Mechanochemical Synthesis of UiO-66

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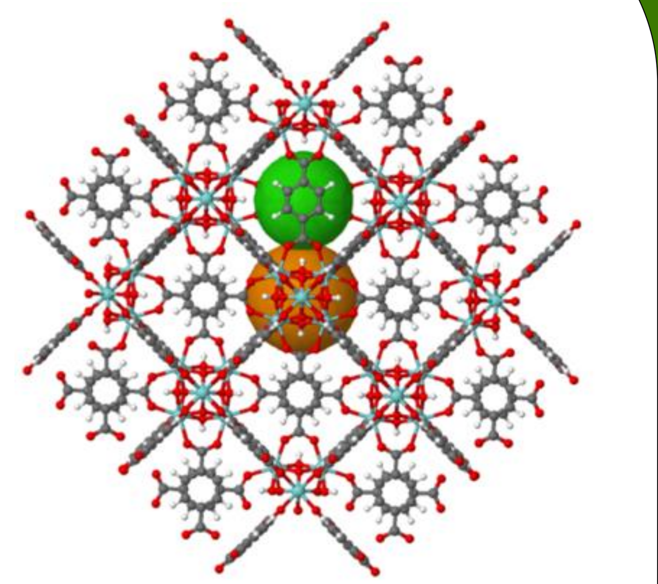
Introduction

- The current solvothermal synthesis of UiO-66 is costly and wasteful.
- Mechanochemical synthesis has emerged as a sustainable alternative, aligning with green chemistry principles.
- UiO-66 was synthesized using mechanochemistry with commercially available materials.
- Characterization of UiO-66 was performed using powder X-ray diffraction (PXRD).
- This synthesis approach will enable sustainable testing of UiO-66's potential applications.



Real World Applications

- Zr-MOFs, like UiO-66, are being studied for their ability to break down:
- Chemical warfare agents (CWAs).
  - Organophosphorus nerve agents through catalytic processes.
  - These MOFs effectively detoxify nerve agent stimulants by enabling rapid hydrolysis.[3]
- Zr-based MOFs' potential to capture per- and polyfluoroalkyl substances (PFAS) show:
  - High adsorption rates for PFAS.
  - Potential as an alternative to traditional degradation methods.

Green Chemistry

- MOF research focuses on 4 of the 12 principles of green chemistry: design, synthesis, activation, and application[1]
- Mechanochemical synthesis reduces energy input, is scalable, and time efficient (under 30 minutes)
- It uses less organic solvent, making it more cost-efficient

Mechanochemistry

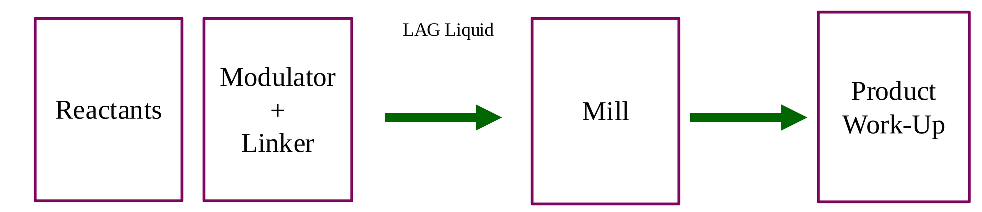
- In a general sense, chemical and physical reactions are induced by applying mechanical force
- Aqueous chemical by-product
- The use of LAG reduces the amount of amorphous material[2]

Procedure

- The milling jars are loaded into the mill with the UiO-66 starting materials and LAG solution
- Milled at a frequency of 30 Hz for 30 minutes
- Teflon milling jars with zirconium balls are used

Retch™ MM400 Electric Ball mill

Teflon Milling Jars and Zr Infused Ceramic Balls



Mechanochemical vs. Solvothermal Processes

Solvothermal Process
- Starts from a zirconyl cluster
- The whole synthesis process, including drying, takes days
- Uses large amounts of organic solvent

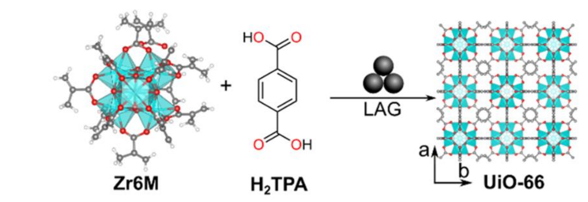
Mechanochemical
- Used 100 uL of organic solvent
- Reaction time of 30 minutes on the mill and 2 hours in the oven
- Made from commercially available starting materials

UiO-66

- Zr- based MOF
- Crystalline structure with a large surface area (approximately 1211 m^2/g)[2]
- High thermal stability at 300°C and decomposes at 500°C[2]
- Two primary pore structures with gas adsorption capabilities
- Stable in water and acidic conditions

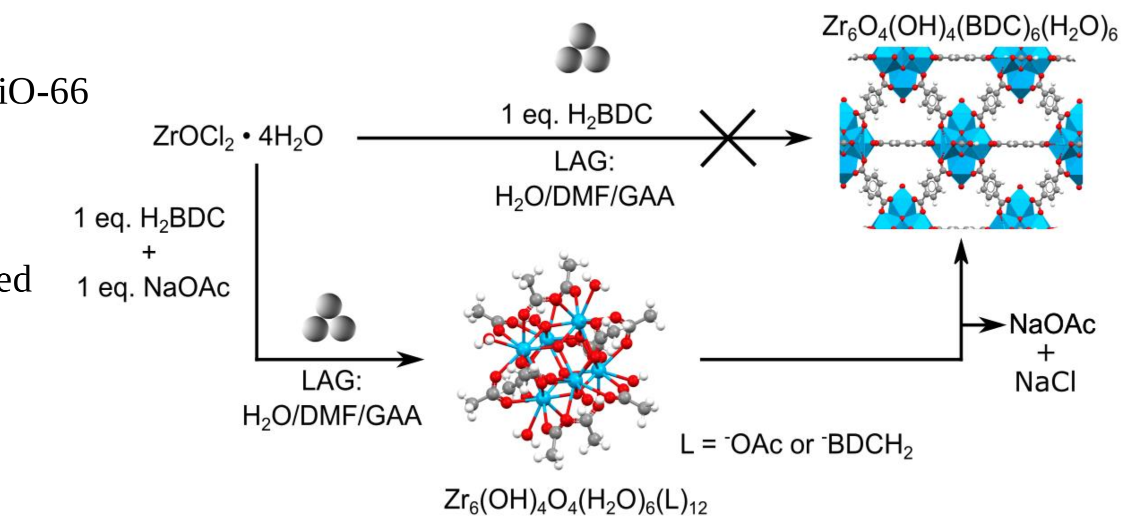
Previous studies

- UiO-66 has been synthesized mechanochemically, but in previous studies, the synthesis starts from a Zirconyl methacrylate cluster [$Zr_6O_4(OH)_4$] and adds terephthalic acid (H_2BDC) organic linkers[4]



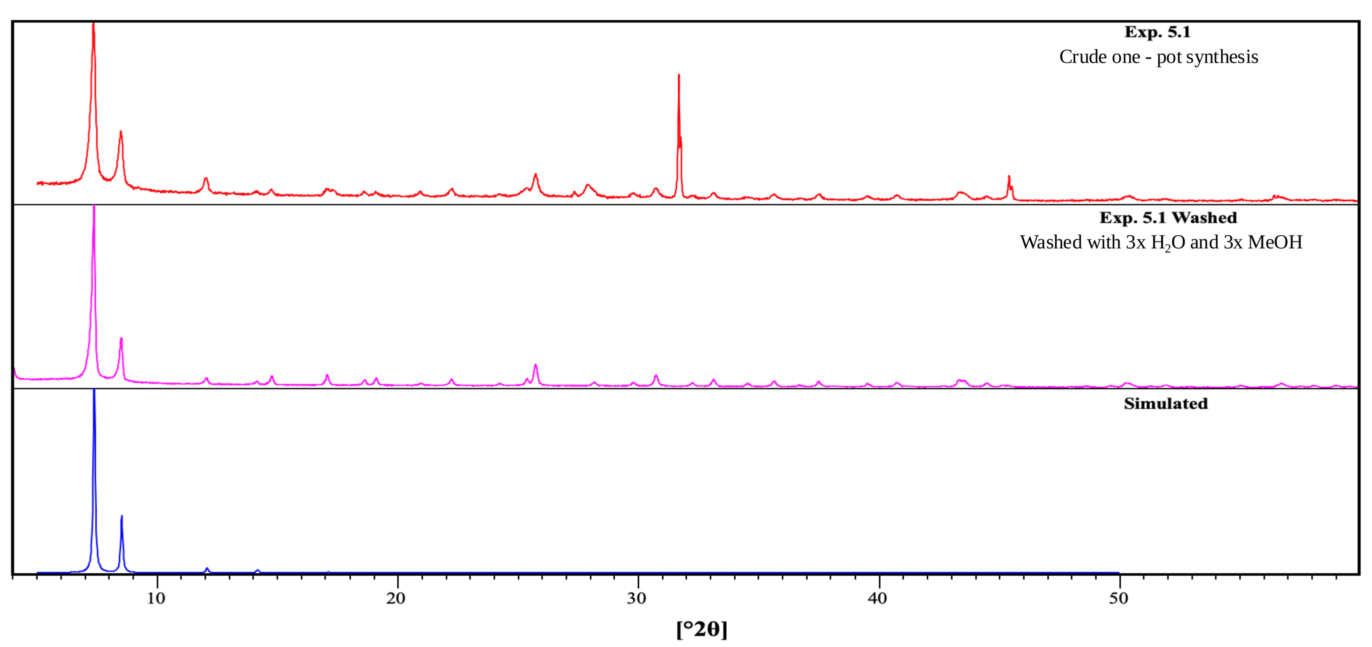
Our Approach

- We aimed to make UiO-66 using commercially available $ZrOCl_2$ and H_2BDC
- In a one-pot modulated synthesis



Results and Discussion

Characterization Data

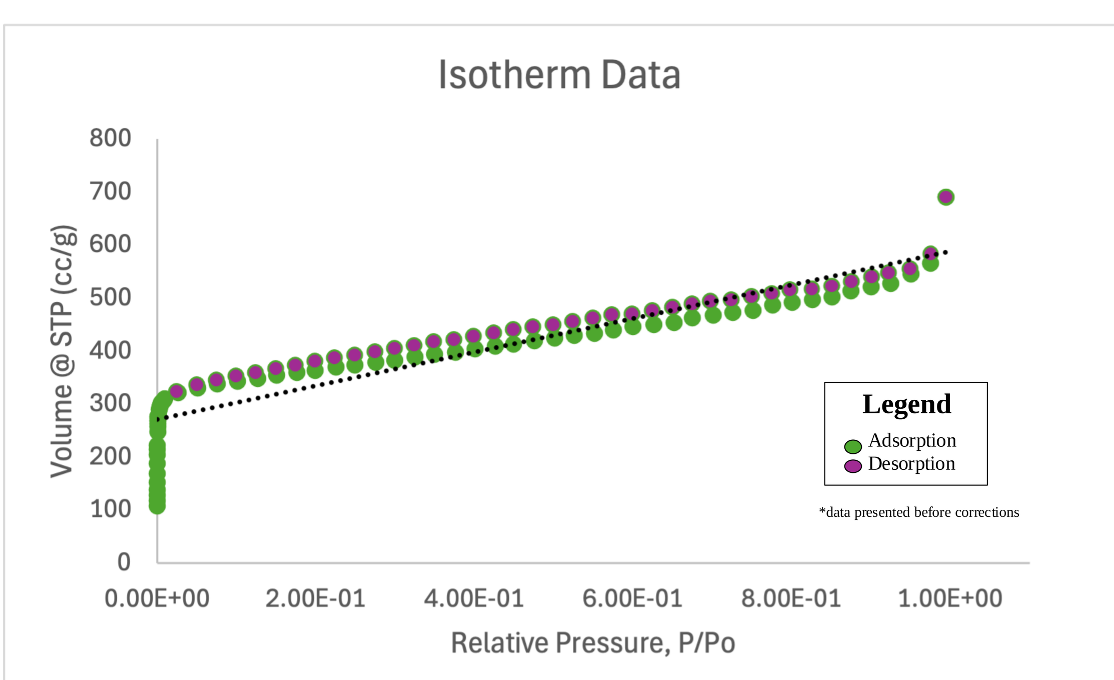


Wash Product

- MOFs need to be washed to activate porosity: before the wash, they are full of salt
- First was was done with 15 mL of H_2O x3 to remove the salt
- Second wash was done with 15 mL of EtOH x3 to remove the organics

PXRD

- One-pot synthesis
- The crude mixture of UiO-66 resembles the simulated product
- Washed product indicates that we have successfully created UiO-66



Brunauer-Emmett-Teller (BET) Analysis

- BET analysis explains the physical adsorption of gas molecules on a physical surface.
- Measuring the surface area of the samples using the nitrogen sorption isotherms at 77 K for 24 hours [5]

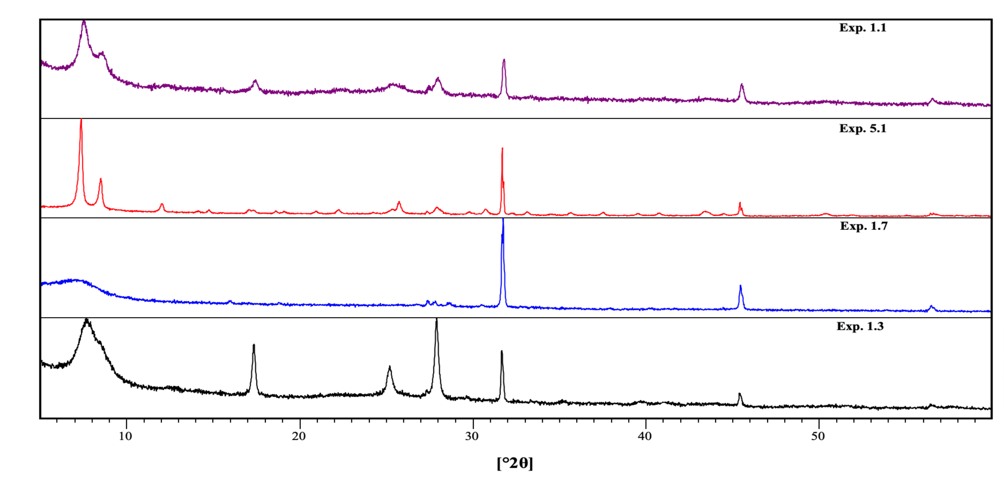
Surface Area

- MOFs are renowned for their high surface area
- Uncompressed solvothermal samples report surface areas reaching 1125 m^2/g [5]
- The mechanochemical synthesis yielded a surface area of 866.01 m^2/g before corrections

Varying the Stoichiometric Ratio

Based on MOF-74, we started with a 1:1:1 ratio. All reactions had the same conditions following (except 5.1*): a 1:1 LAG ratio of DMF&H2O, 1x Milling Balls, Milled for 30 min @ 25 Hz, and no pre-heating

The 1:2:1 ratio produced the best product. The next step was to optimize the LAG solvent.



Exp 4.3			
Stoichiometric Ratio	1	1	0.5
Compounds	$ZrOCl_2$	H_2BDC	NaOAc

Exp 5.1			
Stoichiometric Ratio	1	1	2
Compounds	$ZrOCl_2$	H_2BDC	NaOAc

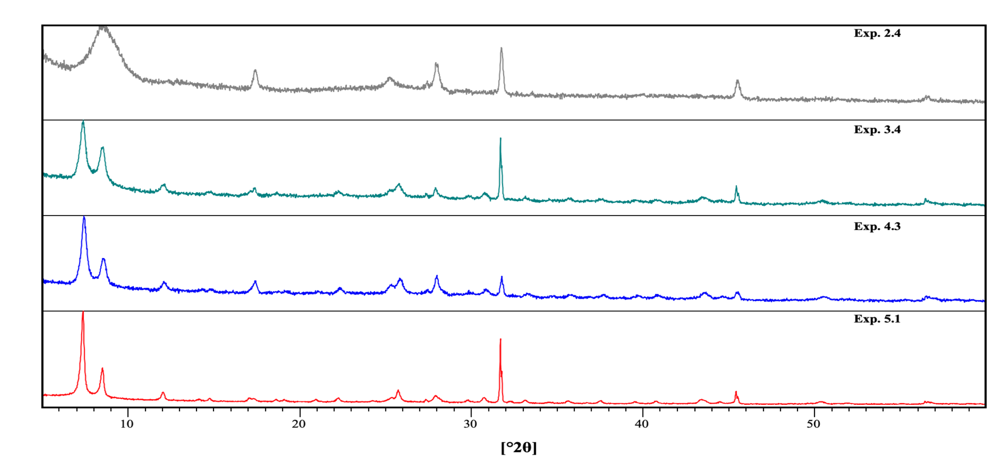
Exp 1.7			
Stoichiometric Ratio	1	1	1
Compounds	$ZrOCl_2$	Na_2BDC	NaOAc

Exp 1.3			
Stoichiometric Ratio	1	2	1
Compounds	$ZrOCl_2$	H_2BDC	NaOAc

Varying the LAG Solvents

By varying the LAG solvents, we changed the pH of the reaction - UiO-66 forms in acidic conditions (a pH of 4.9); we tried 4 optimizations. The following conditions remained the same in each reaction: a 1:1:1* Stoichiometric ratio of ZrOCl2, H2BDC, and NaOAc, 2x Milling Balls, Milled for 30 min @ 30 Hz, and pre-heated jars.

The LAG with glacial acetic acid produced the best crystalline product. HCl was too acidic for the product to form.



Exp 3.4		
LAG Ratio	1	1
Compounds	H_2O	DMF

Exp 2.4	
LAG Ratio	1
Compounds	MeOH

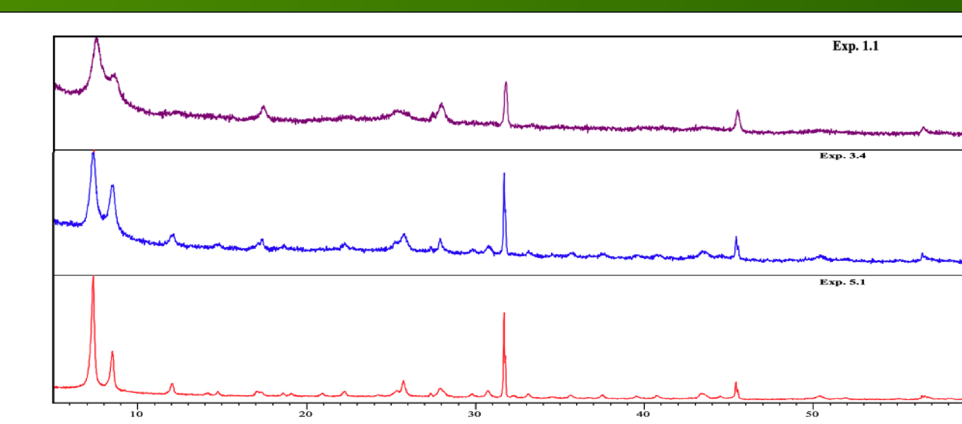
Exp 4.3			
LAG Ratio	1	1	0.5
Compounds	H_2O	DMF	HCl

Exp 5.1			
LAG Ratio	1	1	0.5
Compounds	H_2O	DMF	Glacial Acetic Acid

Multiple Milling Balls

Another theory was that the amounts of balls could affect the product. We theorized that the balls could affect the impact force, which affects the mixing of the reagents, or that they could significantly change the temperature due to friction. The following conditions remained the same in each reaction: Reactants: ZrOCl2, H2BDC, and NaOAc, LAG solvents: H2O, DMF, and glacial acetic acid, milled for 30 min @ 30 Hz, and pre-heated jars.

Overall, we found that the balls had impacted the reaction minimally. The best optimization was 2 balls (M+M), although the jars tended to get warped, causing the ball to get stuck.



Exp 1.1	
Balls	1 medium

Exp 3.4	
Balls	6 small

Exp 5.1	
Balls	2 medium

Conclusions

UiO-66 has been synthesized mechanochemically using LAG mixing milling and commercially available starting materials. The product produced had a good crystalline structure that closely resembled the controlled sample of UiO-66, along with a high surface area. The product was synthesized in 30 minutes and used under 100 μL of organic solvents.

References

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Future Directions

The subsequent characterization steps are to run a thermogravimetric analysis (TGA) and an SEM analysis to prove further that UiO-66 was successfully created using the synthesis. This process is currently ongoing. Once this MOF is fully characterized, we intend to continue this work with subsequent MOFs in the UiO series.

Acknowledgments

The author gratefully acknowledges the support of Dr. Patrick Julien and Dr. Adrian Pang from the Chemistry Department of the Royal Military College of Canada. They also recognize and thank the DRDC for providing funding for this project.

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