work with in the undergraduate laboratory due to a combination of ease of use and preparation and relevance to the student's real-word experience. The use of zeolites in laundry detergents is the easiest application that illustrates the use of zeolites in the introductory laboratory. Modern laundry formulations use zeolites as builders, substances which help lift soil and keep it from redepositing on clothing in the washing machine [1]. They have been a major substitute for phosphates, which to some extent have been removed from detergent formulations because of their suspected role in the deterioration of water quality. While there are naturally occurring zeolites, most of the materials used today are synthetic. Zeolites in laundry detergents are multifunctional in that they not only serve as builders but they act as water softeners by ion exchange and as anticaking or flow agents as well. An excellent historical perspective of zeolite science and technology has been given by Milton [2].

Zeolites are microporous crystalline aluminosilicates with pore dimensions (< 15Å) that are comparable to those of small molecules, such as water, simple hydrocarbons, and gases (e.g., N_2, O_2 and CO_2). Many different types of zeolite can be prepared, and each type has pores with well-defined sizes [3]. The ability to prepare materials with different pore sizes has led to applications in size or shape selective separations and catalysis. If a molecule is small enough to fit in the zeolite's pores it can be adsorbed and separated from a mixture. Alternatively, if the zeolite has catalytically active sites inside its pore system, the reaction pathway is constrained by the requirement that the reactants, transition state, and products must be able to fit inside the pores.

While zeolite structures and formulas can look complicated, their basic architecture is simple. They can all be built up from SiO_4 and AlO_4 tetrahedral units. Figure 1 illustrates how these tetrahedral units are assembled to give the structure of Zeolite A. Formally we can consider the MO_4 tetrahedra (**A**) to be linked up to give secondary building units such as the sodalite cages (**B**) and the double four-ring units (**C**) shown in Figure 1. As there are many atoms in a typical zeolite unit cell it is customary to draw their structures without explicitly indicating the positions of the oxygen atoms. Lines are drawn between the centers of the SiO_4/AlO_4 tetrahedra that make up the structure to indicate the overall connectivity of the secondary building unit or zeolite. **D** and **E** in Figure 1 are representations of the sodalite cage and double four-ring units that do not show the oxygen positions. The final framework structure of zeolite A (**F** in Figure 1) can be constructed by linking together sodalite cages. The zeolite A framework has pores of ~4Å diameter that connect larger cavities inside the material. If there is nothing obstructing these pores they are big enough so that water, straight chain hydrocarbons, and simple ions can move through the cavity system.

Zeolites are sometimes built up entirely from SiO_4 tetrahedra, in which case they would have the empirical formula SiO_2; however, most zeolite structures contain some AlO_4 tetrahedra leading to a framework formula of the type $[Si_{1-x}Al_xO_2]^{x-}$ where x is the fraction of the SiO_4 tetrahedra that are replaced by AlO_4 units. For every AlO_4 tetrahedron that is incorporated into the material, the framework gains a charge of –1 that has to be balanced by the presence of additional, so-called extraframework, cations that sit inside the pores of the zeolite. These species are often ion exchangeable as they are small enough to move through the pore system of the zeolite. Na^+, K^+, NH_4^+, H^+, Zn^{2+}, Mg^{2+}, Ca^{2+} are all examples of ion exchangeable extraframework cations. It is this ion exchange behavior that leads to the use of zeolites for water softening and the removal of some radioactive ions from waste streams.

The use of zeolites as drying agents is also facilitated by the presence of extraframework cations. In the presence of moisture, these cations are coordinated to some of the oxide ions in the framework and to water molecules that also occupy the zeolite pores. On heating under vacuum most of these water molecules can be removed, but this leaves the extraframework cations with very little to coordinate with. Dehydrated zeolites readily take up water from air and "wet" solvents in an effort to properly coordinate their extraframework cations.

Many experiments involving zeolites in the high school and undergraduate laboratory experience are appearing in the

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S1430-4171(02)01533-0, Published on Web 02/01/2002, 10.1007/s00897020533a, 710033dw.pdf

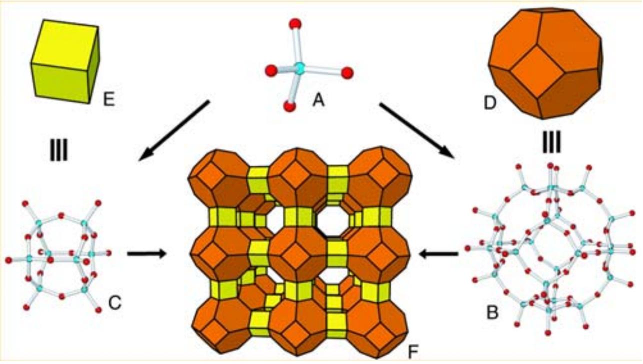

Figure 1. Zeolite structures are built up from corner sharing SiO_4 and AlO_4 tetrahedra. In the case of zeolite A, the tetrahedra (**A**) link up to form secondary building units such as sodalite cages (**B**) and double four rings (**C**). Typically, in drawings of zeolite structures the oxygen positions are not marked. Lines are drawn between the centers of connected tetrahedral so that the sodalite cages and double four rings would be represented as shown in **D** and **E**. These secondary building units are linked together to form the complete zeolite A framework (**F**), which has pores of ~4Å diameter connecting larger cavities.

literature [4–10]. Some involve using zeolites that have been extracted from proprietary laundry detergents[4] while others develop experiments illustrating their catalytic ability[4–7]. The synthesis of zeolites in the undergraduate laboratory has also been the subject of a few papers [8–10], but typically these are better suited for the more advanced courses. True inorganic synthetic experiments are largely omitted from the first-year undergraduate laboratory experience because of complexity, toxicity, waste disposal, and other impediments. We have recently written and used a series of experiments for the first-year undergraduate laboratory that focus on making Zeolite A, the principle builder in many major detergents used in the United States[11]. We have also adapted the following series of experiments involving synthetic Zeolite A to other levels of the chemistry laboratory, from nonmajor courses to more advanced analytical and physical chemistry laboratories, and, of course, to the inorganic synthesis laboratory. The intention of this report is to give the framework for a zeolite synthesis and analysis laboratory experiment that we have been using for the past few years in one of our first-year general laboratory courses.

Experimental

All chemicals were used as obtained from the supplier without further purification. Powder diffraction patterns were recorded to verify the identity of Zeolite A using a Scintag X1 diffractometer or a Rigaku Miniflex system. They were compared to published data from the International Zeolite Association[3] or the International Center for Diffraction Data (ICDD) Powder Diffraction File.

Zeolite Synthesis [12]

A solution of 40 g of NaOH (Baker) and 300 mL of distilled water was prepared in a 500-mL beaker with a magnetic stirring bar and placed on a stirrer hotplate. Another beaker containing 200 mL of distilled water was placed on the hotplate and both beakers were heated. To the NaOH solution 12.8 g of $NaAlO_2$ (Fisher Scientific) was added with stirring until dissolved. To the other beaker 10.6 g $Na_2SiO_3 \cdot 5H_2O$ (Fisher Scientific) was added with stirring until dissolved. Both solutions were brought to a boil. The sodium silicate solution was then added to the sodium aluminate solution with stirring just after the solutions began to boil. A thermometer was placed in the reaction beaker, and the temperature was maintained at ca. 90°C for 90 min. Care must be taken in heating because the mixture tends to have a thick paste-like consistency and can bubble out of the beaker due to localized superheating. The solution was filtered while still hot, and the filter cake was rinsed four times with distilled water. The filter cake was then spread out on a watchglass and allowed to dry over the week in the student's drawer. The mass of the product isolated was 8.07 g (99.4% yield). The final product's empirical formula is $Na_2Al_2Si_2O_8 \cdot 4.5H_2O$ ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.5H_2O$), known as "Zeolite A"or Linde Type A (LTA) zeolite. LTA is actually $[Na_{12}(H_2O)_{27}]_8 [Al_{12}Si_{12}O_{48}]_8$ (formula for one unit cell of fully hydrated material) and the properties can be found on the International Zeolite Association (IZA-SC) Web site[3].

The product may be characterized by X-ray powder diffraction (XRD) if equipment is available, and the XRD pattern may be compared to a known spectrum to confirm purity [3].

Water Hardness Test

In order to demonstrate the ability of Zeolite A to soften water by sequestering calcium ions, a series of tests was preformed. First, about 5 mL of a ca. 0.13 M $CaCl_2$ stock solution were obtained and placed in one of two small test tubes. In the other test tube was placed 5 mL of tap water. A few drops of soap solution were then added to each, and both tubes were shaken. In the test tube with the calcium present, almost no suds are observed. In the tap-water test tube, suds were observed. A spatula-tip full of dried zeolite was added to both test tubes, which were then shaken. It was observed that both test tubes showed a similar amount of suds.

Example Titrations

A 1.00-mL aliquot of the $CaCl_2$ stock solution (ca. 0.13 M) was placed in a 250-mL Erlenmeyer flask to which was added 50 mL deionized water, 3 mL of a NH_3/NH_4Cl buffer (pH 10), and 7 drops of Eriochrome Black T (Fisher) indicator solution[1]. The solution was titrated with a 0.00864 M ethylenediaminetetraacetic acid (EDTA, disodium salt, Fisher) solution which had been standardized against a 0.1000 M calcium ion standard solution (Orion). The 1.00-mL aliquot required 14.72 mL of titrant, resulting in a calculated molarity of 0.127 M for the stock solution; the indicator going from pink to blue in color denotes the endpoint.

A 2.0 g sample of Zeolite A was stirred with 50 mL of a $CaCl_2$ stock solution for 30 min. The Zeolite A suspension was filtered, and a 1.00-mL aliquot of the filtrate was titrated as above, 7.40 mL of EDTA titrant being required. The resultant molarity of the filtrate after treatment with Zeolite A was 0.0639 M.

Results and Discussion

We have now used parts of this procedure for two years in our introductory laboratories and also in our intermediate inorganic course. The procedures take two three-hour periods to complete with the first session being devoted to the synthetic portion, and the second session is used for the testing and titrations. The synthesis is facile and little difficulty is encountered by the students. The balanced equation is one of the more difficult equations to balance, and this appears to be the largest source of frustration on the part of first-year students [13]. Working with just the empirical formula simplifies the process greatly, and we generally tell the students to determine the limiting reagent by assuming that $NaAlO_2$ and $Na_2SiO_3 \cdot 5H_2O$ react in one-to-one stoichiometry,[2]

Table 1. Powder Diffraction Peak Positions and Intensities for Pure Sodium Zeolite A

2θ	d/Å*	I%
7.26	12.17	63
10.24	8.63	38
12.54	7.05	26
16.18	5.47	21
17.76	4.99	1
20.50	4.33	5
21.72	4.09	49
22.94	3.87	2
24.04	3.70	71
26.16	3.40	21
27.16	3.28	79
29.10	3.07	2
30.00	2.98	100
30.86	2.90	15
32.58	2.75	23
33.40	2.68	7
34.24	2.62	80
35.76	2.51	9
36.54	2.46	8
38.02	2.36	7
39.49	2.28	1
40.16	2.24	5
41.54	2.17	18
42.22	2.14	11
42.88	2.11	7
43.52	2.08	6
44.18	2.05	25
44.85	2.02	1
47.34	1.919	21
47.94	1.896	10
49.14	1.853	2
49.74	1.832	7
52.02	1.757	7
52.60	1.739	45
53.18	1.721	7
54.32	1.688	25
54.82	1.673	5
56.48	1.628	12
57.02	1.614	1
57.56	1.600	18
58.58	1.574	17

* The d-spacing, *d*, is calculated from the scattering or Bragg angle 2θ using Bragg's law $2d\sin\theta = \lambda$, where λ is the X-ray wavelength (1.54056 Å for Cu $K\alpha_1$).

and then assume a yield based on half the number of moles of the limiting reagent. Outside of this minor challenge, the students appear to enjoy making something that has an application in their everyday life [13].

A powder X-ray diffraction pattern from Na zeolite A is shown in Figure 2. This pattern is just a plot of the X-ray intensity scattered from the sample versus the scattering angle (Bragg angle, 2θ). The positions and intensities of the peaks in the diffraction pattern are a fingerprint of the crystalline components that are present in the sample. In Table 1 we list the peak positions and intensities (areas under each peak) that can be expected for a pure sample of Na Zeolite A. Additional peaks in the powder diffraction pattern would indicate the presence of a crystalline impurity. The nature of the impurity could be established by comparison with the International Center for Diffraction Data's database of powder patterns for known compounds. While it is not essential that the identity of the sample be confirmed by powder diffraction as the synthesis is reliable [12], there is value in introducing students to the technique as it is the primary method for identifying most solid materials[14]. Earth science/geology programs frequently have powder diffraction equipment and the purchase of instruments such as the Rigaku Miniflex units that we use in upper-level undergraduate laboratories at Georgia Tech can, in some cases, be justified.

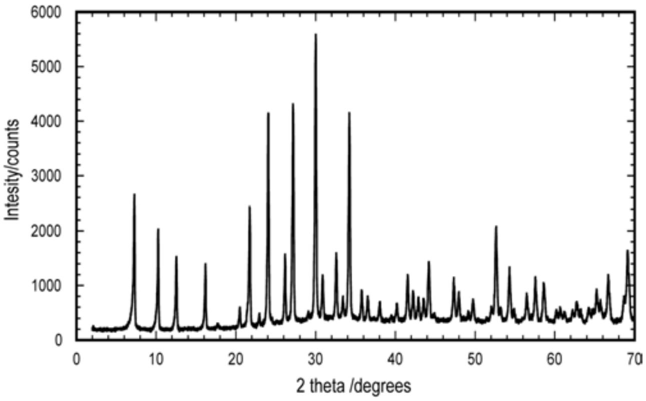

Figure 2. A powder diffraction pattern for sodium zeolite A recorded using one of the Miniflex diffractometer systems that are employed for instruction in the undergraduate laboratories at Georgia Tech (Cu kα radiation, variable divergence slits). The peak positions and intensities act as a finger print of the crystalline components in the sample. A crystalline impurity in the sample would lead to the appearance of extra peaks.

The water hardness test using soap solution is very useful in drawing the student's attention to the application of zeolites as water softeners. We explain that hardness is due, generally, to the presence of two ions, Ca^{2+} and Mg^{2+}, in natural surface or ground waters although other ions such as iron can also contribute. They see the effect of calcium ion on the sudsing of a soap solution. Then they see the effect with the removal of calcium using the zeolite. This area of Georgia gets all of its tap water from surface waters on granitic bedrock, and the water tends to be naturally soft or low in Ca^{2+} (20 ppm or less) [15]. Thus, tap water here provides a good "control" for how soap is supposed to suds in the absence of water-hardening ions. The students note that adding zeolite to tap water alone does not effectively change the sudsing action, but addition of zeolite to the calcium ion test tube allows sudsing that appears similar to the tap water both with and without the zeolite. The logical conclusions drawn from this experiment are that their tap water is already naturally soft, and that zeolites soften hard water. In areas of naturally hard water such as South Florida or Northeast Ohio, definite conclusions could also be drawn. The students would see that the calcium tube and the tap-water tube behaved similarly with the addition of soap, and they would conclude that their water is naturally hard. They would see the effect of adding the zeolite to both, once again observing similar results. One may wish to include a third test tube of deionized water and soap to show what the sudsing would look like in the absence on any additive to underscore the effect of zeolite as an ion exchanger. It should be emphasized to the student, however, that this experiment is not quantitative and that they are only seeing a relative effect.

Complexometric titrations are also quite simple to illustrate with these experiments, and the results can be interesting. In the experiments described above, synthetic Zeolite A removed about half of the calcium from the 0.127 M stock solution because the molarity dropped to about 0.0637 M. We also have the students calculate the number of millimoles of calcium removed for every gram of zeolite, which from the values reported above would be 31.2 millimoles per gram. Based on potentiometric titrations done using a calcium ion specific electrode and a suspension of the zeolite with a more dilute calcium solution, it takes about 10 min for the calcium to be absorbed [16]. Although our experiments recommend 30 min in the procedure, the stirring can be shortened if time constraints are an issue. We use 30 min simply to allow students to get their titration apparatus set up and do the nonzeolite treated samples first. Otherwise, the shorter stirring times are not problematic, and, in fact, more closely mimic what one would expect in the typical wash cycle of most household washing machines.

Acknowledgments. The authors wish to thank Brennan Price for help in developing these procedures. APW is grateful to the NSF for assistance with the purchase of powder diffraction equipment for use in undergraduate laboratories (DUE-9950700) and a CAREER award (DMR-9623890).

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17. 1. Water-hardness test kits, such as those produced by Hach Chemicals, have an indicator-and-buffer-powder mixture already prepared and packaged in small plastic pillows for immediate use. They will tend to increase the expense of the experiment per student, but they are much more convenient and safer to use.
18. 2. The balanced equation for the empirical formula is as follows:

$$2NaAlO_2 + 2Na_2SiO_3{\cdot}5H_2O \rightarrow Na_2Al_2Si_2O_8{\cdot}4.5H_2O + 4NaOH + 3.5H_2O$$