Infrared spectroscopy as a compliment to X-ray diffraction for zeolite examination

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Abstract

X-ray diffraction is commonly used to examine zeolite structure, but it is unable to see small changes in the long- or short-range structure. Infrared spectroscopy is used to examine changes in the long- and short-range structure of zeolite.

Structural changes in zeolite CIT-6 and derivatives upon chemical treatment are identified with mid- and far-infrared spectroscopy. Differences in the local structure of the sample are observed in the mid- and far-infrared spectra.
Zeolites

- Molecular sieve
  - Regular crystalline structure
  - Composed to TO$_4$ tetrahedra
  - Change uses and structure by changing T-atoms
  - Structure examined with X-ray diffraction
- Widely used in industry

Image from: http://www.personal.utulsa.edu/~geoffrey-price/zeolite/beta-a.jpg
Zeolite structure

- X-ray diffraction (XRD) 
  - most common tool
  - Easy to use
  - Long-range structure
- See distance between layers of atoms
  - Gives structure and composition
- Short-range changes not visible with XRD

How to see short-range changes in structure?

- Infrared spectroscopy (IR)
  - Fourier Transform IR widely used
    - Easy to use
    - Full spectrum quickly
  - Identify atomic bonds in molecules
  - Sensitive to changes in environment
    - Composition
    - Structure
Methods

Sample treatments

- As-made CIT-6 (zincosilicate, Li⁺ cation, contains SDA)
- Pure Si CIT-6 (pure silicate, Li⁺ cation, no SDA)
- Calcined CIT-6 (zincosilicate, Li⁺ cation)
- Zn CIT-6 (zincosilicate, Zn²⁺ cation)
- Si *BEA – with SiOH (pure silicate, Li⁺ cation, no SDA)
- Aluminum *BEA (aluminosilicate, Li⁺ cation, no SDA)

Spectra collected with Mattson Cygnus FT-IR
- Diffuse-reflectance IR used
- Samples mixed with CsI at 1:5 ratio
Results – Mid-infrared

- Differences between 1250 to 975 wavenumbers
- Show changes in O-T-O stretching from treatments
  - Chemical or heating treatment of zeolite
- Short-range structure changed for Calcined and Acetic acid samples
  - More like Pure Si CIT-6
- Aluminum sample changed to be more similar to original CIT-6
- IR does see changes not visible in XRD
Short-range O-T-O changes

- Pure Si CIT-6
- Aluminum
- Acetic acid
- Calcined
- Original
Results – Far-infrared

- Long-range
  - Double-ring modes
    - 700 to 500 cm\(^{-1}\)
- See long-range changes in zeolite
- Calcined and acetic acid samples more like Pure Si CIT-6
- Aluminum sample changes back to be more similar to Original
- IR again sees changes not visible in XRD
Long-range structure changes

- Pure Si CIT-6
- Aluminum
- Acetic acid
- Calcined
- Original
Conclusions

- Mid-infrared shows evidence of short-range changes
- Far-infrared shows evidence of long-range changes
- IR a useful tool for zeolite structure examination
  - Development of new zeolites
  - Modifying existing zeolites
References

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