Particle Size and Morphological Effects on Surface Catalysis with ZIF-8

Oliver M. Linder-Patton[a], Kenji Sumida[a], Christian J. Doonan[a] and Christopher J. Sumby[a]
[a] *The University of Adelaide, Centre of Advanced Nanomaterials, School of Physical Sciences*

Metal-Organic Frameworks as Catalysts

Metal-organic frameworks (MOFs) are a class of porous crystalline materials.

- Synthesised from metal ions (nodes) and organic ligands (linkers).
- Containing large internal surface area and tuneable pore sizes.

MOFs are ideally suited as heterogeneous catalysts or as scaffolds for catalytically active molecules. Zeolitic Imidazolate Framework-8 (ZIF-8), comprised of zinc nodes and 2-methylimidazole (2MeIm) linkers, can catalyse transesterification reactions at Lewis acidic sites on its surface.[1]

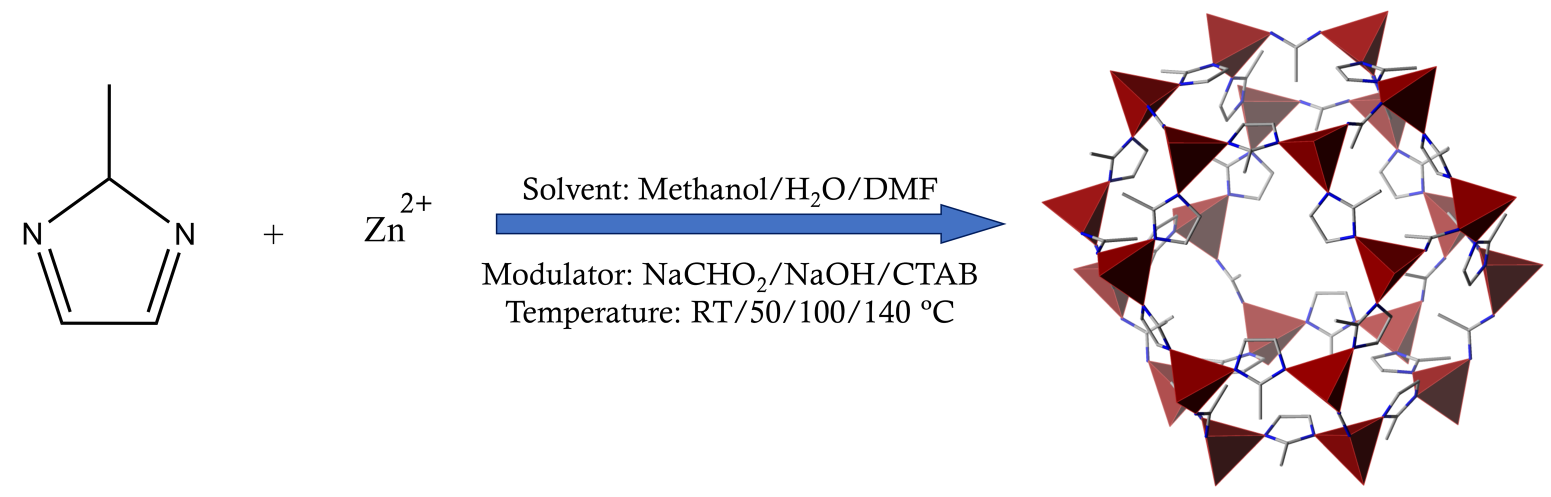


Figure 1: Zinc and 2-methylimidazole (2-MeIm) (left) are the building blocks of the ZIF-8 framework (right)

Particle Size Effect

The industrial scale synthesis of MOFs will utilise techniques (flow reactors etc.) that will likely produce sub-micron crystallites.[2]

- Decreasing particle size leads to decrease in diffusion time and an increase in the amount of external surface area.
- MOF catalysts may be more efficient at smaller particle sizes.

Morphological Effect

The morphology of ZIF-8 determines the accessible surfaces which will have different terminating functional groups.[3]

- Lewis acidic sites on ZIF-8 occur at Zn-2MeIm linkages.[3]
- [100] and [211] miller planes in ZIF-8 have the highest concentration of Zn-2MeIm sites.[3]
- Exposing more active sites leads to increased catalytic activity.

The effect of particle size and morphology on catalysis with MOFs was investigated.

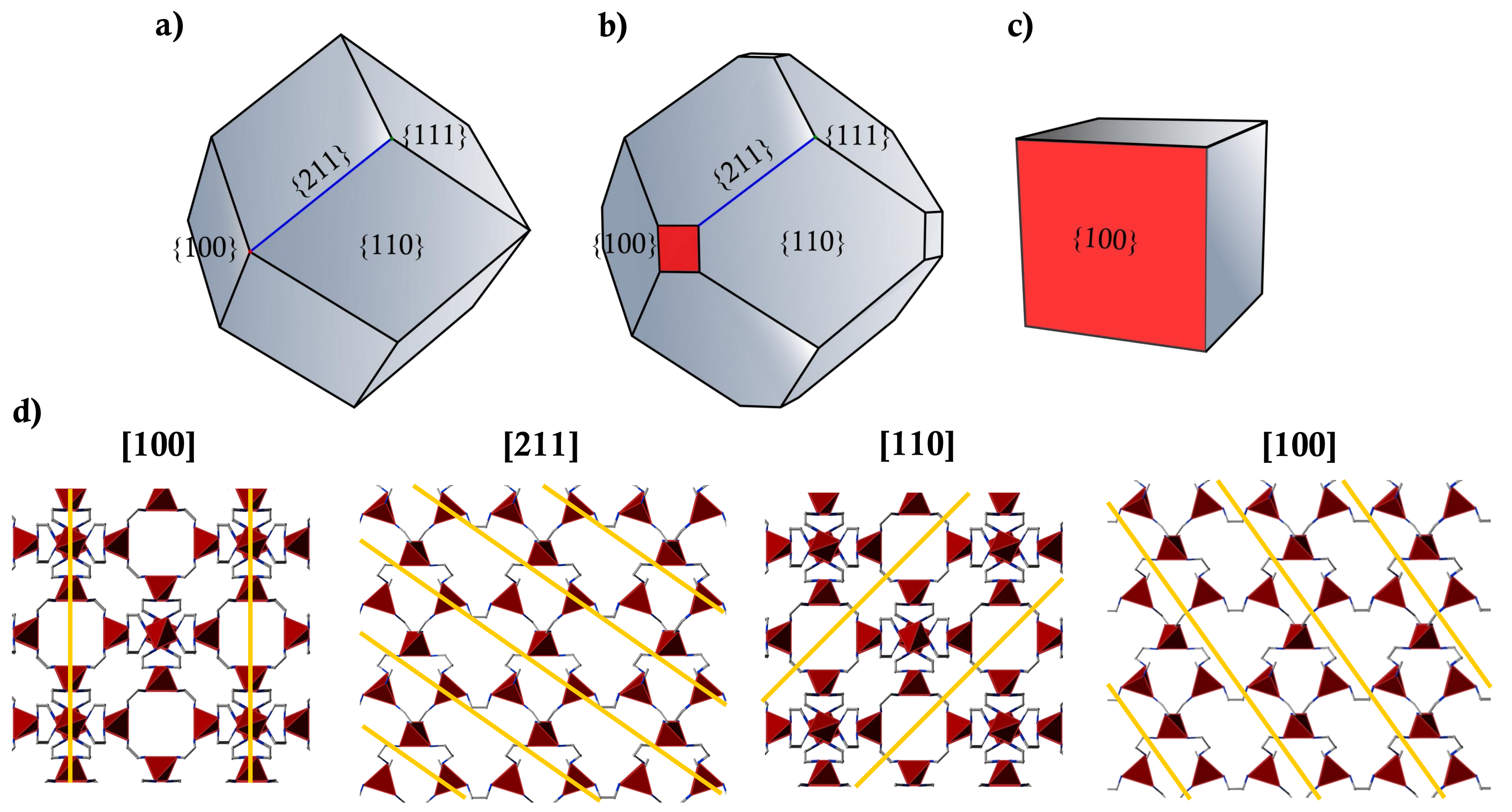
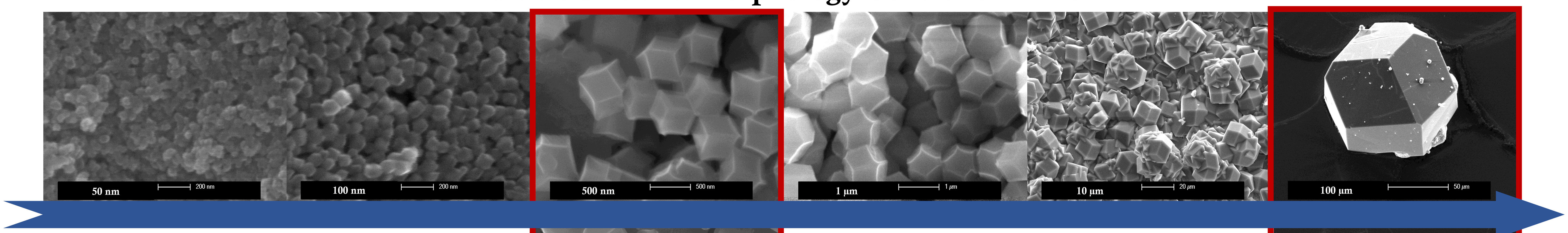
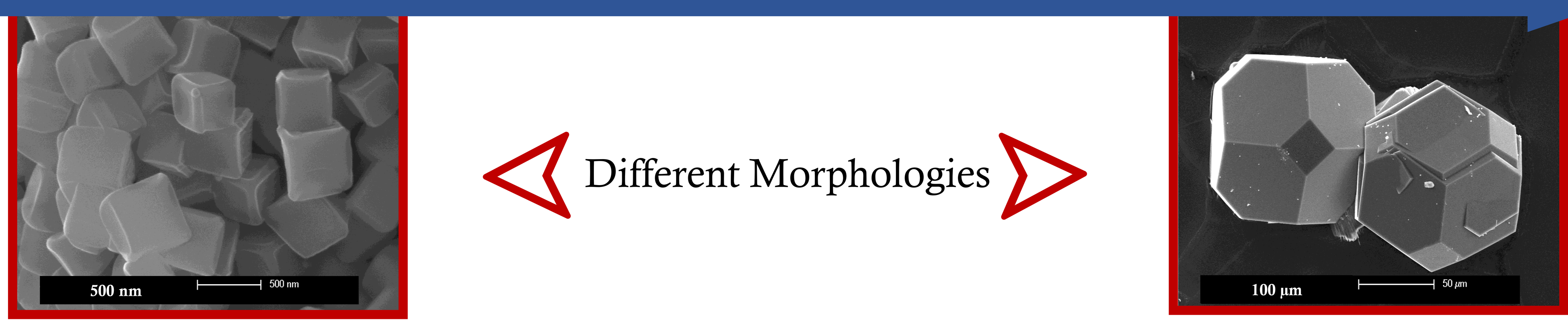


Figure 2: Morphologies of ZIF-8; a) Rhombic Dodecahedron, b) Truncated Rhombic Dodecahedron, c) Cubic and d) the miller planes associated with the crystal surfaces of ZIF-8. [100] and [211] planes contain highest density of Zn-2MeIm linkages.[3]

Particle Size and Morphology Control of ZIF-8





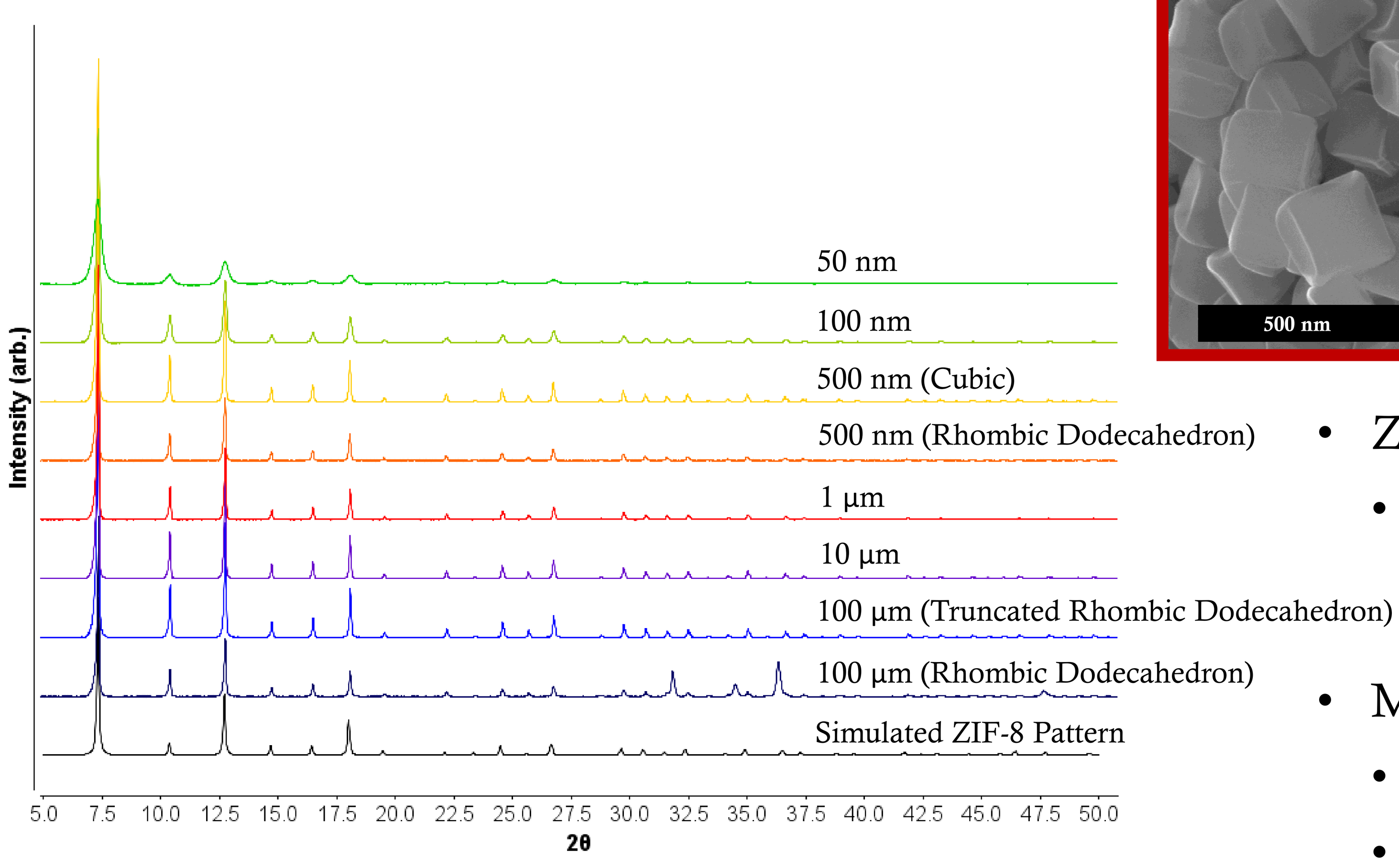


Figure 3: Powder x-ray diffraction patterns of all sizes and morphologies of ZIF-8 that were synthesised

- ZIF-8 was synthesised at 6 different sizes between 50 nm - 100 µm
  - Particle size controlled via addition of modulators (NaOH, 1MeIm and $NaCHO_2$), varied temperature (RT, 50 and 140 °C), different solvents (DMF and MeOH) and Zn:2MeIm (1:8, 1:4, 1:2, 1:1).
- Morphological control at 500 nm and 100 µm.
  - Cubic 500 nm: Cetyltrimethylammonium bromide (CTAB) was used as a capping agent.
  - Truncated Rhombic Dodecahedron 100 µm: Sodium formate ($NaCHO_2$) used as a modulator.

Application: Surface Catalysis

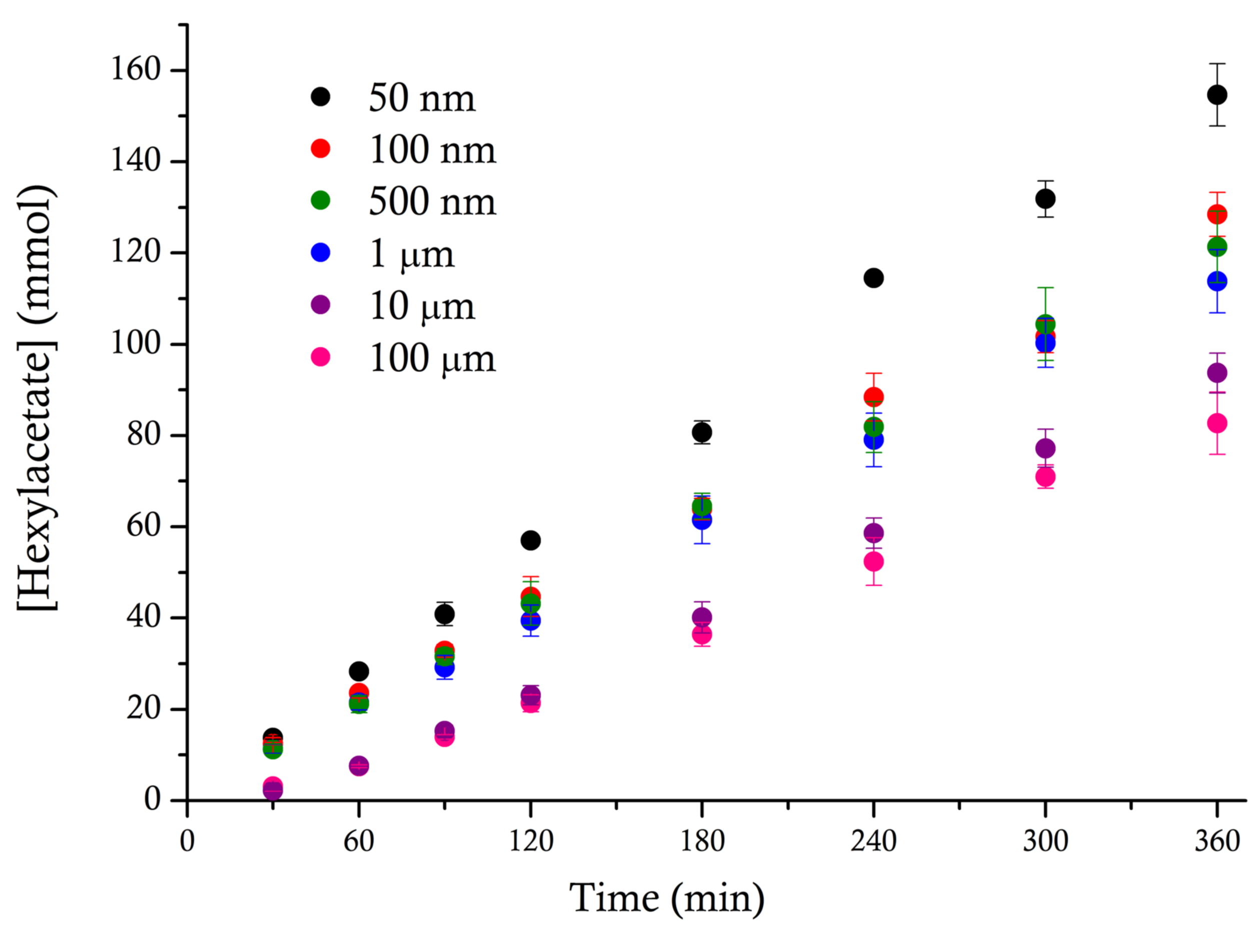
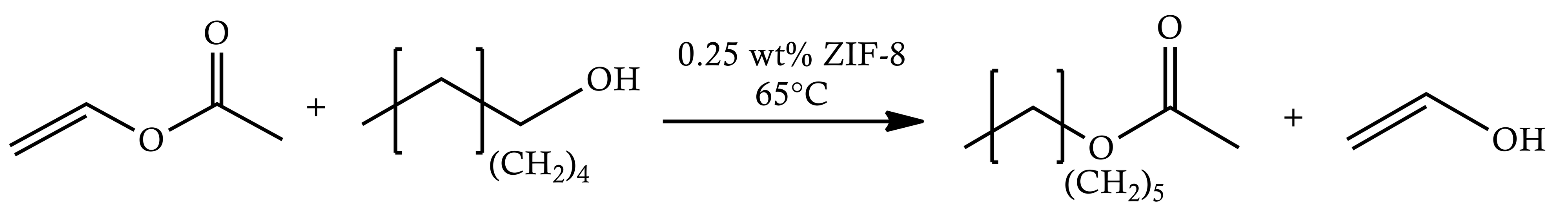


Figure 4: Production of hexylacetate vs. particle size over 6 hrs for a transesterification reaction catalysed by ZIF-8, analysed via GC-MS



Reaction Scheme 1: Transesterification of vinylacetate and hexanol, catalysed by ZIF-8 at 65 °C, to hexylacetate and vinylalcohol

Surface transesterification on ZIF-8 progress followed via [hexylacetate] (GC-MS).

Conclusions

- Particle size and morphological control of ZIF-8 was achieved between 50 nm - 100 µm and at 500 nm and 100 µm respectively.
- There is an inverse relationship between particle size and hexylacetate production (Figure 4).

References

1 Chizallet, C. l. et. al., *J. Am. Chem. Soc.* **2010,** *132*, 12365-12377.
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Acknowledgements

The Sumby-Doonan-Sumida-Keene Group, The University of Adelaide, Adelaide Microscopy, The Australian Research Council