Exp. 1 (Text #3): The Molecular Sieve Zeolite X

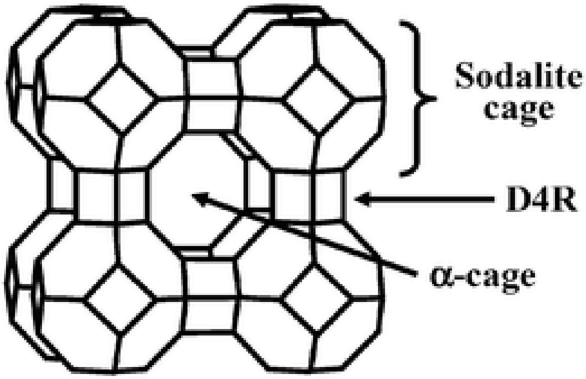
What is a zeolite?

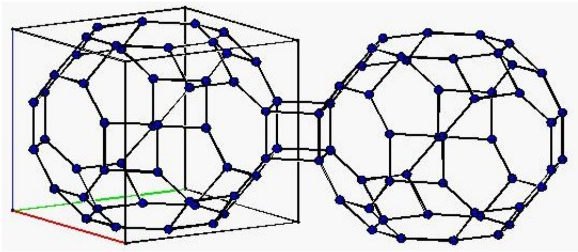
- A microporous solid, containing pores or channels in its structure that can accommodate guest molecules
- An aluminosilicate
  - Framework stoichiometry: $(Si, Al)_nO_{2n}$
  - Si or Al atoms are tetrahedrally coordinated to bridging O's ("vertex-sharing" tetrahedra)
  - Cations (e.g., Na^+, K^+) *required for charge balance*

Si^{4+} vs. $(Al^{3+} + Na^+)$

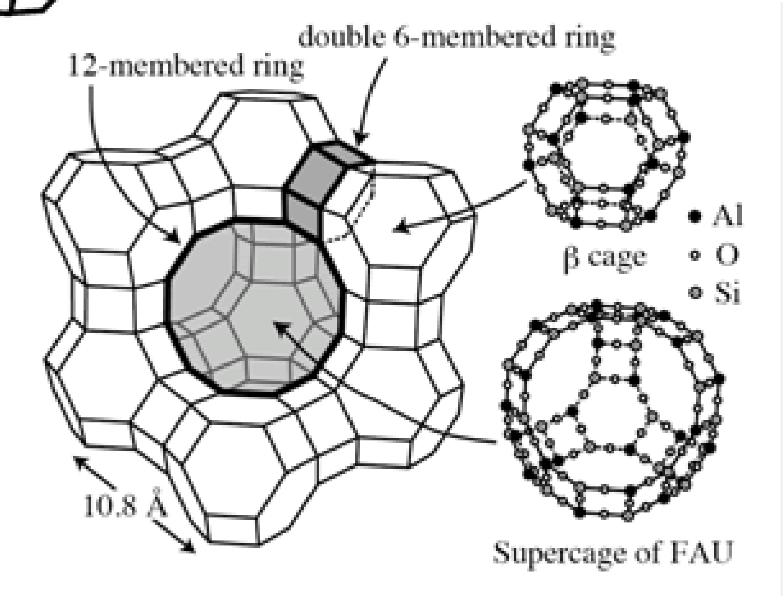
Zeolite Structure

Several aluminosilicate structures are based on a **truncated octahedron** with stoichiometry $\mathbf{M_{24}O_{36}}$ (where M = Si, Al), also called the **sodalite** or β **cage**:





Zeolite A
(showing connectivity of "octahedra")

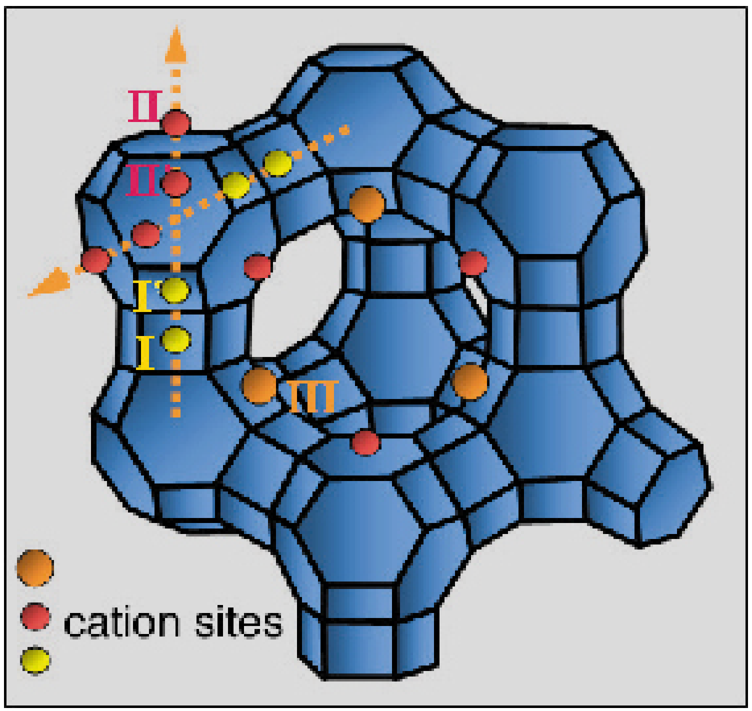


Zeolite X

Zeolite Structure, continued

Cations occupy numerous sites within the framework, and help to determine the size of the pores (α- or supercage).

- Also influenced by Si/Al ratio



We will use Na^+ to balance charge, so the **hydrated sodium ion** helps determine pore size.

How would pore size change if K^+ were used, instead?

K^+ is larger; pore size would be smaller.

Applications of Zeolites

- Molecular sieves (separation by size):
  - Desiccants/Adsorbents

- Ion exchange
  - Water softening

- Catalysis
  - Introduction of transition-metal ions affords numerous sites for catalytic reactions

NaX Synthesis and Ion-Exchange:

Synthesis of NaX:

$$(24\text{-}n)\ SiO_2 + n\ NaAlO_2 \rightarrow Na_nSi_{24\text{-}n}Al_nO_{48}$$

n = 9.6 – 12 for X-type zeolites; For us, ***n* = 10.7** (pore size = 7.4 Å)

Completed by mixing prepared solutions of sodium aluminate and sodium silicate (Solutions 1 and 2 in text)

Characterization by IR spectroscopy (1/25): See Balkus, K. J. et al. *J. Chem. Educ.* **1991**, *68*, 875-877 for published spectra.

Ion-Exchange Reaction:

$$Na_nSi_{24\text{-}n}Al_nO_{48} + x\ CoCl_2 \rightarrow Co_xNa_{n\text{-}2x}Si_{24\text{-}n}Al_nO_{48} + 2x\ NaCl$$

What is the specific ion-exchange process that occurs here?

Uptake of 1 Co^{2+} results in release of 2 Na^+ ions

NaX Synthesis: Procedural Notes and Tips

- You will work in pairs on this experiment.
- We will perform the experiment at **50% scale**.
- Next week, we will complete Part A to the stopping point mentioned in the text (filtering NaX crystals and leaving them in your drawer to dry).
- Our aim is to allow 2 hours for reaction in the oven, ideally starting around 3:00. We cannot begin heating until everyone is ready.
  - Make water bath immediately and start heating (watch temp as directed)
  - Work on Solutions 1 and 2 simultaneously
  - Note that the specified masses are not very precise (e.g., 1.2 g). **Don't** waste time trying for 1.200 g; just record the exact mass you obtain.
- After cooling, you will suction-filter your product using a Buchner funnel and filter paper. Wash the crystals with ~3 portions of water and continue suction as long as possible.
- Be careful when removing crystals from filter paper.

Overview of Activities for Next Week

In Lab Next Week:

1. Determine total mass of dry NaX product

2. Acquire IR spectrum of solid NaX product

3. Perform cobalt-exchange reaction:

$$Na_{10.7}Si_{13.3}Al_{10.7}O_{48} + x\,CoCl_2 \rightarrow Co_xNa_{10.7-x}Si_{13.3}Al_{10.7}O_{48}$$

4. Perform Powder X-Ray Diffraction on your product AND the cobalt exchange product.

   You will need to coordinate with Pam Jaco to do this experiment. She is available all day Friday. Dr. Gelabert is available to help with the analysis.

1. Percent Yield of NaX Product

You prepared two solutions – sources of alumina and silicate – and mixed them together to form NaX:

1. $Al(OC_3H_7)_3 \rightarrow NaAlO_2$

2. Silica gel $\rightarrow$ Silicate (“SiO_2”)

Overall reaction:

$$13.3\ SiO_2 + 10.7\ NaAlO_2 \rightarrow Na_{10.7}Si_{13.3}Al_{10.7}O_{48}$$

How will you calculate the theoretical yield of NaX?

Find limiting reactants from preparation of Solutions 1 & 2 and for the overall reaction

2. Characterization of NaX by IR Spectroscopy

What does IR spectroscopy measure and how is it used as a characterization tool?

Vibrations (stretches, bends) of different bonds; characteristic frequencies for different functional groups

What functional groups (bonds) would be diagnostic of your NaX product?

See Balkus, K. J. et al. *J. Chem. Educ.* **1991**, *68*, 875-877 for published spectra. You can access this from http://pubs.acs.org/journal/jceda8

3. Synthesis of Cobalt-exchanged Zeolite X

$$Na_{10.7}Si_{13.3}Al_{10.7}O_{48} + x\ CoCl_2 \rightarrow Co_xNa_{10.7-x}Si_{13.3}Al_{10.7}O_{48}$$

What role do the Co^{2+} ions assume in the new product?

Charge balance

Similar ion exchange is harnessed in water softening.

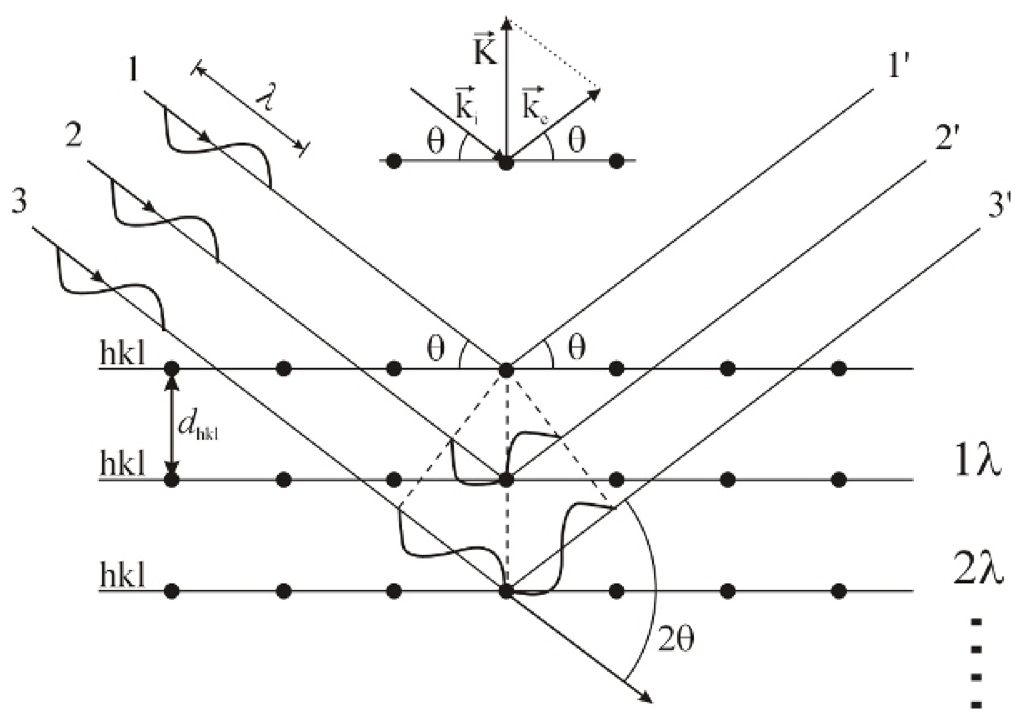
What observations can you use as evidence of successful cobalt exchange?

Color change accompanying ion exchange. *$CoCl_2 \cdot 6\ H_2O$ is pink: as it is incorporated into the zeolite, the white NaX turns pink and the pink solution loses color. (Uptake of Co^{2+} can also be followed by UV-visible spectroscopy.)*

4. Powder XRD Analysis

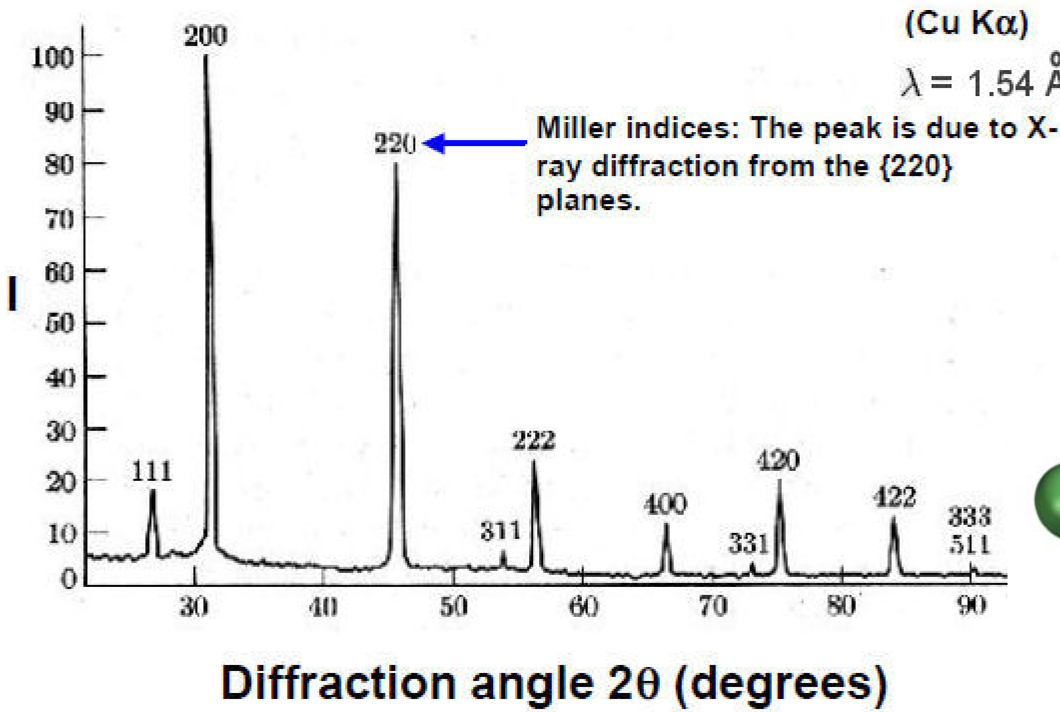
- X-rays are generated by the instrument.
  - These have a very specific wavelength you will need to record
- The X-rays interact with the crystalline sample.
- Planes of atoms in the sample will scatter X-rays constructively only when Bragg's Law is satisfied

$$\frac{2sin\theta}{\lambda} = \frac{1}{d}$$

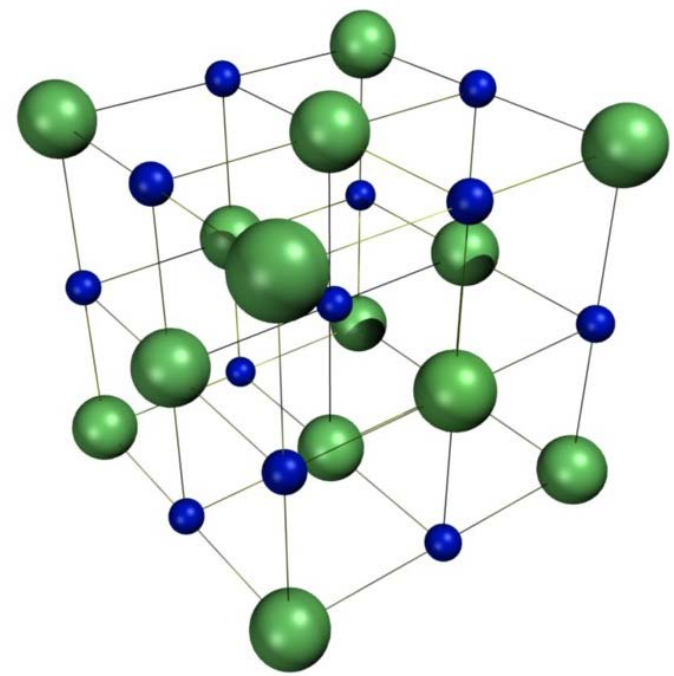


4. XRD Analysis

XRD Pattern of NaCl Powder



$$\frac{2\sin\theta}{\lambda} = \frac{1}{d}$$



200 peak: $2\theta = 31°$ → d = 2.88 Å

Atom planes in the NaCl crystal are 2.88 Å apart.

Procedural Tips

1. Remember that we are still working at **50% SCALE.**

2. Begin by: a) setting up your water bath and b) Determining the mass of dry NaX product. You can then acquire the IR spectrum at any time.

3. Break the NaX product into small pieces (if necessary) to facilitate cobalt exchange. Stir vigorously with a magnetic stir bar. (Make sure your water bath set-up allows this.)

4. You can follow reaction progress by observing color changes in solution and solid. Stop stirring occasionally to permit this.

5. When cobalt exchange is complete, collect product by filtration, wash and dry on the filter paper, and transfer to oven (110-115 °C). A color change should occur. **Why?**

6. Make sure that both samples are dry for XRD analysis.

Formal Lab Report

Title *Be descriptive!*

Abstract *A concise summary of the **entire report**, including results and discussion. One paragraph (150-350 words)*

Intro

*Address all the key questions: **What** did you do (or **What** scientific questions were you hoping to answer)? **Why** is it relevant? **How** did you accomplish the synthesis and characterization? Briefly and generally, **what results** did you obtain?*

Experimental Methods

*Describe **exactly** what <u>was done</u> (using past tense, passive voice). Include sufficient detail so that a fellow chemist could repeat your work.*

Results *The quantitative and qualitative results of your experiment*

- ***Yield and calculated % yield of NaX*** *(show your calculations)*
- ***IR spectrum*** *with peaks labeled (Insert as an Excel spreadsheet; include figure title and caption) – may also tabulate key peaks in the text.*
- ***Observations related to cobalt exchange reaction***
- ***XRD data***

Formal Lab Report (cont.)

Discussion *Interpretations of results to answer questions posed*

- ***Did you successfully synthesize NaX?*** *Explain how your results led you to your answer. Also,* ***discuss your yield and the crystallinity of your product (see J. Chem. Educ. Article).***
- ***Was the*** $\boldsymbol{Co^{2+}}$***-exchange reaction successful?*** *Discuss all observations in support of your answer.*
- ***What did you learn from the XRD analysis?*** *Did the crystalline structure of the zeolite change by exchanging ions?*

Conclusions

A brief ***summary*** *of the* ***entire report****.* ***No new information*** *should be presented here.*

References

Include ***numbered citations*** *in the text for any sources you cite (first source cited = #1, etc.). List citations in numerical order in the References section.*