Contract No:

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Disclaimer:

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

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Overview & Relevance

Timeline:

Project start date: 10/2016

Project end date: 9/2017

Percent complete: *45%*

Budget

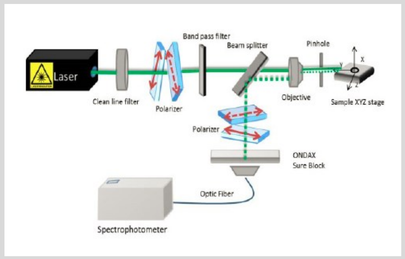
- Total project funding: 235K
- Funding received in FY17: 235K
- Total funding planned for FY18: none

Overall Objectives:

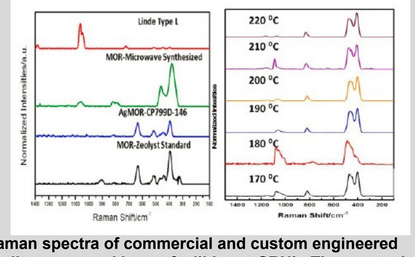
- Optics procurement and instrumental setup completed in Robert Lascola's laboratory. An Ondax THz-Raman probe was installed in order to obtain Raman terahertz spectra of commercially available Zeolites.
- Perform polarized Raman spectroscopy experiments with around 10 different commercial and lab-synthesized zeolites.
- Raman spectra of the commercial zeolites should be acquired with different laser wavelengths to determine which experimental parameters are suited to perform the remainder of the experiments.
- Perform low wavenumber 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 pressurized gas cell to spectroscopically examine zeolite-gas interactions.
- Fundamentally gain a better understanding of the science of site 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.

Significance

The nano- and micro-scale ordering of a zeolite's components largely determine the macroscopic properties of the zeolites. There is a need to study crystal ordering and porosity of the zeolites. The complexity of the state of internal orientation (how they may 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 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 gas) 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 range. 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-function relationships of zeolites used in industry. This work applies to the focus area of non-proliferation and nuclear deterrent: advanced sampling and seeking new/alternative signatures and measurement techniques.



Originally proposed polarized Raman spectroscopy experimental setup



Raman spectra of commercial and custom engineered zeolites prepared in our facilities at SRNL. The spectral panels represent different studies

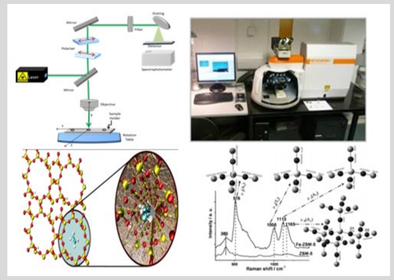
Approach

	Milestones, Deliverables, or Go/No-Go Decision	Progress Notes	% Complete
	• Zeolites currently used in our facilities were fully characterized using polarized Raman spectroscopy and XRD. • Purchased polarization kits: In depth polarized Raman spectroscopy studies with commercial zeolites	• Different instruments and laser lines were used. • 325 nm, 532 nm and 785 nm laser lines were used. • Polarization kits were installed successfully. • 325 nm laser malfunctioned at the time the in-depth polarization studies were initialized.	70 %
	• Procured and installed THz Raman spectroscopy probe. • Purchased a commercially available pressurized Raman cell to study zeolite-gas interactions	• Analyzed around 8 samples with this setup. • Improvements to the instrumentation were addressed. Purchasing a new holographic filter for the spectrograph could not be completed.	50%

Raman Spectroscopy Characterization of Zeolites

Zeolites are widely used in catalysis, adsorption, molecular sieve diffusion, nanoclusters preparation, 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 get important information about parameters of the species, which is impossible to get by other means. There have been several patents of the use of these materials in sampling systems which have paved the way for SRNL to develop noble gas samplers. These zeolites were 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 grab sampling and continuous concentration. As part of this project with polarized Raman spectroscopy we want to fundamentally gain a better understanding of the science behind how non-reactive gases interact with zeolites through structure function relationships. We used commercially sold zeolites, as well as planned to characterize custom-engineered zeolites by polarized Raman spectroscopy. Zeolites are the most well-known family of microporous materials. Often referred to as molecular sieves or open-framework materials, they are a class of inorganic solids that possess regular pores or voids in the size range of 5-20 angstroms. Even though numerous zeolite structures have been successfully synthesized, it is still necessary to rationally design and synthesize more zeolite structures with specific architectures and properties, which requires a full understanding of the crystallization process and the formation mechanism of zeolites.

Technical Approach



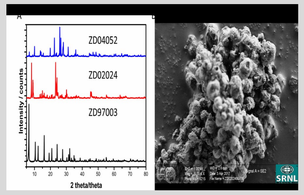
Experimental polarized Raman spectroscopy setup and examples of acquired Raman Spectra of structurally diverse zeolites

Technical Progress (Accomplishments)

FY-17 Accomplishments

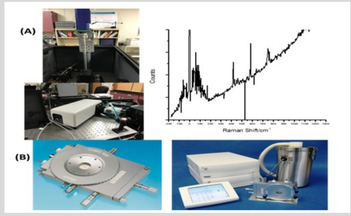
- **Polarized Raman spectroscopy measurements have been done with around 10 commercially available zeolites.**
- **We have performed experiments using three different instruments for spectral validation.**
- **Three laser wavelengths were used to perform our experiments (325nm, 532nm and 785 nm).**
- **Different laser wavelengths were used to correct for fluorescence, which impedes 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 customized probe arrived at the end of April 2017.**
- **Improvements to the instrumentation have been addressed. We have purchased a new holographic filter for the spectrograph.**
- **We procured and purchased a commercially available pressurized Raman cell to study zeolite-gas interactions.**
- **Experiments could be performed as well at cryogenic and variable temperatures.**
- **Measured commercial zeolite vibrational information in terms of the vibrational frequencies and modes.**

XRD and SEM Characterization



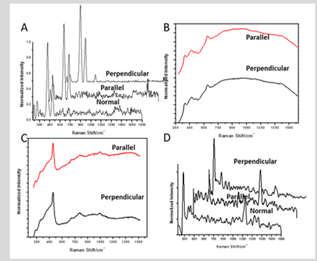
p-XRD of different commercially available zeolites and SEM image of ZD02024

Future Experiments

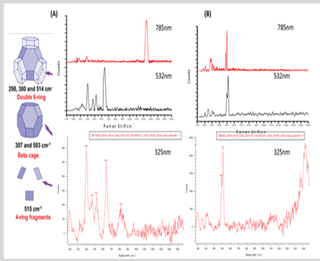


(A) CBV-10ADS THz Raman spectra with the purchased probe and (B) Specialized Raman cell for the use of zeolite-gas interaction studies

Polarized Raman Spectroscopy Experiments



Polarized Raman spectra of different commercially available zeolites



Raman spectra of two commercially available mordenite zeolites taken at three different laser wavelengths

Experimental peak positions of all the observed Raman vibrational modes of different zeolites

Raman shift (cm^{-1}) (no polarization)	Raman shift (cm^{-1}) (0^o)	Raman shift (cm^{-1}) (90^o)	Band Assignment
158	158	158	Lattice modes
207	207	207	Lattice modes
247	247	247	Lattice modes
406	406	406	5-membered ring breathing, stretching
465	465	465	4-membered ring breathing
			Al-O-Si bending and symmetric stretching of framework
525	525	525	
648	648	648	8-or 10-membered ring vibration
799	799	816	Si(Al)-O symmetrical stretch
895	895		Si(Al)-O symmetrical stretch
970			Si(Al)-O asymmetrical stretch
950-1250			Si(Al)-O asymmetrical stretch

Collaborations

Savannah River National Laboratory

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

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**
- **Experimentation with the pressurized gas cell to spectroscopically study zeolite-gas interactions.**

Proposed Future Work

- **Computational DFT studies calculations can provide not only the energetics/kinetics of possible zeolite structures and chemical reactions, but also the vibrational information in terms of the vibrational frequency which can be used to compare with available experimental data.**

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 analyzed.**
- **Different instruments and laser lines (325 nm, 532 nm and 785 nm) were used.**
- **THz-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.**

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