Contract No:

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Synthesis of Zeolite Materials for Noble Gas Separation

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Project ID # LDRD-2016-00062

Overview & Relevance

Timeline:

Project start date: 10/2015

Project end date: 9/2017

Percent complete: *100%*

Budget

- Total project funding: $600k
- Funding received in FY16: $250k
- Funding received in FY17: $350k
- Total funding planned for FY18: none

Overall Objectives:

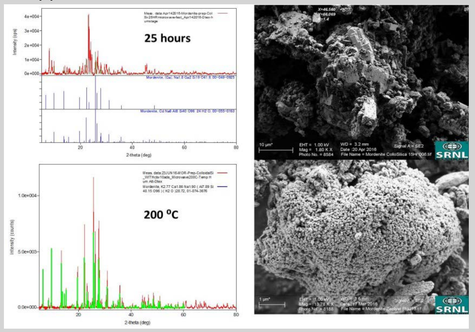
- Currently used zeolites will be characterized using gas sorption analysis, SEM, XRD and Raman spectroscopy
- Microwave-assisted and conventional hydrothermal synthesis will be used to make a variety of zeolites tailored for noble gas separation.
- Candidate materials will be down-selected based on highest available surface area, maximum overall capacity for gas adsorption and best selectivity for noble gases (or optimum exclusion of noble gases).
- Boronation and/or silanation modifications will be tested on commercial materials and new materials for fine-tuning of pore size and adsorption properties.

Partners:

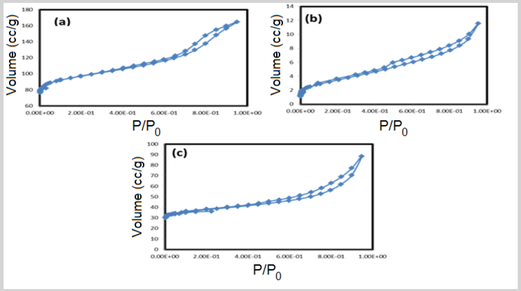
- Naval Research Laboratory

Significance

There is a need for a better fundamental understanding of how non-reactive gases selectively adsorb to the surface and diffuse through the pore structure of zeolites. End user requirements necessitate improved noble gas samplers with smaller size, weight and power requirements and higher efficiency. Advances in analytical techniques and the science of zeolites since the development of the materials that are currently used at SRNL for noble gas sampling give the opportunity to improve the understanding of how zeolites separate noble gases from air and open the door to the synthesis of better zeolites. Data collected in the first year of this two-year strategic LDRD has been used to help guide the synthesis of these new materials. Microwave-assisted and conventional hydrothermal synthesis have been used to make a variety of zeolites tailored for noble gas separation in the final year of the project. Boronation modifications have been tested on commercial materials and new materials for fine-tuning of pore size and adsorption properties. Candidate materials have been down-selected based on highest available surface area, maximum overall capacity for gas adsorption and best selectivity for noble gases (or optimum exclusion of noble gases). The creation of improved adsorbent materials initiated in this project will lead to development of more compact, efficient and effective noble gas collectors and concentrators. SRNL has been a leader in noble gas collections using adsorbent materials for nonproliferation activities for over 20 years. This project will build the foundation to maintain this leadership in the future. The development and characterization of novel adsorbent materials that was accomplished in this project is being prepared for submission in two publications. The work performed in this project will be used as a foundation for funding proposals for further material development from NNSA, DoD and OGA, as well as possible industrial applications.



XRD scans and SEM micrographs of synthesized Mordenite samples



Adsorption isotherms for (a) silver mordenite, (b) boric acid modified mordenite, (c) silver chabazite

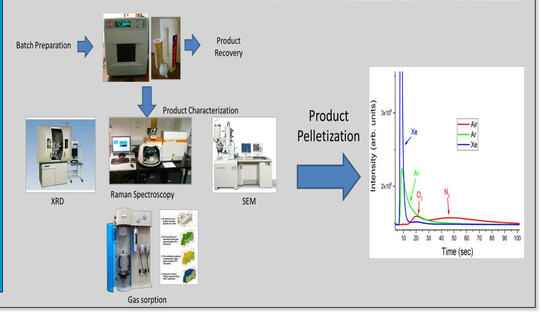
Approach

Milestones, Deliverables, or Go/No-Go Decision	Progress Notes	% Complete
Characterization of current and new zeolites to improve understanding of the physical/chemical properties of zeolites and how non-reactive gases interact with the surfaces and pores	Completed analysis of samples using SEM, XRD, gas sorption, NMR	100
Synthesis and testing of new zeolite materials Down select 3-5 candidate zeolites. Pelletize, test and optimize recipes for candidates	Down selected three candidate samples (offretite, mordenite, Linde Type F)	80

Microwave-assisted and conventional hydrothermal synthesis of zeolites

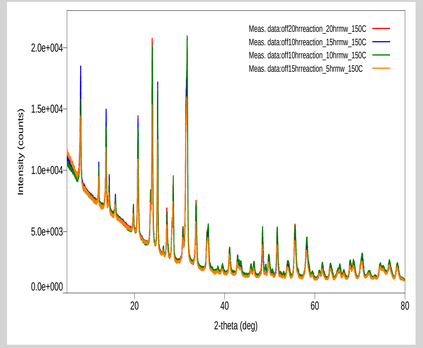
As part of this project, zeolites were synthesized and/or modified to give improved performance in noble gas separation processes. The use of a microwave oven to heat the mixture of reactants facilitated the synthesis of zeolites as compared to traditional hydrothermal synthesis in conventional ovens. We used microwave-assisted hydrothermal synthesis of known recipes of mordenite and Linde type L as initial trial syntheses. SEM measurements revealed crystal morphology for the different types of mordenites we synthesized. X-Ray crystallography was used to determine the type of zeolite synthesized based on comparing the diffraction pattern of the powder sample with a reference library of diffraction patterns for the zeolites synthesized. Solid-state NMR analysis has given information on bonding environments of various elements in the crystal lattice. Candidate materials have been down-selected based on highest available surface area, maximum overall capacity for gas adsorption and best selectivity for noble gases (or optimum exclusion of noble gases).

Characterization using XRD, Raman, SEM, gas sorption analysis, gas chromatography, NMR

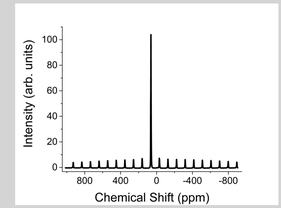


Technical Progress (Accomplishments)

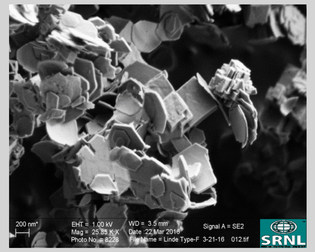
- Syntheses of known zeolites have been performed using microwave and conventional oven hydrothermal synthesis.
- We have performed syntheses of the following compounds: offretite, chabazite, faujasite, mordenite, Linde type F, Linde type L and EMC-2.
- Results of this work were presented at the ACS Southeast Regional meeting as a poster in October 2016.
- Two manuscripts are in the preparation stages focusing of some of these results for submission to peer-reviewed journals.
- Variations in reaction conditions and recipes of the offretite zeolite have been tested for improvements in separation characteristics through gas chromatography.
- Currently used zeolites have been characterized using gas sorption analysis, SEM, XRD and NMR spectroscopy.
- Characterization and trial modifications of commercial zeolites have been performed.
- We have performed gas chromatography experiments with around 11 commercial and natural zeolites.
- An MPO interagency agreement (IAA) has been approved for subcontract for NMR analysis by NRL.
- Initial results of the solid state NMR experiments were obtained from NRL. Si-NMR and Al-NMR spectra were obtained of synthetically customized zeolites at SRNL.



XRD scans of Offretite samples



^{27}Al MAS NMR spectrum of Linde Type F 20 hr microwave reaction product



SEM micrograph of Linde Type F 20 hr microwave reaction product

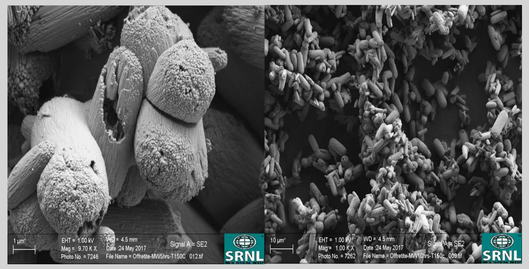
Gas Sorption Experiments-Microwave synthesis at T=160^{0}C

Zeolite-Offretite	Surface Area m^2/g	Pore Volume (cc/g)(DFT)	Average Pore size(Å)
t=15 hr	147.123	0.081	9.37
t=20 hr	219.559	0.107	8.65
t=25 hr	410.443	0.166	8.03
t=30 hr	361.799	0.142	7.96

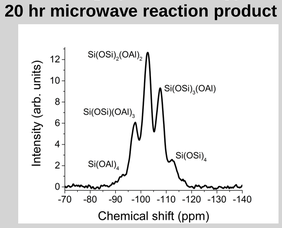
Gas Sorption Experiments-Microwave synthesis at T=150^{0}C (aged for 1 day)

Zeolite-Offretite	Surface Area m^2/g	Pore Volume (cc/g)(DFT)	Average Pore size(Å)
t=5 hr	433.998	0.161	7.72
t=10 hr	487.003	0.197	7.74
t= 15hr	468.051	0.196	7.84
t=20hr	475.604	0.221	8.21

Gas sorption analysis results of porosity and surface area for Offretite



SEM micrographs of Offretite 5 hr and 10 hr samples



^{29}Si MAS NMR spectrum of Offretite 15 hr microwave reaction 160° C product

Collaborations

Savannah River National Laboratory

- **Nonproliferation Technologies**

Naval Research Laboratory

- **Subcontract to NRL**
- **Christopher Klug**
- **NMR analysis of samples**

Remaining Challenges and Barriers

- **Pelletize candidate zeolites for testing in sampling systems**
- **Scale synthesis of selected zeolites for production**

Proposed Future Work

- **Computational DFT studies can provide not only the energetic/kinetics of possible zeolite structures and chemical reactions, but can also simulate gas sorption experiments and gas-zeolite interactions.**
- **^{11}B spectra of boric acid modified Z900Na.**
- **^{109}Ag spectra of silver-exchanged mordenite and chabazite.**
- **^{29}Si and ^{27}Al spectra of different batches of Ag-CHA, various sealed dry/activated samples.**

Project Summary

- **Completed characterization of currently used zeolites**
- **Successfully synthesized a variety of zeolite structures and characterized them with XRD, SEM, NMR, gas sorption analysis**
- **Identified potential commercial zeolites for modification to perform separations**

This work was supported by the SRNL LDRD Program

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