Developing an Engineered Form of MOFs

CaSDB and HKUST–1

Nuclear Technology
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Summary

Selective krypton (Kr) and xenon (Xe) capture experiments for various adsorbents have been performed extensively at Idaho National Laboratory (INL). As part of the Off-Gas Sigma Team efforts, Pacific Northwest National Laboratory (PNNL) has suggested the use of metal-organic frameworks (MOFs) in place of more traditional inorganic sorbents. In 2016, PNNL developed compressed and ground engineered forms of calcium–4,4’–sulfonyl dibenzoate (CaSDB) MOF which was subsequently tested at (INL). The tests revealed that the CaSDB had a sufficient saturation capacity, but a low breakthrough capacity. The larger issue was that the CaSDB form was not robust enough to withstand the handling necessary for installation in a flow through column.

In 2018, PNNL sent two untreated MOFs, CaSDB and Hong Kong University of Science and Technology–1 (HKUST–1), to INL. INL’s goal was to develop an engineered form that maintained adsorption properties comparable to the original MOFs with mechanical strength desired for use in a column. Initial testing consisted of batch-wise contacts of the MOFs with aprotic solvents and water, to ensure that the material did not dramatically degrade. Brunauer, Emmett and Teller (BET) analyses confirmed that the MOFs could be exposed to water and DMSO without significant losses in surface area. MOF engineered forms were successfully produced, CaSDB–EF1 and HKUST–EF2, using the INL-patented procedure for composite manufacture (USA Patent No. 8,686,083, 2013). BET analyses performed on the engineered forms yielded surface areas of 148 m^2/g and 1487 m^2/g for CaSDB–EF1 and HKUST–EF2 respectively, nearly all of the surface area of the respective untreated materials. These engineered forms were also qualitatively evaluated for mechanical stability. Both engineered form MOFs are deemed acceptable for further study to determine efficacy for selective Kr and Xe capture.

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Acronyms

1M2P	1–methyl–2–pyrrolidinone
BET	Brunauer, Emmett and Teller
CaSDB	Calcium–4,4'–sulfonyl dibenzoate
DMSO	Dimethyl sulfoxide anhydrous
DMAC	Dimethylacetamide
EF1	First engineered form
EF2	Second engineered form
HKUST–1	Hong Kong University of Science and Technology MOF made up of copper nodes and 1, 3, 5 – benzenetricarboxylic acid linkages
INL	Idaho National Laboratory
MOF	Metal–organic framework
PAN	Polyacrylonitrile
PNNL	Pacific Northwest National Laboratory

Developing an Engineered Form of MOFs CaSDB and HKUST–1

1. Introduction

As part of the Off-Gas Sigma Team, INL has been conducting research focused on the removal of Kr and Xe in gas effluents generated from nuclear fuel reprocessing activities. The research focused on physisorption techniques utilizing thermal swing and pressure swing conditions. Unfortunately, commercially available engineered form sorbents typically have low surface areas and are therefore, not conducive to physisorption of noble gases. This fact resulted in the development of new sorbent manufacturing techniques to prepare engineered forms that retain the characteristic high surface areas contained in the active ingredients by incorporating them into a polyacrylonitrile (PAN) binder. Two mordenite powders were successfully incorporated into the PAN and tested at INL. Additionally, MOF materials have been developed and investigated at PNNL with reportedly higher pore surface areas than inorganic compounds.

The primary reason for development of these new adsorbent materials is to test the selective partitioning of Kr and Xe from air, which is the bulk carrier gas of nuclear facility emissions. In 2016, PNNL synthesized a CaSDB MOF (Banerjee, et al., 2016) and produced an engineered form by compressing it into a puck and then grinding it to size. The resultant material was tested at INL. Initial testing concluded that CaSDB had a sufficient saturation capacity for Xe, but a low breakthrough capacity (Welty, Garn, & Greenhalgh, 2018). The physical examination of the material in the 2016 report refers to CaSDB as being easily friable to a fine dust, which will pose engineering challenges when designed for use in a flow through process.

For the MOF materials to be viable in a flow through system they must be converted into a robust engineered form. The ideal engineered form will possess a capture capacity comparable to the original material but have a more durable physical form that will not easily migrate through a flowing system or form restrictions resulting in over-pressurization. In 2018, PNNL sent two MOF samples, CaSDB and HKUST–1 in untreated forms to INL for conversion into engineered forms. This report summarizes the approach and formation of two engineered forms of these materials utilizing the INL patented method of forming a composite PAN material (USA Patent No. 8,686,083, 2013).

2. Characterization of Material

Each as received MOF was physically studied and weighed. Kr and Xe capture with the MOFs is a physisorption process, which means adsorption occurs when a gas molecule gets trapped in a pocket or pore in the MOF micro-structure. Capacity can therefore be linked to the MOF’s surface area. The initial BET surface areas of both materials were obtained from a nitrogen adsorption isotherm in the relative pressure range (P/P_0) of 0.05-0.3 using a Micromeritics ASAP 2020 analyzer.

2.1 CaSDB

The as received CaSDB was a very fine dusty powder, white or light grey in color (Figure 1). The initial mass of the material received from PNNL was 9.4936 grams. A small sample was degassed at 150°C for 4 hours in preparation for a BET analysis. The BET analysis concluded that the material had a surface area of 219 m^2/g. For comparison, BET analyses on previous batches of the compressed CaSDB yielded surface areas of 4 m^2/g and 81 m^2/g (Welty, Garn, & Greenhalgh, 2018).

2.2 HKUST–1

HKUST–1 was a larger particle size crystalline MOF that appeared to be very sticky. In the presence of ambient air, it was observed that the material changed from a deep purple color to a teal color. It is speculated that the material almost instantaneously adsorbs moisture from the air which causes the oxygens from the water to coordinate around the MOF's copper centers thus, changing its color (Kim, et al., 2015). BET analysis on this material resulted in a surface area of 1777 m^2/g.

3. Initial Testing: Solvent Effects on MOF Surface Area

The patented process to convert fine solid material into a robust engineered form by incorporation into PAN utilizes an aprotic solvent and water (USA Patent No. 8,686,083, 2013). Based on this process, the MOF materials were contacted batch-wise with various aprotic solvents and water at ratios typically used in the formation process to ensure that the surface area would not change significantly after exposure. The batch contacts consisted of 0.2 grams of MOF and 0.600 mL of respective solvent in a test tube that was gently agitated on a Glas-Col rotary mixer for one hour. Nanopure water was used to wash down any material stuck to the sides of the test tubes. The samples were centrifuged, and the liquid was decanted. Nanopure water was added to each tube to wash any remaining solvent off of the MOF. The tubes were agitated for 20 seconds on a Fisher Scientific vortex mixer. The samples were centrifuged again, and the water was decanted. This wash cycle was repeated for a total of three washes. Samples were uncapped and placed into a 100°C oven to dry. BET analyses were then performed on the dried samples.

3.1 CaSDB

CaSDB was contacted with both nanopure water and di-methyl sulfoxide (DMSO). Upon initial contact no drastic changes were observed (Figure 1). After contacting for one-hour black solids were observed in both samples. In Figure 2 it can be observed that the water contact contained several smaller black specks while the DMSO contact had a single large black flake. This could be an indication of MOF decomposition when introduced to liquids or impurities in the MOF sample. Quantity of the black material was deemed insufficient for analytical determination.

During the washing of the test tubes the mixture in the water contact became cold, indicating an endothermic reaction, whereas the DMSO/ water mixture became warm, indicating an exothermic reaction. Temperature changes were not observed in subsequent washes. It was noted that the material remained partially suspended after centrifugation due to the fine nature of the powder. The suspensions made it difficult to remove only the supernate. The CaSDB solid losses are documented in **Error! Reference source not found.**.

Table 1. Mass of CaSDB in each tube, pre and post contact.

	Untreated	**H_2O**	**DMSO**
Initial Mass (g)	0.1973	0.2075	0.2037
Post Oven Mass (g)	0.1862	0.0862	0.1107
% Loss	5.6%	58.5%	45.7%

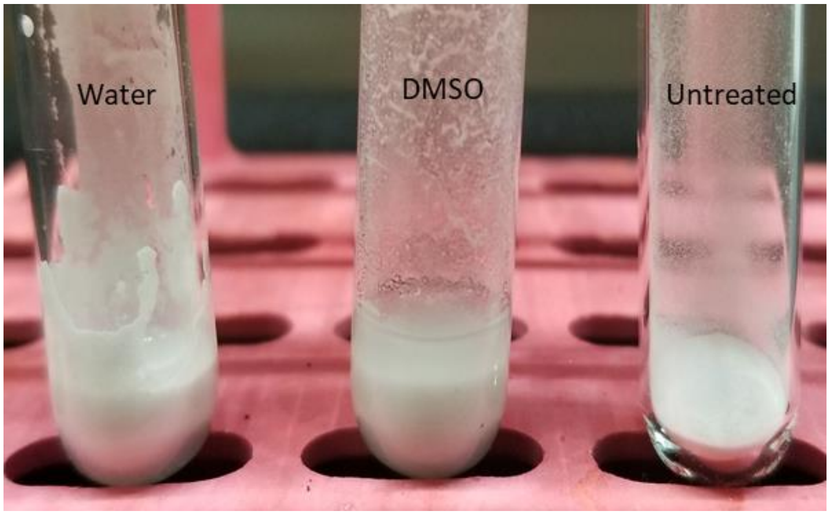

Figure 1. CaSDB contacts immediately after the addition of each solvent compared to untreated material.

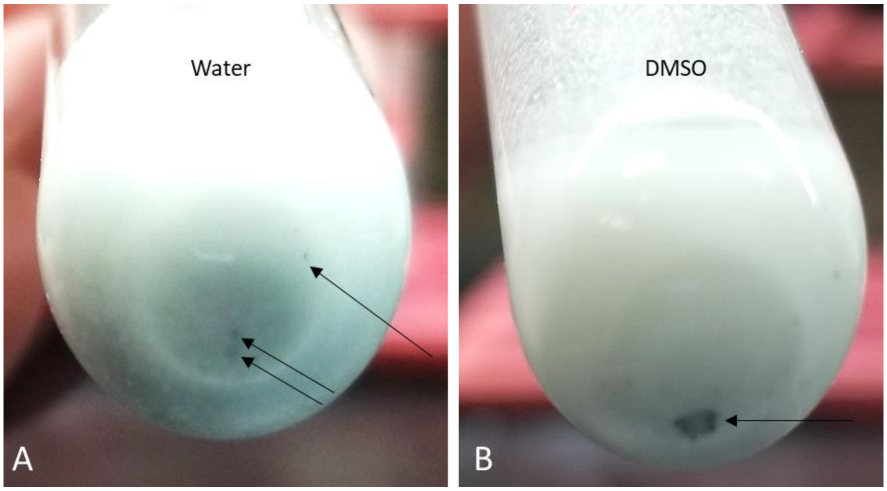

Figure 2. A) CaSDB water contact after one-hour of agitation. Multiple small black specks were observed. B) CaSDB DMSO contact after one-hour of agitation. A large black flake was visible at the bottom of the test tube.

Following solid-liquid separation, the solids were placed in an oven and dried for 48 hours. Solid samples were then transferred to a BET tube and weighed. The BET samples were degassed in accordance with section 2.1. BET analysis of the batch contacts yielded surface areas of 187 m^2/g for CaSDB contacted with water and 125 m^2/g for CaSDB contacted with DMSO. Though a 43% decrease in surface area was observed with the sample contacted with DMSO, the post contact surface area was still found to be higher than previously received batches of CaSDB.

3.2 HKUST–1

HKUST–1 was tested with water and three solvents: DMSO, 1–methyl–2–pyrrolidinone (1M2P) and dimethylacetamide (DMAC). Initial contact of the material with water immediately caused it to change to a teal color (Figure 3A). Contact with DMAC yielded a darker teal color whereas in the DMSO and 1M2P contacts the material remained deep purple (Figure 3B).

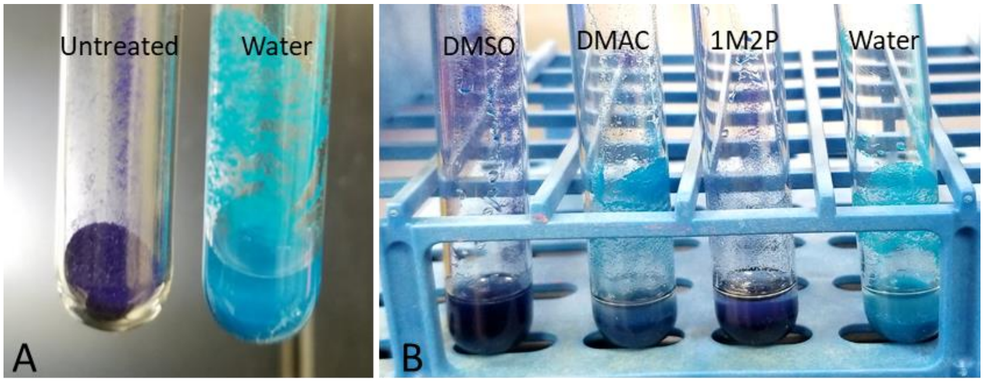

Figure 3. A) HKUST–1 immediately after contact with water compared to untreated HKUST–1. B) HKUST–1 immediately after contacting each solvent.

After samples were removed from the rotary mixer, it was noted that the HKUST–1 naturally separated from the solution. The water contact remained its original teal color and the DMSO contact changed to the teal color. The DMAC and 1M2P contacts changed slightly to a dark blue color (Figure 4). The samples were centrifuged, and the remaining liquid was decanted.

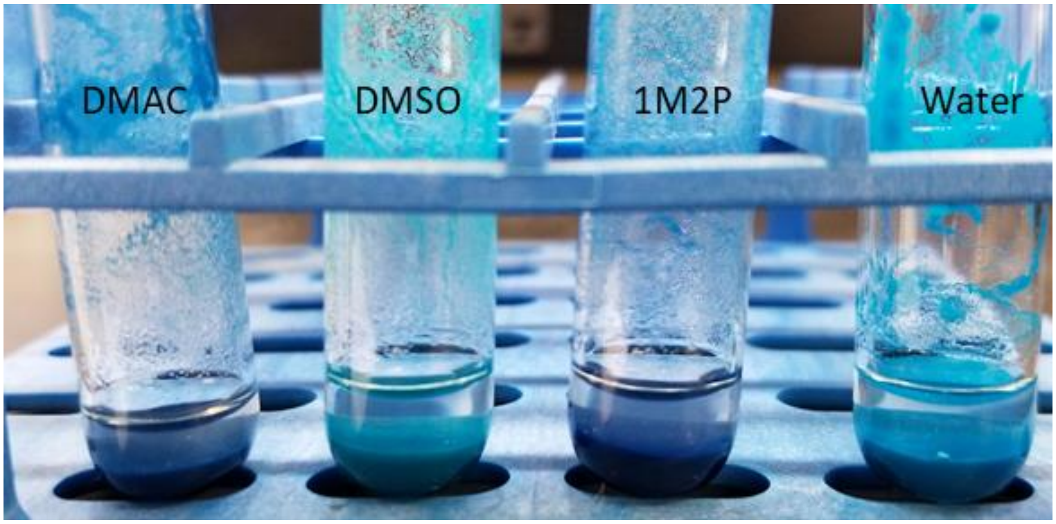

Figure 4. HKUST–1 contacted with respective solvents after one- hour agitation.

Sample tubes were rinsed using water, then agitated. The HKUST–1 in each tube turned teal after contact with the water. Following agitation, the DMSO and 1M2P contacts produced bubbles that lifted material from the bottom of the tube throughout the solution. Two solid phases were observed. The material being lifted through solution was teal and had a fluffy coagulated appearance, whereas the material at the bottom of the tube remained teal and grainy (Figure 5A). The DMSO contact ceased to produce bubbles after centrifugation; however, the 1M2P contact continued to produce small bubbles (Figure 5B). White flakey solids were settled on top of the material (Figure 5C). It was present in all samples, but most prevalent in the water contact.

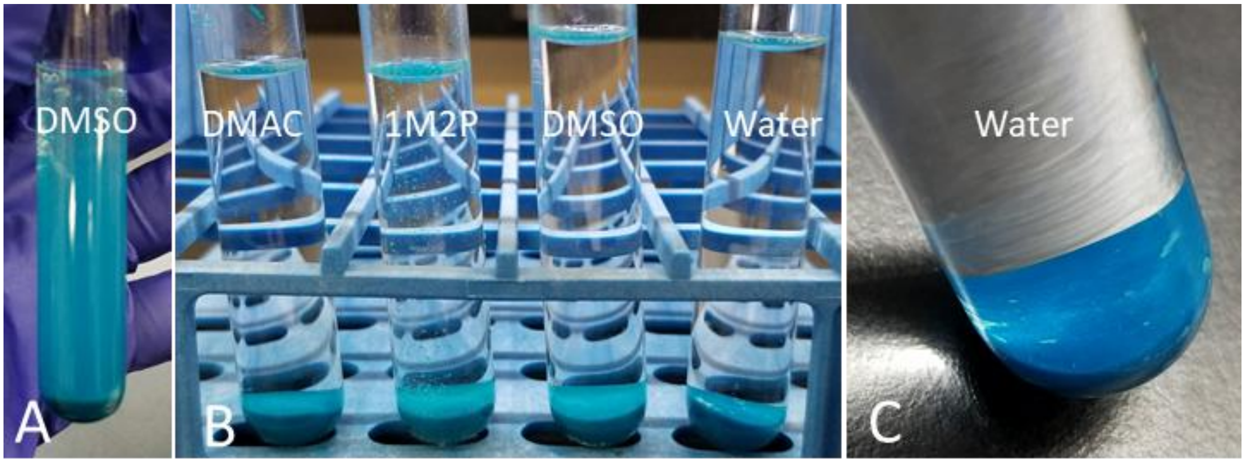

Figure 5. A) Two solid phases, and large bubbles visible in the HKUST–1/ DMSO contact after the first rinse and agitation. B) Samples after the first rinse and centrifuge. The HKUST–1/ 1M2P contact produced small bubbles that carried HKUST–1 throughout the solution. C) Close up of white flakey solid present in the HKUST–1/ water contact.

The solid samples were washed three times with water and then placed in an oven to dry overnight. After drying, all the samples turned to a rich royal blue color (Figure 6). Samples were degassed at 200°C for 6 hours before BET analysis. Degassing restored the material's original deep purple color, which would affirm that the color changes are a result of water interaction with the HKUST–1. Surface areas were obtained for each sample (**Error! Reference source not found.**). HKUST–1 recovered from the 1M2P contact lost almost 55% of its original surface area. After the DMSO/ water contact, HKUST–1 maintained approximately 70% of its initial surface area.

The surface area analysis results obtained from these preliminary batch contacts suggested that an effort to prepare engineered forms of CaSDB and H-KUST-1 using DMSO/ H_2O was feasible. Due to the limited mass of each received MOF, only one attempt at an engineered form could be made for each MOF.

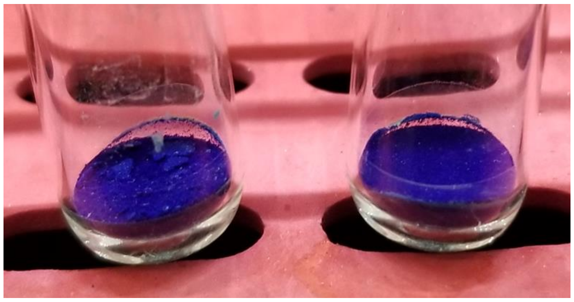

Figure 6. HKUST–1 contacts after drying in a 100 °C oven overnight.

Table 2. Surface area after HKUST–1 contact with various solvents.

	Untreated	**Water**	**DMSO**	**DMAC**	**1M2P**
Surface Area (m^2/g)	1777	1215	1232	1190	811
% Loss	-	31.6%	30.7%	33.0%	54.4%

4. Engineered Form Development

The appropriate amount of MOF to achieve approximately 80% weight loading was added to 15 mL of DMSO. The mixture was heated to approximately 80°C. PAN fibers were slowly dissolved into the mixture and it was heated and stirred until the desired consistency was obtained. A custom glass apparatus was used to dispense drops of the mixture into an agitated pool of water. The pool quenched the drops into the desired engineered form.

Ideally, the engineered form would be consistent in shape and size. The engineered forms were dried and weighed before being sieved. Particles between 425 and 1400 µm were deemed acceptable for further testing. To verify that the MOFs retained sufficient surface area during processing, a BET analysis was performed on the new material. A qualitative agitation test was also performed on the new engineered materials as well as the compressed CaSDB MOF to test the robustness. An appropriate amount of material was placed in a 25 mL test tube that was then agitated on a Glas-Col rotary mixer set to approximately 18 rpm for one-hour. Particles were observed before and after agitation.

4.1 CaSDB Preparation

DMSO and 5.0073 grams of CaSDB were combined in a beaker. The mixture was stirred and heated to approximately 80°C. When the mixture was homogeneous, 1.0080 grams of PAN fibers were slowly added. The complete mixture was stirred and heated until it reached the desired viscosity. The mixture was cooled for 2 min and then processed through the glass apparatus. The CaSDB engineered form (CaSDB–EF1) beads were collected and rinsed to remove excess DSMO. The material was dried overnight in an oven and the yield of CaSDB–EF1 was 3.6696 grams. A mass loss was expected and attributed to coating of glassware used during solid formation. Most of the engineered form was spherical, larger than 425 µm and had a measured BET surface area of 148 m^2/g (Figure 7).

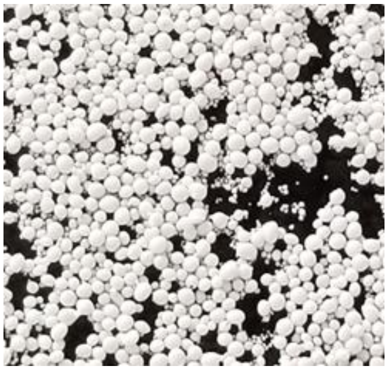

Figure 7. CaSDB–EF1 after being dried

4.2 HKUST–1 Preparation

DMSO and 5.0079 grams of HKUST–1 were combined in a beaker. The mixture turned teal, produced bubbles, and the beaker became warm. Though bubbles were observed in the small HKUST–1/ DMSO solvent contact, no heat was observed. Heat generation could have been overlooked because it rapidly dissipated from the mixture. After cooling to room temperature, the mixture was placed on a hotplate set to 80°C. The PAN fibers were slowly dissolved into the mixture. Once the PAN had dissolved, the mixture appeared to be more viscous than the CaSDB mixture. When this mixture appeared homogeneous, it was transferred to the glass apparatus. Because the mixture was thick, it clung to the walls of the glass drop device which made droplet size and shape difficult to control. The resulting engineered form varied greatly in size and shape. Most commonly, tadpole-shaped particles were observed (Figure 8A).

It was determined that the HKUST–1 engineered form (HKUST–EF1) should be re-dissolved and the engineered form remade. The HKUST–EF1 particles and films were collected in a beaker. A separate beaker of 15 mL of DMSO was heated to 80°C and the HKUST–EF1 material was slowly added to the hot solvent to allow the large pieces to dissolve. Once all the HKUST–EF1 was dissolved by the solvent, the mixture was observed to be very similar to the original mixture. The hotplate temperature was increased to 85°C and the mixture was stirred for approximately one-hour in an attempt to thin the solution. The resultant mixture was a slightly less viscous solution than desired, so it was cooled for one minute before pouring into the glass dropper device. The resulting engineered form, HKUST–EF2, had a more uniform size and shape than the previous batch (Figure 8B). The teal solid was dried in a 100°C oven where it became a lavender color. A BET analysis was performed, and a surface area of 1487 m^2/g was obtained.

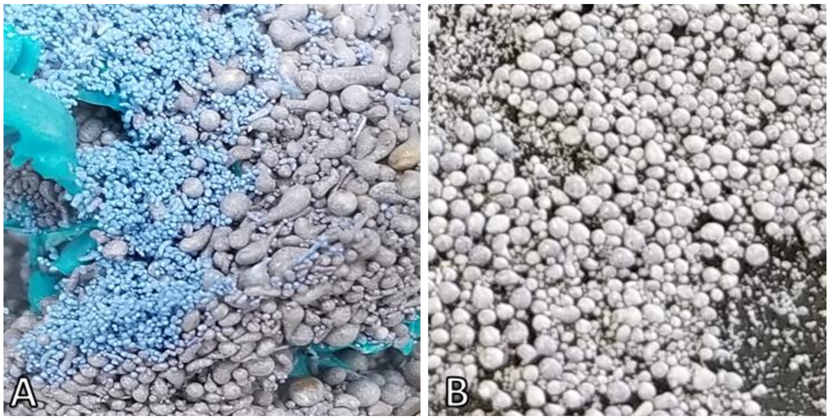

Figure 8. A) HKUST–EF1 collected in a beaker in preparation for dissolution. The various materials are: the film that coated the inside of the dropper (teal), particles less than 425 µm (light blue), and particles between 425 and 1400 µm. B) HKUST–EF2 after drying. Notice the nearly spherical shape as compared to the purple material in Figure A.

4.3 Engineered Form Mechanical Stability

Small samples of the original compressed CaSDB, CaSDB–EF1 and HKUST–EF2 were placed into 25 mL glass test tubes and rotated on the Glas-Col rotary mixer at approximately 18 rpm for one-hour. The compressed CaSDB formed a powder that dusted the sides of the test tube after only a few rotations. The material before and after agitation are shown in Figure 9.

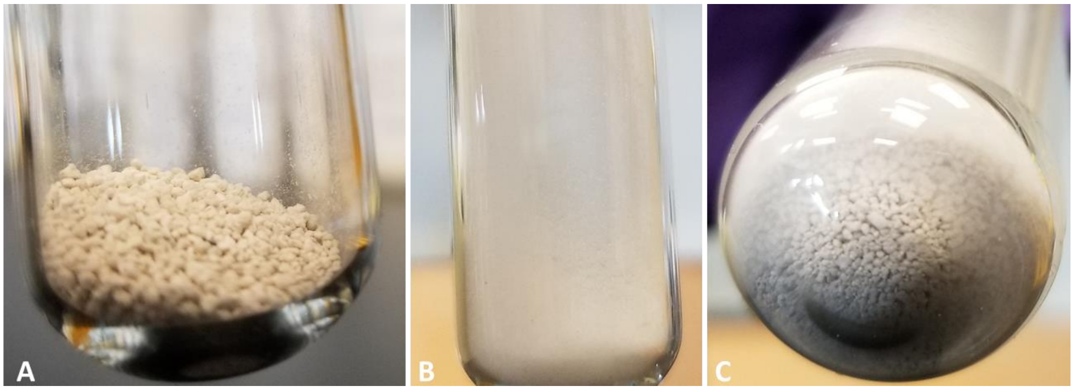

Figure 9. A) Compressed CaSDB engineered form before agitation. B) Compressed CaSDB engineered form after agitation. The test tube was very dusty, indicating that the material was not in a stable engineered form. C) After agitation a wide range of particle sizes were observed.

In both the CaSDB–EF1 and the HKUST–EF2 tubes, no significant changes in particle size or dust were observed, indicating the desired mechanical strength. The before and after of CaSDB–EF1 can be seen in Figure 10 and HKUST–EF2 can be seen in Figure 11.

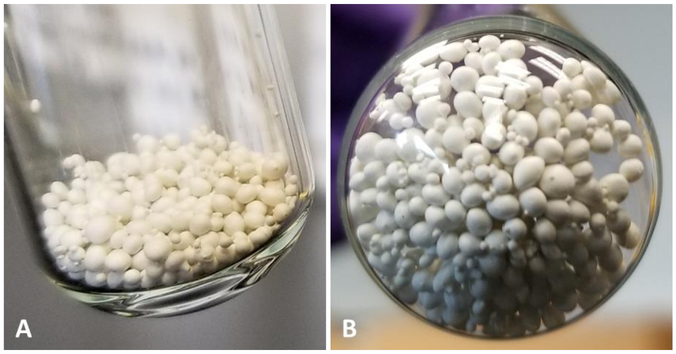

Figure 10. A) CaSDB–EF1 before agitation. B) CaSDB–EF1 after agitation. The particles appear to be comparable in size to the particles in A.

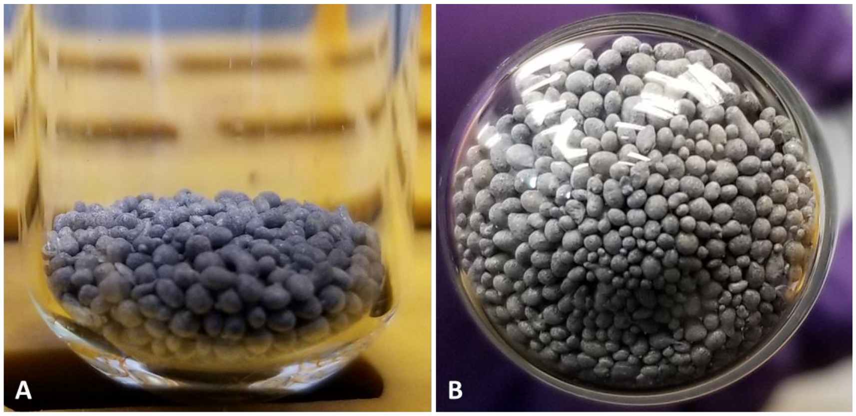

Figure 11. A) HKUST–EF2 before agitation. B) HKUST–EF2 after one hour of agitation. Particle size remains unchanged.

5. Conclusions

Initial batch contacts of the CaSDB and HKUST–1 indicated that both MOFs could be contacted with DMSO and water without causing significant loss of surface area. Engineered forms of both MOFs were successfully produced. A qualitative agitation test of the new materials confirmed the engineered forms were more robust than starting materials and previous engineered forms. Both CaSDB–EF1 and HKUST–EF2 maintained sufficiently high surface areas of 148 m^2/g and 1487 m^2/g respectively. Since the production of the MOF engineered forms was considered successful, further testing will be conducted to investigate the efficacy of the engineered forms.

6. References

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