

# Synthesis of metal-organic framework membranes

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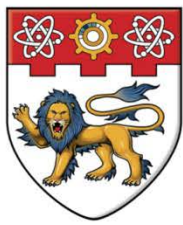
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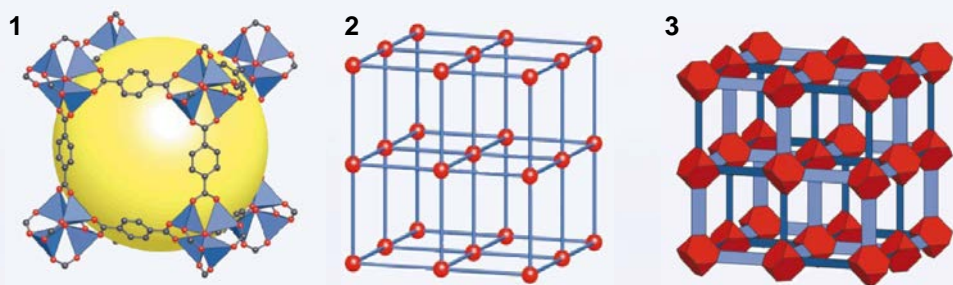
# Synthesis of Metal-Organic Framework Membranes

## Introduction

Metal-organic frameworks are hybrids of organic ligands as connectors and metal oxides as the joints all held together by strong chemical bonds, or molecular scaffolds. The crystalline structures have no internal walls and are essentially porous and light, yet strong and rigid. MOFs have some of the largest recorded surface areas and pore volumes. The use of organic linkers also presents the potential for the design of different functional groups, which would allow for many different applications.

## Aim

We wish to grow MOFs as a compact layer on porous alumina substrates for use in gas/ vapour separation. We have chosen MOF-5 since extensive research on its synthesis has been recorded. MOF-5 is a framework made out of zinc nitrate ( $\text{Zn}(\text{NO}_3)_2$ ) and benzene dicarboxylic acid ( $\text{H}_2\text{BDC}$ ). MOF-5 has a pore size of  $\sim 11\text{\AA}$ , which is suitable for hydrocarbon separations.



### MOF-5 Structure and topology

- 1) The MOF-5 structure shown as  $\text{ZnO}_4$  tetrahedral (blue polyhedral) joined by benzene dicarboxylate linkers (O, red and C, black) to give an extended 3D cubic framework. The yellow sphere represents the hollow space or size of the cavity in one unit of the crystal.
- 2) The topology of the structure (primitive cubic net) shown as a ball-and-stick model.
- 3) The structure shown as the envelopes of the  $(\text{OZn}_4)\text{O}_{12}$  cluster (red truncated tetrahedron) and benzene dicarboxylate (BDC) ion (blue slab).  
(O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, 423, 705;)

## Experimental

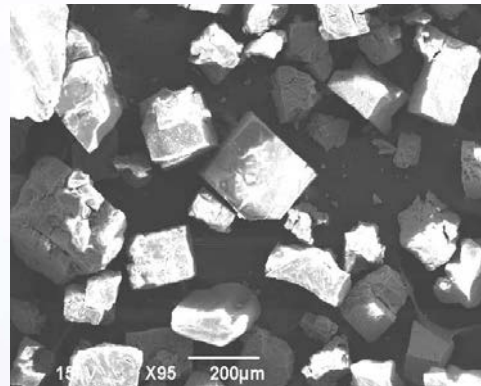
Synthesis of MOF-5 were carried out under hydrothermal conditions.

1. Both  $\text{Zn}(\text{NO}_3)_2$  and  $\text{H}_2\text{BDC}$  dissolved in appropriate solvent
2. Solution was put into autoclave at prescribed temperature conditions for a certain time period (typically 24 hrs)
3. Mixture was allowed to stand and cool to room temperature
4. Crystals were filtered out in a glove box and washed with DMF
5. X-ray diffraction was done to confirm the identity of the crystals

### Sample Experimental data on MOF-5 Synthesis

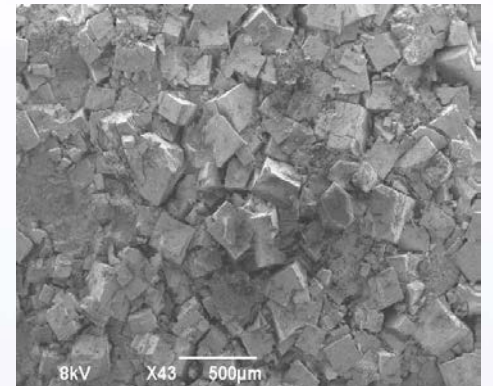
No	$\text{Zn}(\text{NO}_3)_2$	$\text{Zn}^{2+}/\text{H}_2\text{BDC}$	Solvent	Time (h)	Temp. ( $^\circ\text{C}$ )	Result
1	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	3:1	DEF	24	105	Yes
2	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	3:1	DMF	24	105	No
3	$\text{Zn}(\text{NO}_3)_2$ After dehydration	3:1	DMF	24	105	Yes
4	$\text{Zn}(\text{NO}_3)_2$ After dehydration	3:1	DMF Very small amount of $\text{Et}_3\text{N}$	24	105	Yes
5	$\text{Zn}(\text{NO}_3)_2$ After dehydration	3:1	DMF	24	105	No
6	$\text{Zn}(\text{NO}_3)_2$ After dehydration	3:1	DMF	12	105	No
7	$\text{Zn}(\text{NO}_3)_2$ After dehydration	3:1	DMF	24	105	No
8	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	3:1	DEF	24	105	Yes

## Results



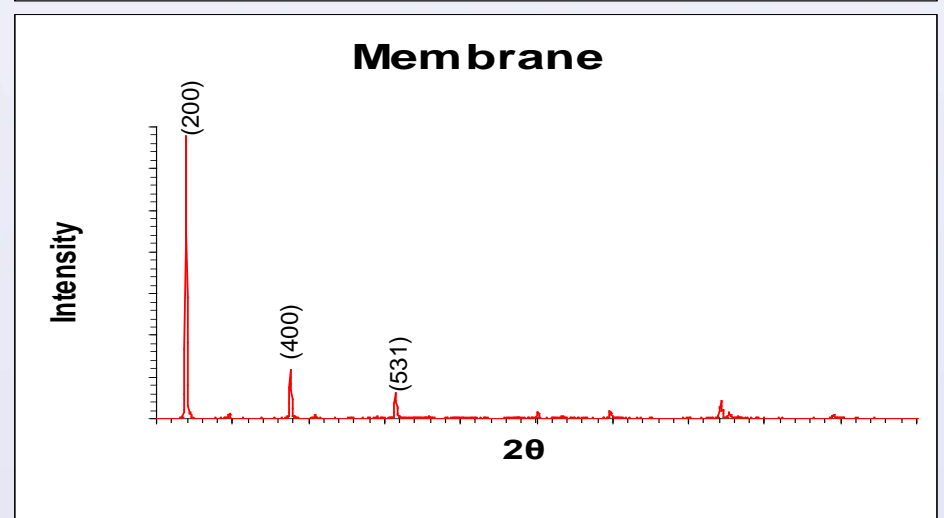
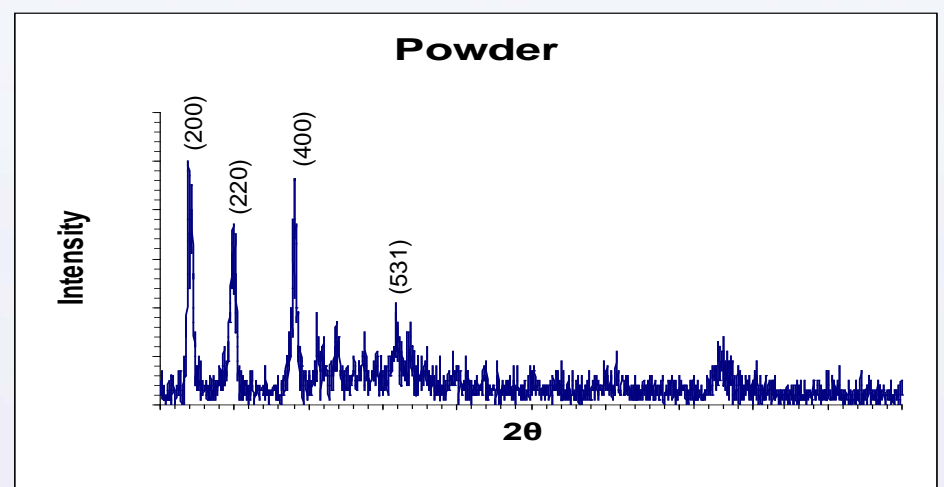
### MOF-5 crystals

SEM images of the crystals synthesized in the lab



### MOF-5 crystals loaded on alumina substrate

SEM images of MOF-5 crystals that are loaded on an alumina substrate



### XRD images

The first XRD confirms that the crystal grown is MOF-5. The second image shows the pattern that is derived when MOF-5 is grown on alumina substrates.

## Discussion

1. MOF-5 crystals were successfully synthesized. MOF-5 on alumina substrates were made by in situ crystal growth.
2. The MOF-5 membranes synthesized were very thick.
3. Reproducibility of the results is an issue since the synthesis of pure MOF-5 crystals require very precise conditions.
4. As seen in the SEM photos, the crystals are too large and have visible defects on them.

## Future goals

1. To grow smaller crystals of MOF-5 with less defects.
2. To grow membranes of MOF-5 by seeded growth.
3. Explore the optimum synthesis condition for MOF-5 crystals.
4. Study the applications of MOF-5 membranes in gas separations