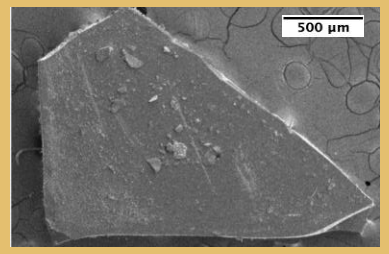
Developing Hierarchical Structures in MOF Glasses

Toni Renz. Dr Celia Castilo Blas. Emily Shaw. Dr Tom Bennett.
Hybrid Materials Group-Department of Materials Science and Metallurgy.

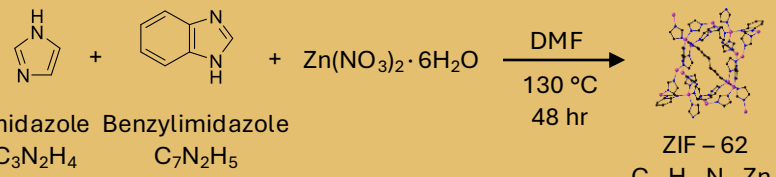
Introduction: Crystalline metal organic frameworks (MOFs) have very high porosity which makes them desirable in application such as gas absorption and separation, catalysis and drug delivery. MOFs are composed of metallic ion clusters joined by organic linkers which form large pores in the structure. Recently, a few MOFs has exhibit glass ability via melt-quenching and forming glasses. However, the porosity of the resulting glass has been compromised despite their mechanical properties, stability and processability are improved. Therefore, reintroducing porosity to a MOF glass is highly desirable to exploit their better mechanical properties and make them suitable for porous applications.

Aim: Fabricate a composite combining a MOF glass and an inorganic glass as template that can be dissolved to reintroduce porosity forming hierarchical pores into a MOF glass to significantly improve the gas sorption uptake of the MOF glass.

Materials – ZIF-62 glass



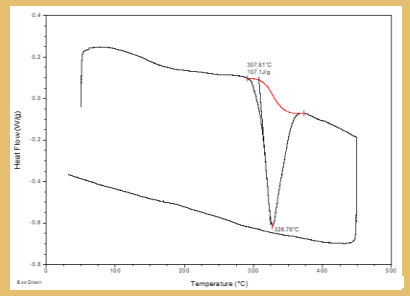
Advantages
- Meltable over 350°C
- Simple synthesis
- Well studied



Imidazole $C_3N_2H_4$ Benzylimidazole $C_7N_2H_5$

ZIF – 62 $C_{28}H_{26}N_{16}Zn_4$

Materials – Inorganic glass 50% Na_2O 50% P_2O_5

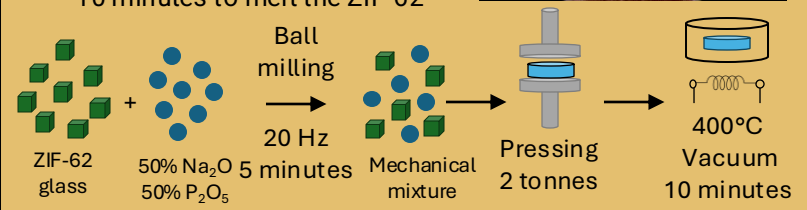


Advantages
- Very soluble in aqueous solutions
- Hygroscopic
- Easily processable
- Relatively low T_g

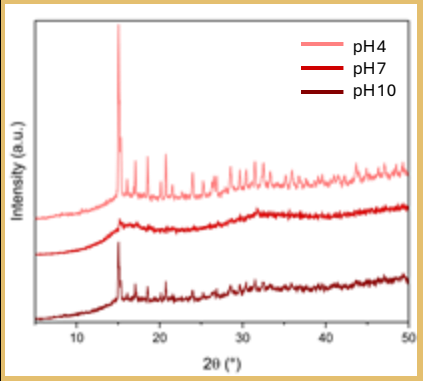
The inorganic glass was characterised by differential scanning calorimetry and showed a recrystallisation temperature of 307°C.

Composite Fabrication

Process
- Ball mill materials together
- Pelletise mechanical mixture
- Heat to 400°C under vacuum for 10 minutes to melt the ZIF-62



Dissolving 50% Na_2O 50% P_2O_5



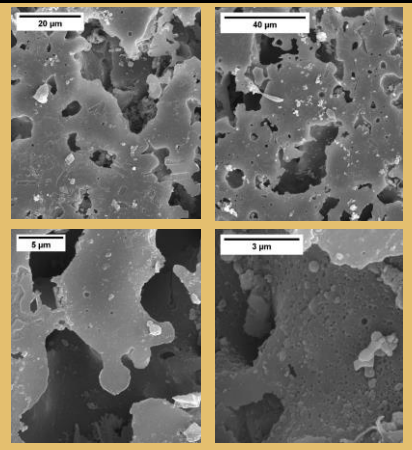
Aqueous solutions at pH = 4, 7 and 10 were tested for efficacy of dissolve the inorganic glass.

The solution with pH=7 was the most effective, leaving just the ZIF-62 glass with pores where the inorganic glass was. The powder X-ray diffraction of this sample is fully amorphous, showing no sharp peaks, in contrast to the pH=4 and10 samples from the recrystallised phosphate glass.

Porosity in the MOF glass

The porosity of the pH7 sample was explored with scanning electron microscopy across multiple length scales.

Pores of micro sizes were observed. Indicating that the composite process was successful in generate hierarchical porosity into the ZIF-62 glass and potentially to incorporate a better gas sorption ability.



Conclusions and Further Work

The PXRD and SEM results proved that hierarchical structures are generated into ZIF-62 glass using an inorganic glass as template that can be dissolved – combining the superior mechanical properties of the MOF glass and the hierarchical porosity generated.

Further work may focus on gas absorption capacity by the collection of N_2 and CO_2 isotherms, mechanical testing and exploring the scalability of the process.