Contract No:

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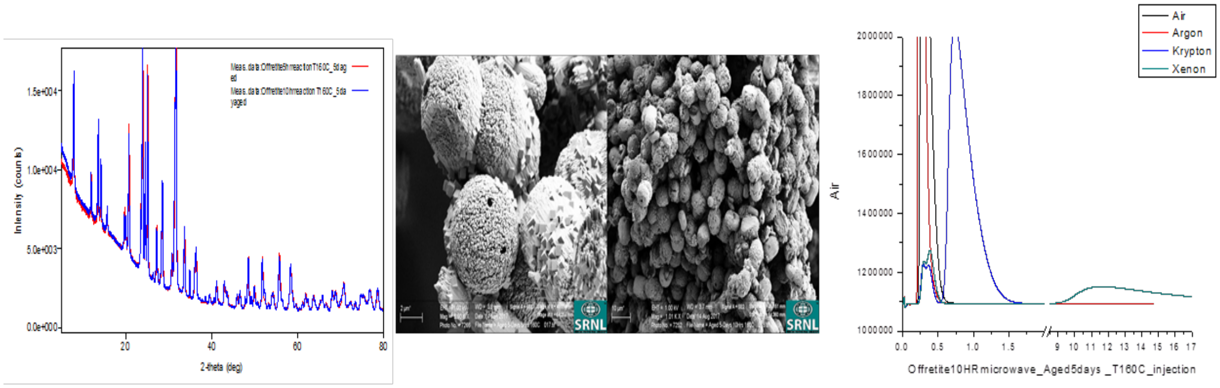
Synthesis of Zeolite Materials for Noble Gas Separation

Microporous zeolite adsorbent materials are widely used as a medium for separating gases. Adsorbent gas separation systems can run at ambient temperature and require minimal pressure to flow the input gas stream across the adsorbent bed. This allows for low energy consumption relative to other types of separation systems. Specific zeolites also have a high capacity and selectivity for the gases of interest, leading to compact and efficient separation systems. These characteristics are particularly advantageous for the application of signatures detection for non-proliferation, which often requires portable systems with low power draw. Savannah River National Laboratory currently is the leader in using zeolites for noble gas sampling for non-proliferation detection platforms. However, there is a constant customer need for improved sampling capabilities. Development of improved zeolite materials will lead to improved sampling technology. Microwave-assisted and conventional hydrothermal synthesis have been used to make a variety of zeolites tailored for noble gas separation. Materials characterization data collected in this project has been used to help guide the synthesis of improved zeolite materials. Candidate materials have been down-selected based on highest available surface area, maximum overall capacity for gas adsorption and highest selectivity. 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. The work performed in this project will be used as a foundation for funding proposals for further material development as well as possible industrial applications.



Offretite zeolite XRD and SEM characterization and gas chromatographic performance testing of the product

Awards and Recognition

None to date

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

Signature **Date**

Synthesis of Zeolite Materials for Noble Gas Separation

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Subcontractor: MPO interagency agreement (IAA) with NRL

Thrust Area: Non-Proliferation & Nuclear Deterrent

Project Type: Standard

Project Start Date: October 1, 2015
Project End Date: September 30, 2017

Microporous zeolite adsorbent materials are widely used as a medium for separating gases. SRNL currently is the leader in using zeolites for noble gas sampling for non-proliferation detection platforms. However, there is a constant costumer need for improved noble gas sampling capabilities. The zeolites that are currently used for noble gas separation have been characterized to understand which properties are most important for noble gas separation. This knowledge was used to develop improved zeolites which will allow the building of a new generation of noble gas samplers.

FY2017 Objectives

- Microwave-assisted and conventional hydrothermal synthesis will be used to make a variety of zeolites tailored for noble gas separation.
- Boronation modifications will be tested on commercial materials and synthesized materials for fine-tuning of pore size and adsorption properties.
- Currently used zeolites will be characterized using gas sorption analysis, SEM, XRD and NMR spectroscopy
- 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).

Introduction

Advances in analytical techniques and the science of zeolites since the development of zeolites 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. Characterization data collected in the project has been used to help guide the synthesis of these new materials. Microwave-assisted and conventional hydrothermal synthesis has been used to make a variety of zeolites tailored for noble gas separation. Characterization data collected in the project has been used to help guide the synthesis of these new materials. A thorough understanding of the properties of the existing zeolites has been gained through characterization of the materials with XRD, SEM, and gas sorption analysis. Such characterization has revealed which properties of our zeolite materials are most important for separating noble gases from air. Custom engineered zeolites have been synthesized from raw materials with chemistry designed to give optimal adsorption characteristics and pore structure that are best for noble gas separations while maintaining robust mechanical properties and hydrothermal stability. Post-synthesis modification of the zeolites has been tested with boronation to fine tune the sorption characteristics. Full characterization of the synthesized materials has been used to determine the suitability of the synthesized zeolites for noble gas separation as well as compare their properties with the existing materials.

Approach

There are several zeolite materials that are currently used at SRNL for noble gas sampling. These zeolites were developed many years ago. They have a proven record of consistent and reliable performance. These zeolites are used in two different ways: one time grab sampling and continuous concentration. The grab sampling method relies on capture of the noble gas by the zeolite, while the continuous concentration method uses zeolites that exclude noble gases and adsorb the other gases in air. As part of this project, zeolites have been synthesized and/or modified to give improved performance in both sampling methods. For the continuous concentration sampling zeolite, materials were synthesized with the aim of improving size exclusion of noble gases from the pores, and the composition of the zeolite surface was designed to increase the heat of adsorption for nitrogen and oxygen to give better separation and higher capacity(1-3). Microwave assisted and conventional hydrothermal synthesis of zeolites from raw materials was used to prepare the materials(4-6).

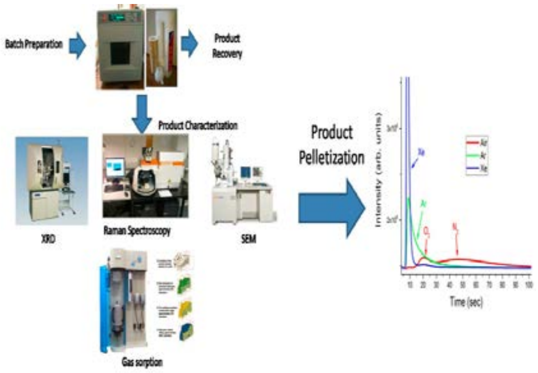

Figure 1. *Zeolite synthesis and characterization strategy*

Zeolite synthesis was performed at SRNL. Samples synthesized include mordenite, Linde type F, Linde type L, offretite, chabazite, faujasite and EMC-2. Powder x-ray diffraction crystallography (XRD), scanning electron microscopy (SEM), Raman spectroscopy, gas sorption analysis and nuclear magnetic resonance (NMR) spectroscopy were used for zeolite characterization. SEM has revealed crystal morphology for the different types of mordenites and offretites we have synthesized so far. XRD 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 known zeolite materials. Solid-state NMR analysis gave information on bonding environments of various elements in the crystal lattice. ^{27}Al and ^{29}Si NMR analysis has been performed on several custom engineered zeolites as well as commercially available products. 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).

Results/Discussion

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. Syntheses of known zeolites and variations on zeolite recipes 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. A series of mordenite samples were sent to NRL to be analyzed through solid state NMR. All NMR spectra were obtained using a Varian NMR500 spectrometer operating at a magnetic field strength of 11.7 T where the ^{27}Al and ^{29}Si resonance frequencies were roughly 130.3 and 99.4 MHz, respectively. A 4 mm triple resonance MAS NMR probe was used for all experiments and samples were loaded into the 4 mm rotors under ambient conditions. The typical sample mass was 50 mg. For the ^{27}Al MAS NMR spectra the spinning frequency was 12.5 kHz and a simple single-pulse excitation was used where the pulse length was 1 μs and the wait time between scans was 4 s. For the ^{29}Si MAS NMR spectra the spinning frequency was 10 kHz and rotor-synchronized Hahn spin echoes with proton decoupling were used with π/2 and π pulse lengths of 5 and 10 μs, respectively, and a delay between scans of 64 s. Chemical shifts were referenced to $AlCl_3$ (aq) and tetramethylsilane for ^{27}Al and ^{29}Si, respectively.

Initially variations on a mordenite synthesis were performed at 190^{o}C for five days in a Teflon lined pressure vessel within a conventional heating oven. To improve the synthesis, microwave heating was used in order to reduce the time of the reaction and increase sample purity. This reaction was performed by transferring the reaction mixture into a Teflon lined vessel and then heating in a microwave at a temperature of 220^{o}C. The purpose of this first set of syntheses was to study how long it takes to obtain a pure product tailored for our purposes. The microwave reactions were run at time lapses of five hours. After one lapse had passed an aliquot of the sample was removed, then the same process was repeated every five hours. The reaction concludes at the thirty hour mark. Figure 2 shows the ^{29}Si and ^{27}Al NMR spectra of the mordenite aliquots extracted every five hours(5). ^{27}Al and ^{29}Si MAS NMR spectra were obtained for mordenite samples synthesized in the microwave with reaction times of 10, 15, 20 and 30 hours. The masses of sample used for the NMR experiments were 43.6, 55.3, 66.0 and 65.7 mg, respectively. Each sample showed a single strong ^{27}Al peak around 55 ppm with spinning sidebands. The 10 hour (Fig. 2A) mordenite sample showed weak spinning sidebands, which implies a high degree of amorphous environment for the ^{27}Al, while the other three mordenite samples showed strong spinning sidebands, indicating a high degree of crystallinity. The chemical shift value is consistent with tetrahedrally coordinated aluminum with four bridging bonds through oxygen to silicon, which shows that the aluminum detected is incorporated into the zeolite framework. A small peak around 0 ppm, corresponding to octahedrally coordinated aluminum, implies that there is little extraframework aluminum, though it is possible that some extraframework aluminum could have an NMR peak broadened so much as to escape detection. The ^{29}Si spectra are similar for each sample, showing three overlapping peaks. The strongest peak around -112 ppm corresponds to silicon with no bridging bonds (Si-O-Al) to aluminum. The second peak around -105 ppm, roughly half the intensity of the first, is from silicon with one bridging bond through oxygen to aluminum. The weakest peak at -97 ppm is from silicon with two bridging bonds to aluminum.

A different study focused on mordenite microwave synthesis at temperatures ranging from 170-220°C. All reactions were completed in under 3 hours. A few milligrams of mordenite powder was added as a seed, CBV10ADS from Zeolyst Corporation, to catalyze the rate of growth of the synthesized mordenite. Figure 3 shows the ^{29}Si MAS NMR spectra obtained for synthesized mordenites where there is a clear evolution from a broad peak to a spectrum dominated by peaks at -106 ppm and -112 ppm corresponding to corresponding to $Si(OAl)(OSi)_3$ and $Si(OSi)_4$ respectively. The spectrum of the 180°C sample has much broader lines, indicating a poorly crystallized sample, while there are considerably narrower peaks for the 190, 200 and 210°C samples. The Si/Al ratio of the samples appears to increase (lower intensity of the peak at -106 ppm relative to the peak at -112 ppm) as the reaction temperature increases and the crystallinity of the sample improves, i.e. as the reaction moves further to completion. The signal as a function of delay between scans was fit to a stretched exponential indicative of a distribution: initially T_1~160 s and stretching exponent β~0.5, but gradually the T_1 shortened to ~40 s while the stretching exponential increased to ~0.7 (7-13).

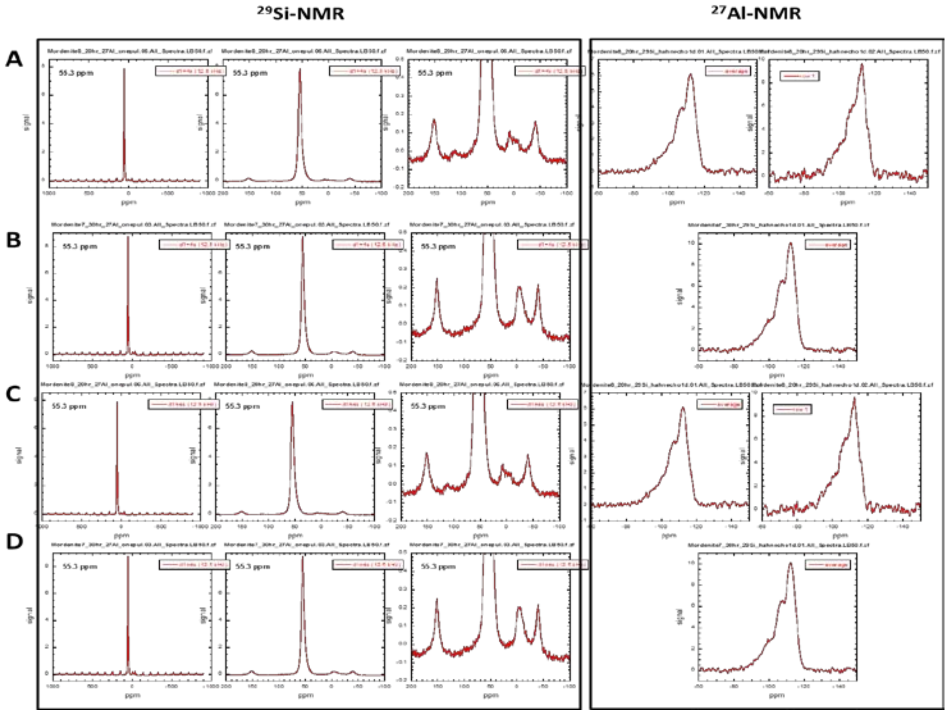

Figure 2. ^{29}Si MAS NMR and ^{27}Al MAS NMR spectra for mordenites synthesized for reaction times of (A) 10 hours, (B) 15 hours, (C) 20 hours and (D) 30 Hours. The spectra were obtained using a spinning speed of 12.5 kHz.

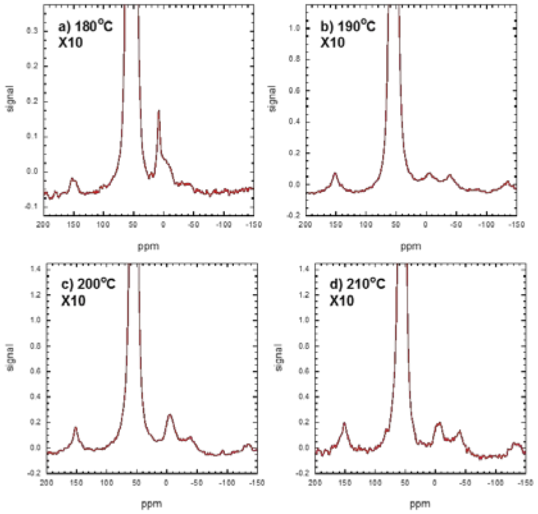

Figure 3. ^{27}Al MAS NMR spectrum for synthesized mordenites with masses of a) 50.3 mg, b) 39.4 mg, c) 49.6 mg, d) 50.5 mg. The spectra were obtained using a spinning speed of 12.5 kHz. A single pulse of 0.8 µs was used to excite the spins, with a wait time between scans of 2.0 s and a total of 256 scans.

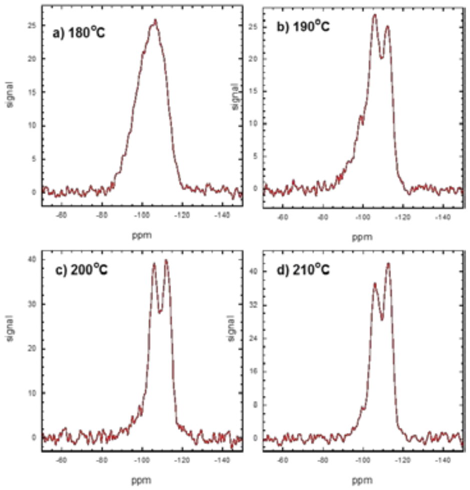

Figure 4. ^{29}Si MAS NMR spectrum for synthesized mordenites with masses of a) 50.3 mg, b) 39.4 mg, c) 49.6 mg, d) 50.5 mg. The spectra were obtained using a spinning speed of 12.5 kHz. A spin echo pulse sequence with pulses of length 2.5 µs and 5.0 µs was used to excite the spins, with a wait time between scans of 512 s and a total of a) 192 scans, b) 96 scans, c) 32 scans, d) 96 scans.

Microwave synthesis of the zeolite offretite(14) was performed at temperatures of 140-180°C. Seen in Fig. 5 are XRD scans and SEM micrographs of the syntheses of offretite at 160°C. We employed microwave heating in order to reduce the time of the reaction and increase sample purity. The reaction was performed by transferring the reaction mixture into a Teflon-lined vessel and heating in a microwave to temperature for a specified reaction time. The purpose of this first set of syntheses was to study how long it takes to obtain a pure product tailored for our purposes. The microwave reactions were run at time lapses of five hours. After one lapse had passed we removed an aliquot of the sample to be characterized by p-XRD. As seen on the left panel of Fig. 5, from the p-XRD, we reached the conclusion that the sample reached its highest degree of crystallinity at approximately 20 hours of the reaction. At this reaction time the diffraction pattern peaks reached maximum intensity. The XRD results obtained experimentally were compared to a database managed by the ICDD. All XRD peaks matched with those registered for offretite(15). The SEM images from (A) to (C) show a progression of the morphology of offretite. The structures are composed of long cylinders of porous fibrous type structures. At higher synthesis times, Fig. 5 (D) and (E), we see the formation of the fibrous type structures taking more of a conglomerate dome structure with a high degree of porosity.

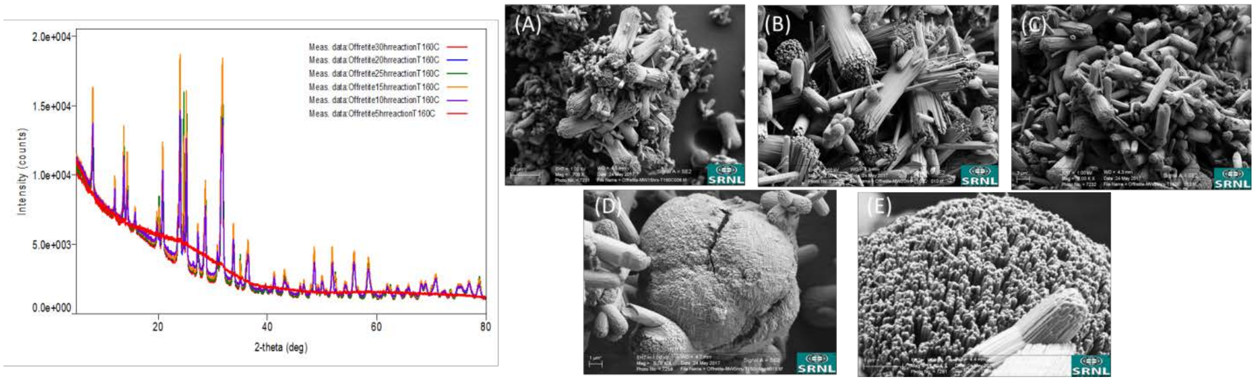

Figure 5. XRD scans of offretite (left) and SEM micrographs of offretite (right) synthesized at different reaction times. The right panel represents the SEM micrographs of Offretite (A) 10 hours, (B) 15 hours, (C) 20 hours, (D) 25 hours and (E) 30 hours.

The nitrogen adsorption isotherms for offretite synthesized at three different times are shown in Fig. 6A. Nitrogen adsorption isotherms of all the offretite samples synthesized showed type IV(b) isotherms in accordance with the latest IUPAC classification.(16) It indicates that for all samples, the initial steep increase in volume adsorbed at low relative pressure $(p/p_0)<0.02$ is ascribed to the monolayer-multilayer adsorption. The second uptake of nitrogen close to the saturation pressure via a multilayer adsorption indicates the presence of mesoporosity by condensation of nitrogen in the pores. Analysis of the adsorption isotherms of the offretite samples synthesized by microwave heating at treatment of 15 hours to 25 hours reveal that the surface area of the samples is 147 m^2/g, 220 m^2/g, and 410m^2/g, respectively, as seen in Table 1. The increase of the surface area shows the increase in the number of adsorption sites and sample crystallinity when the microwave reaction time was prolonged. The enhancement of crystallinity leads to a lower probability of aggregate formation and the minimization of amorphous phases. It was noticed as well that the micropore volume increases when the samples are exposed to longer microwave reaction times, which suggests that porosity between the particles decreased at longer synthesis times (17). A separate study was performed by leaving the reaction mixture aging from one day to 5 days prior to microwave heating treatment. The best results were obtained with samples aged for one day prior to microwave heating treatment. There was an increase in surface area when the sample was aged for one day versus a reaction at the same temperature with no aging, as seen in Table 2. Offretite was also synthesized at different temperatures at a fixed reaction time with the reaction mixture aged for one day. For the samples aged one day, an increase in specific adsorption volume and microporous volume with increasing reaction time up to 20 hours was seen, as shown in Table 2. Those trends also indicate an increase in the number of adsorption sites and sample crystallinity when the microwave heating time was increased.

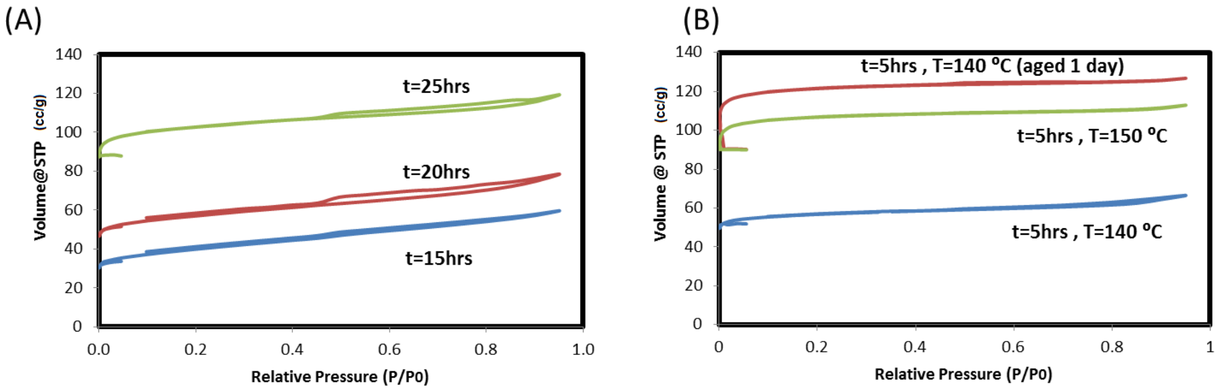

Figure 6. Gas sorption isotherms of offretite: (A) synthesized in the microwave at a temperature of 160^{o}C with varying reaction time, (B) reaction mixture aged for one day prior to microwave synthesis for five hours at different temperatures.

Table 1. Gas sorption analysis results of offretite synthesized at 160^{o}C at different microwave heating treatment times

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

Table 2. Gas sorption analysis results of offretite synthesized at 150^{o}C, with the sample batch aged 1 day prior to microwave heating

Gas Sorption Experiments-Microwave synthesis at T=150^{o}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

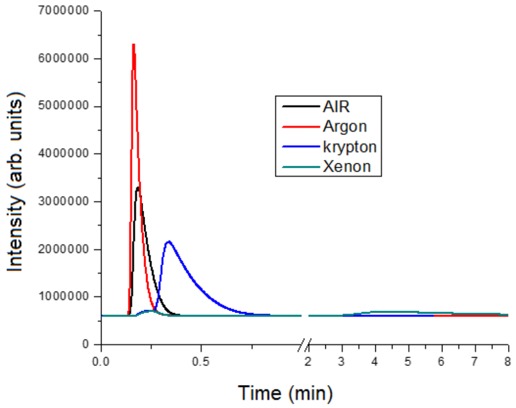

Figure 7: Chromatograms of various gases on column made with offretite 20 hr reaction at 160°C.

Chromatographic testing was performed on synthesized offretite samples. Figure 7 shows chromatograms of air, argon, krypton and xenon on a column made with an offretite sample synthesized for 20 hours at 160°C. The offretite zeolite samples show promising separation of krypton and xenon. Based on the performance of the samples in gas sorption and gas chromatographic separation experiments, offretite samples have been selected as the best candidate for pelletization and testing in separation systems. Due to having the best crystallographic structure results from XRD analysis, as well as crystallinity and sample purity from NMR analysis, synthesized Linde Type F and mordenite samples are the next most likely candidate samples for pelletization and separation testing.

FY2017 Accomplishments

- Syntheses of known zeolites have been performed using microwave and conventional oven hydrothermal synthesis.
- The following compounds have been synthesized: 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 for submission to peer-reviewed journals.
- Variations in reaction conditions and recipes of offretite 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.
- Gas chromatography screening for separation characteristics has been done on 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.

Future Directions

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

FY 2017 Publications/Presentations

- Two publications are in the preparation stages for submission to peer-reviewed journals.
- ACS Southeast Regional meeting as a poster in October 2016.

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Acronyms

DFT : Density functional theory
NMR: Nuclear Magnetic Resonance
SEM: Scanning Electron Microscope
XRD: X-ray Diffraction

Intellectual Property

None

Total Number of Post-Doctoral Researchers

None