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Overview & Relevance

Significance

The nano- and micro-scale ordering of a zeolite’s components largely determine the macroscopic properties of the zeolite. There is a need to study crystal ordering and porosity of the zeolites. The complexity of the state of internal orientation (how they spatially vary) plays an important role in material functionality. A non-invasive spectroscopic way to probe the “crystallinity” at various locations within a given sample is tremendously useful. Characterization through polarized Raman spectroscopy could give us fundamental insight into the states of internal orientation of zeolites which can lie on either of the two ideal states that lie at the ends of the crystallinity spectrum: “crystalline,” in which the molecules are arranged periodically in well-defined unit cells, or random orientations in which the molecules are freely rotating (as in a liquid) or randomly oriented. By analyzing the polarization dependence of selected peaks, we can further characterize the crystal structure of zeolites. As means of characterization of the presence of transition metals present in the zeolite framework, Terahertz Raman scattering measurements on commercially sold zeolites will be analyzed, extending the spectral range to the low frequency region. This new method of zeolite characterization should not only allow SRNL to meet customer needs in providing more insight into the materials used in noble gas samplers but also provide a wider capability of better understanding the local structure of zeolite characterization should not only allow SRNL to meet customer needs in providing more insight into the materials used in noble gas samplers but also provide a wider capability of better understanding the local structure of zeolites. This work was supported by the SRNL LDRD Program.

Project Summary

• Zeolites currently used in our facilities were fully characterized using polarized Raman spectroscopy. This project, focused on the different Raman techniques, and the performance of a few different experiments using the tools of polarized Raman spectroscopy. For different Raman techniques, the different modes of different zeolites were obtained experimentally and were compared with the spectra of two commercially available zeolites. These experiments were conducted at different instruments for spectral validation. Three laser wavelengths were used to perform our experiments (520nm, 515nm and 785 nm).

• Different laser wavelengths were used to correct for fluorescence, which impeded us from obtaining the spectral signatures we are looking for.

• Procurement for the Thz Raman spectroscopy probe was started October 2016 and purchase order issued January 2017. The instrument arrived and was used at the time the in situ experiments were conducted.

• Improvements to the interpretation have been made. We have purchased a new holographic filter for the spectrometer.

• We procured and purchased a commercially available pressure Raman cell to study zeolite-gas interactions.

• Experiments could be performed as well as cryogenic and variable temperature.

• Measured commercial zeolite vibrational information in terms of the vibrational frequencies and modes.

Remaining Challenges and Barriers

• In depth Polarized Raman Spectroscopy studies.

• Commercial zeolite experimental vibrational information in terms of the vibrational frequencies and modes.

• Gain new insights on the differentiation of the symmetric modes of the zeolite crystals

Collaborations

Understanding of local structure-function relationships of zeolites used in industry through polarized Raman Spectroscopy

Collaborations

Savannah River National Laboratory
- Nonproliferation Technologies
- Analytical R&D and Material Characterization
- Ross Smith – Trace Nuclear Measurement Technology Group

Project ID # LDRD-2017-00015

Approach

Technical Approach

Projected polarized Raman spectroscopy setup and examples of acquired Raman Spectra of structurally diverse zeolites

Future Experiments

Experimental peak positions of all the observed Vibrational modes of different Zeolites

Polarized Raman Spectroscopy Characterization of Zeolites

Zeolites are widely used in catalysis, adsorption, molecular Sieve diffusion, nanoliter interferometers, etc. For all these applications, information about the structure and orientation of the molecules and clusters inside zeolite cavities is very important. Moreover, zeolites are unique matrices for ordering and keeping adsorbed species. Studying the ordered species in zeolites, we can gain an understanding of the behavior of the species in the cavities. These techniques have been developed many years ago. They have a proven record of consistent and reliable performance. These zeolites are currently used in two different ways: one-time shot sampling and continuous gas flow. These experiments were conducted at the time the in situ experiments were conducted. As means of characterization of the zeolites which can take on either of the two ideal states that lie at the ends of the crystallinity spectrum: “crystalline,” in which the molecules are arranged periodically in well-defined unit cells, or random orientations in which the molecules are freely rotating (as in a liquid) or randomly oriented. By analyzing the polarization dependence of selected peaks, we can further characterize the crystal structure of zeolites. As means of characterization of the presence of transition metals present in the zeolite framework, Terahertz Raman scattering measurements on commercially sold zeolites will be analyzed, extending the spectral range to the low frequency region. This new method of zeolite characterization should not only allow SRNL to meet customer needs in providing more insight into the materials used in noble gas samplers but also provide a wider capability of better understanding the local structure of zeolite characterization should not only allow SRNL to meet customer needs in providing more insight into the materials used in noble gas samplers but also provide a wider capability of better understanding the local structure of zeolites. This work was supported by the SRNL LDRD Program.

Project Summary

• Zeolites currently used in our facilities were fully characterized using polarized Raman spectroscopy and XRD.

• Experimental peak positions of all the observed Raman vibrational modes of different zeolites were obtained experimentally and were compared with available experimental data.

• Different instruments and laser lines (325 nm, 532 nm and 785 nm) were used.

• Raman probe was installed in order to obtain the spectra of commercially available Zeolites

• Polarization kits were installed successfully.

• Purchased polarization kits: In depth polarized Raman spectroscopy studies with commercial zeolites will be done experimentally.

Overall Objectives:
- Optical procurement and instrument setup completed in Robert Lascola’s laboratory. An Ondas THz Raman probe was installed in order to obtain Raman terahertz spectra of commercially available Zeolites.
- Perform polarized Raman spectroscopy experiments with around 10 different commercial and lab-synthesized zeolites.
- Determine the high frequency vibrations of different laser wavelengths which vary experimentally, which can be used to define the state of internal orientation of zeolites.
- Perform X-ray wavelength Raman spectroscopy to determine the presence of internal metal cations found in the structural framework of the zeolite. This information and technique could be used when characterizing custom-engineered zeolites.
- Set up pressured gas cell out to spectroscopically examine zeolite-gas interactions.
- Fundamentally gain a better understanding of the state of specific interaction of zeolites and non-reactive gases.
- Install polarization kits in order to perform in depth Polarized Raman Spectroscopy studies.
- Measure spectroscopic behavior of the framework of commercial zeolite vibrational information in terms of the vibrational frequencies and modes.
- Gain new insights into the differentiation of the symmetric modes of the zeolite crystals.

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