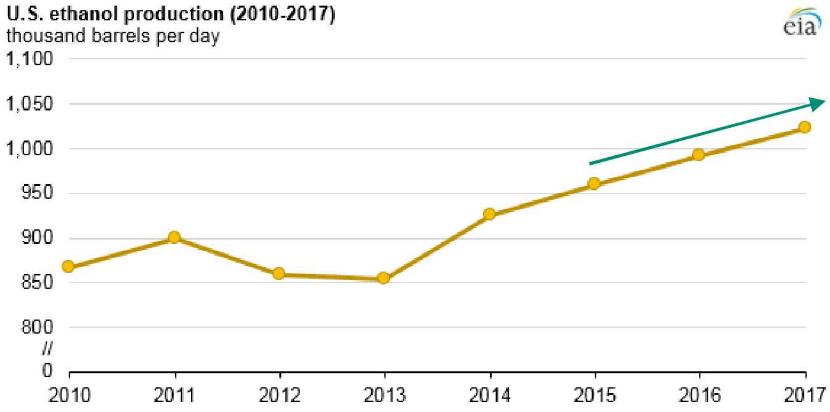
SAND2019-3684C

Metal-Organic Frameworks for Catalytic Biomass Upgrading : Investigation of C—C Bond Formation by Aldol Condensation in a Pre-Defined Pore Space

PRESENTED BY

Timothy C. Wang

Excess Bioethanol Production



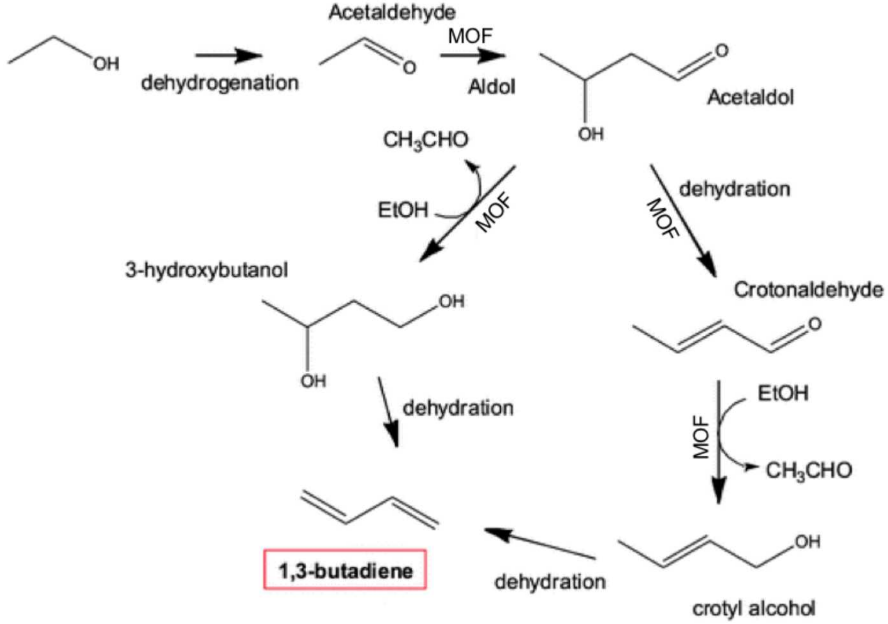
Bioethanol production in U.S.: steady increase and is outpacing the demand of gasoline

Blend wall: conventional engine and refueling facility cannot handle gas with more than 10% ethanol

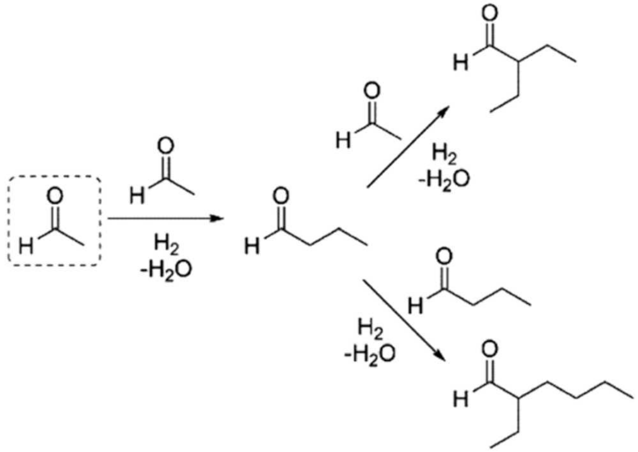
Ways to utilize the excess ethanol is needed!

Upgrading Ethanol to Valuable Chemicals

Butadiene Production (Guerbet Reaction)

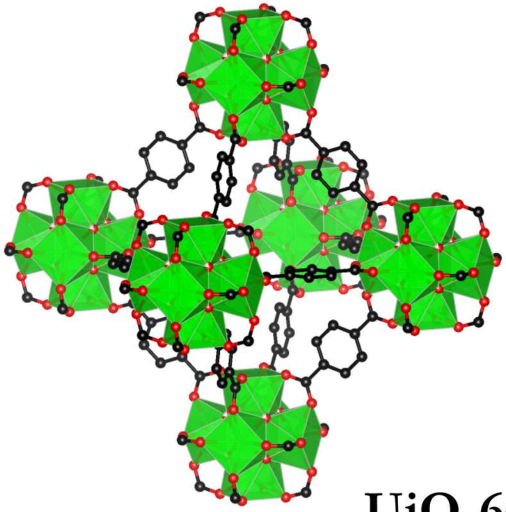


2-Ethylhexanal Production (Aldol+hydrogenation)



Both targets require C—C bonds formation by Aldol condensation

Metal-Organic Frameworks (MOFs) for Catalysis

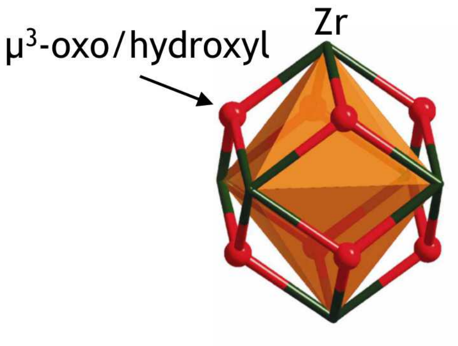


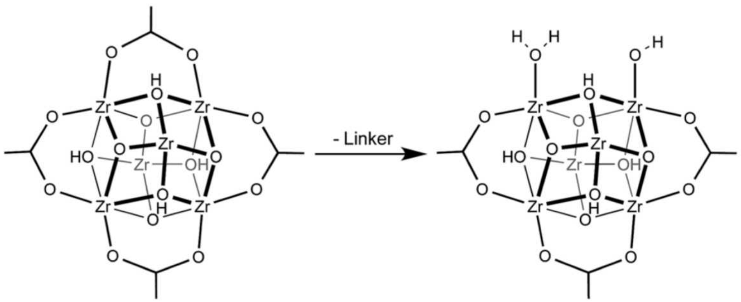
UiO-66

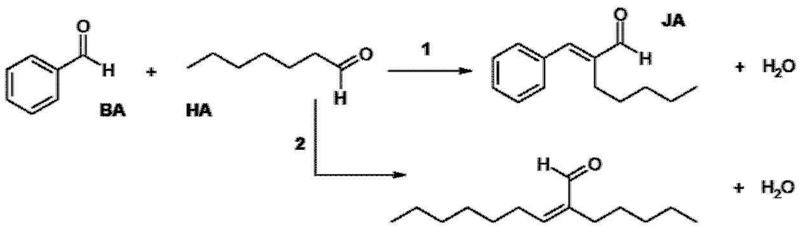
- Consist of metal nodes and multi-topic linker
- Porous, crystalline materials that exhibited potential applications, including catalysis
- Essentially hetrogeneous catalysts w/ high density of accessible active sites
- Highly tunable:
  - -Intrinsically by selection of metal and ligands
  - -Extrinsically by ligands exchange/ incorporation or metallation on the nodes
- Predictable from computational modelling

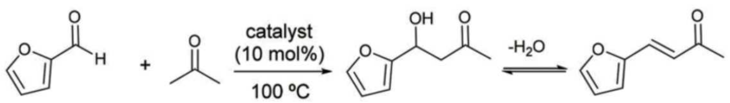
Zr-based MOFs as Catalysts for Aldol Reactions

Brønsted Acid is necessary for catalyzing aldol condensation.









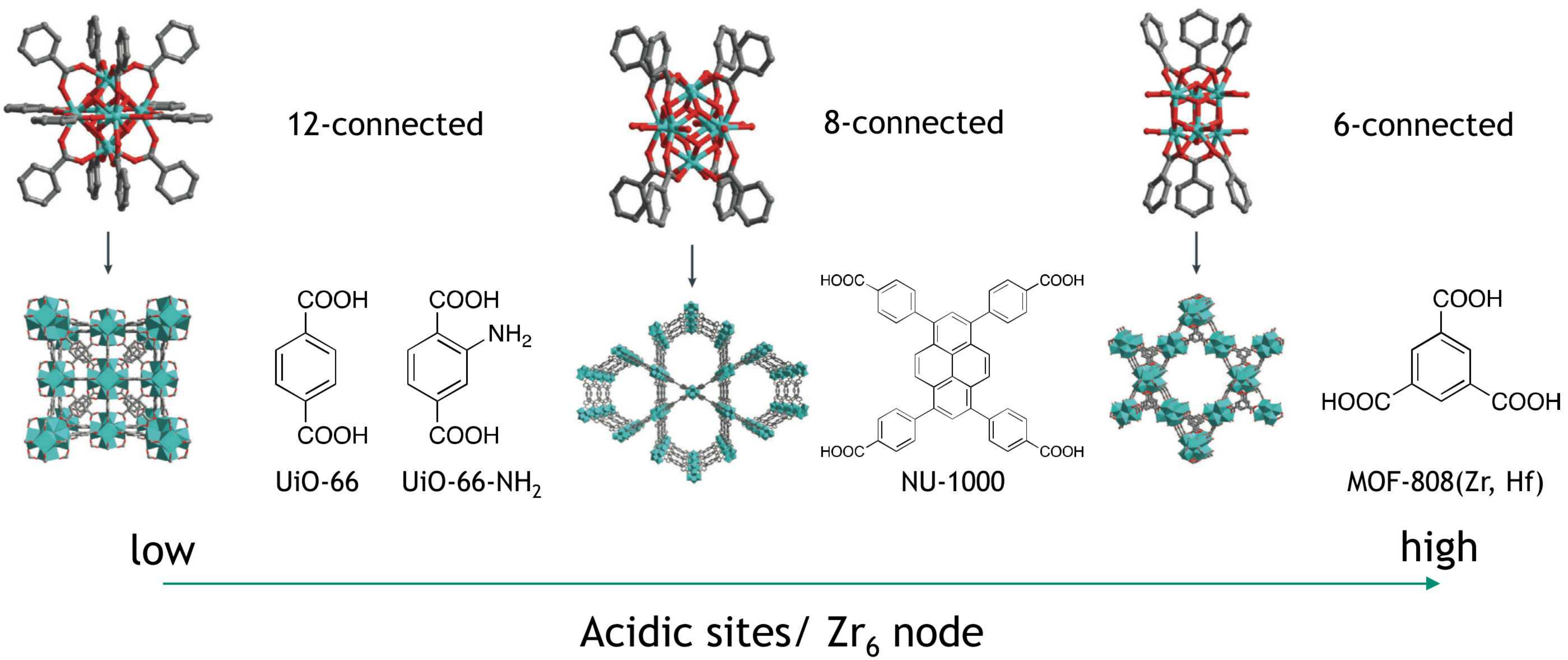
1b 1a

Catalyst	TON	TOF (h^{-1})
UiO-66(Hf)	9.8	9.7
Hf-MOF-808	9.3	5.2
Zr-MOF-808	9.3	4.8
UiO-66(Zr)	7.7	1.7
UiO-66-NH_2(Hf)	7.5	1.5
$HfCl_4$	4.4	1.3
UiO-67(Hf)	2.5	0.6

An amino-modified Zr-terephthalate metal–organic framework as an acid–base catalyst for cross-aldol condensation
Vermoortele, F.; Ameloot, R.; Vimont, A.; Serre, C.; De Vos, D.
Chemical Communications **2011,** *47* (5), 1521-1523.

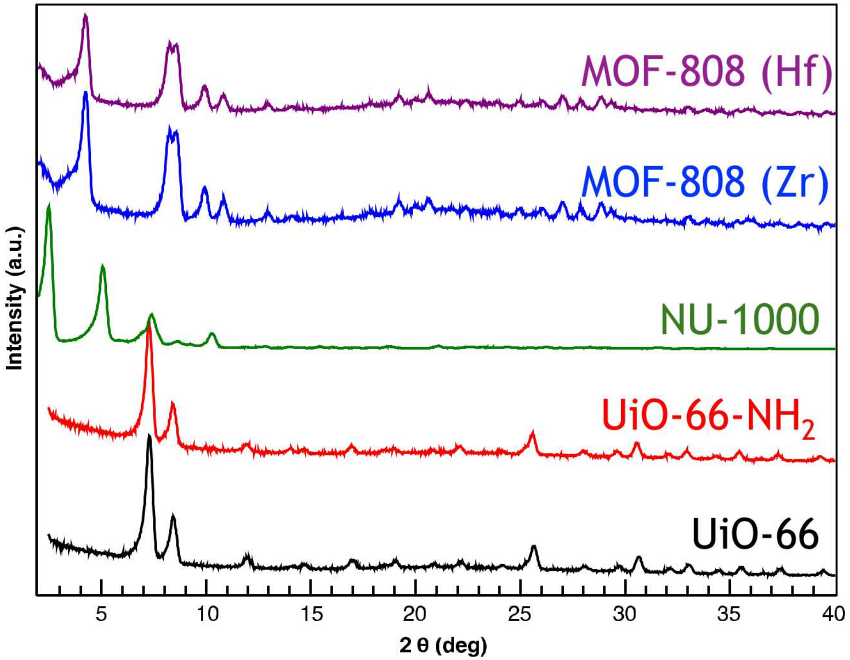
Hf-based metal–organic frameworks as acid–base catalysts for the transformation of biomass-derived furanic compounds into chemicals
Rojas-Buzo, S.; García-García, P.; Corma, A.
Green Chemistry **2018,** *20* (13), 3081-3091.

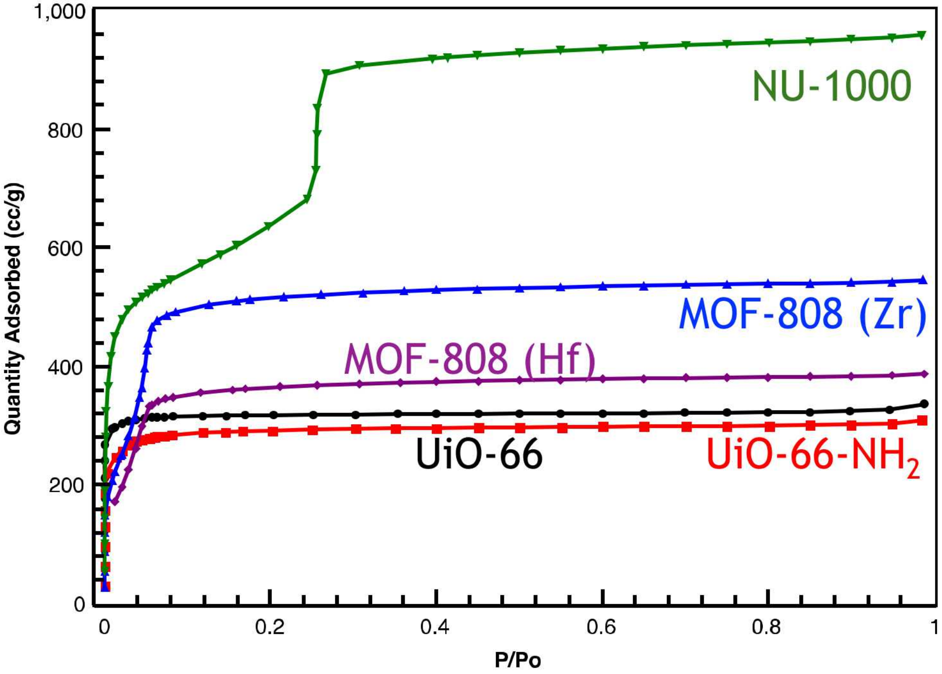
Controlling Density of Catalytic Sites in Zr-MOFs



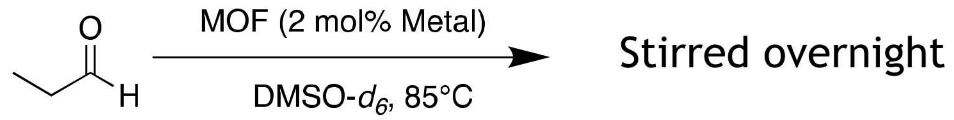
Characterization of MOFs Materials

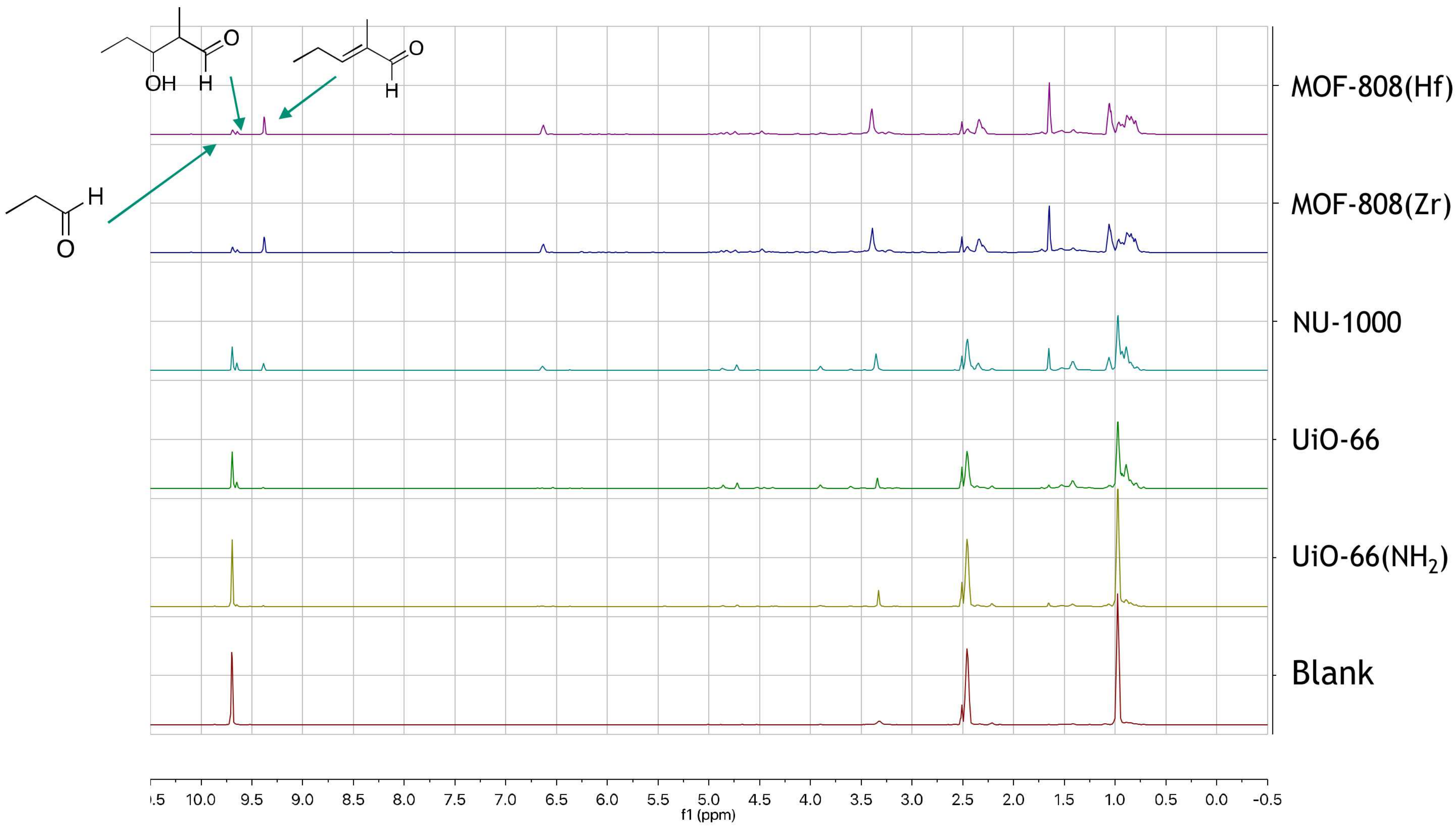
All MOFs are synthesized following literature procedures



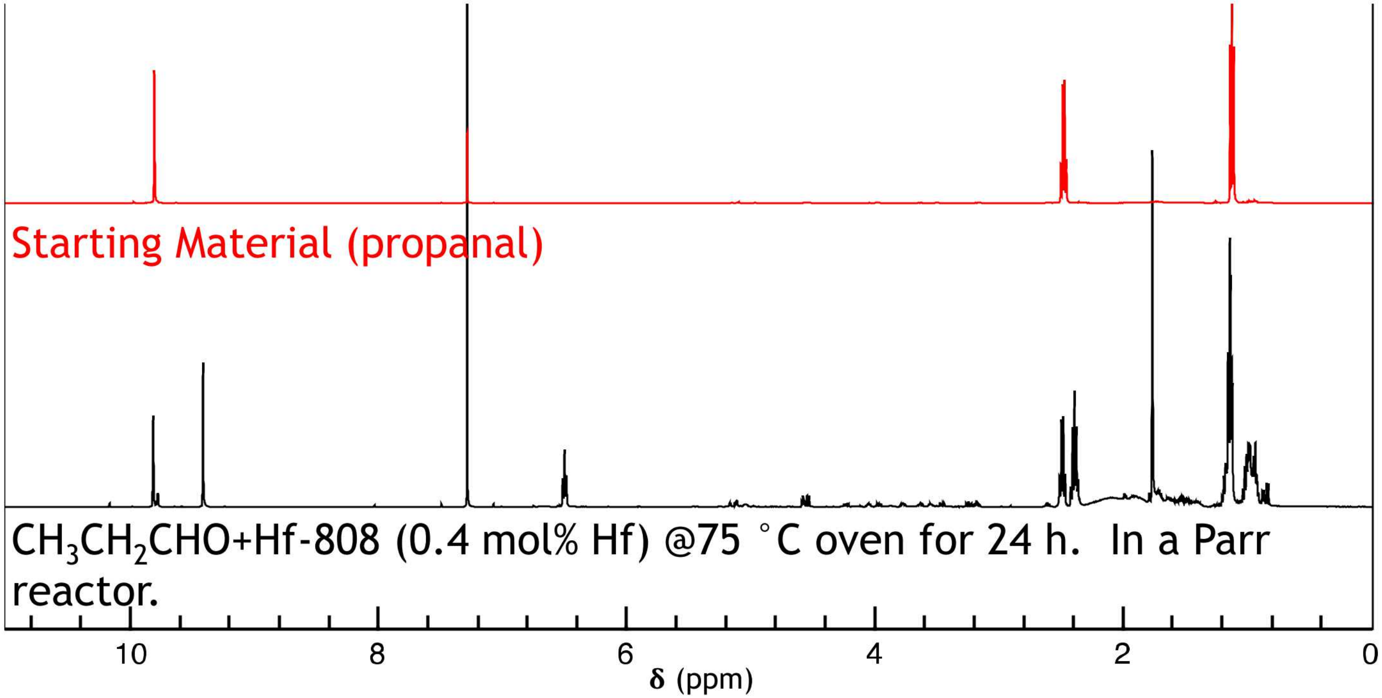


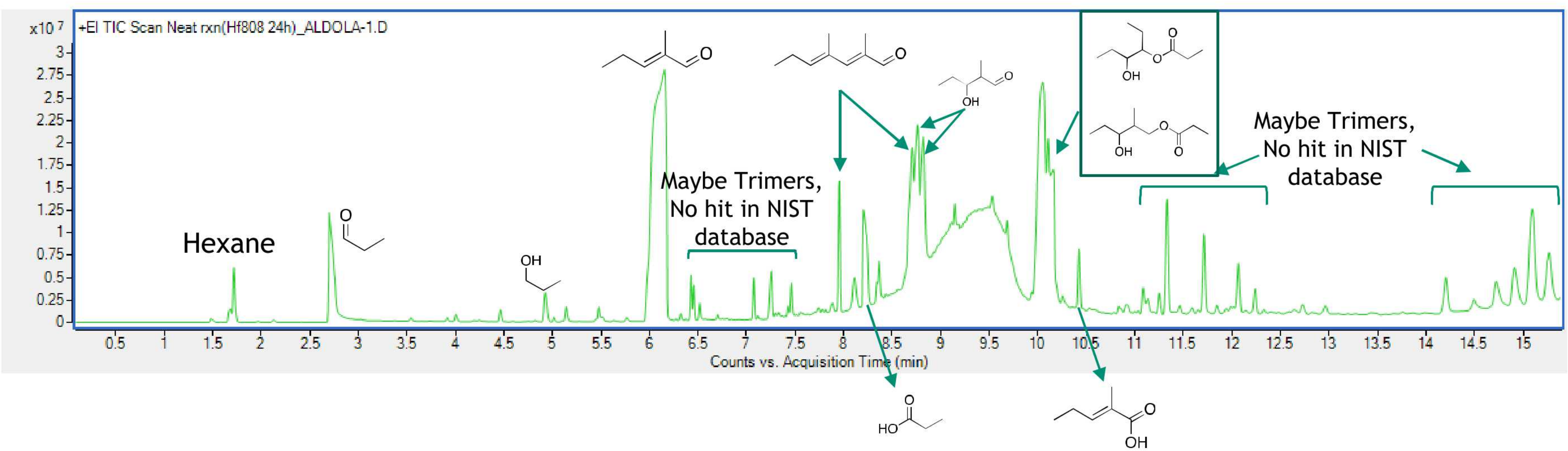
Model Reaction for Self-Aldol Reaction





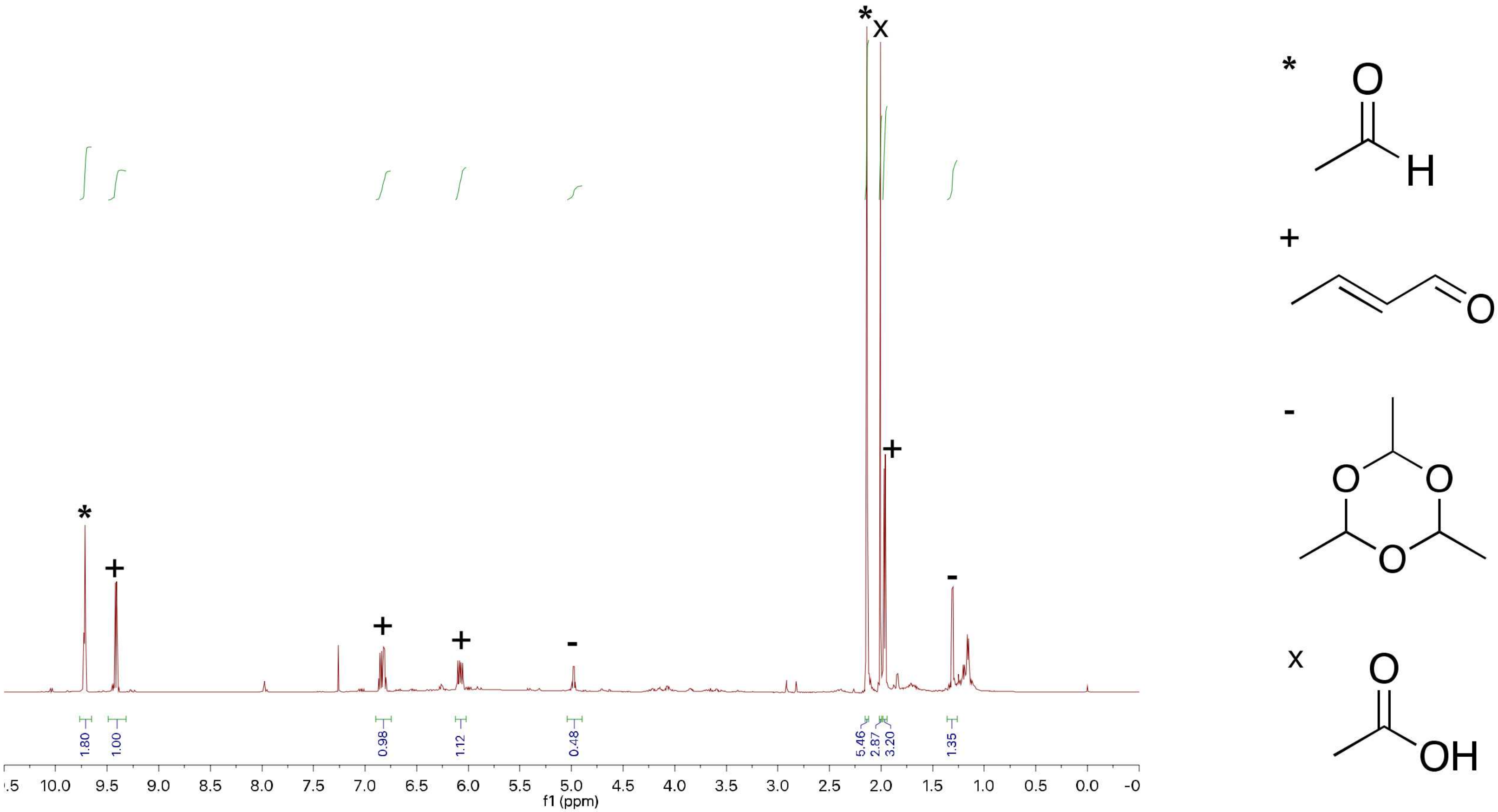
Product Analysis of Propanal Model Reaction



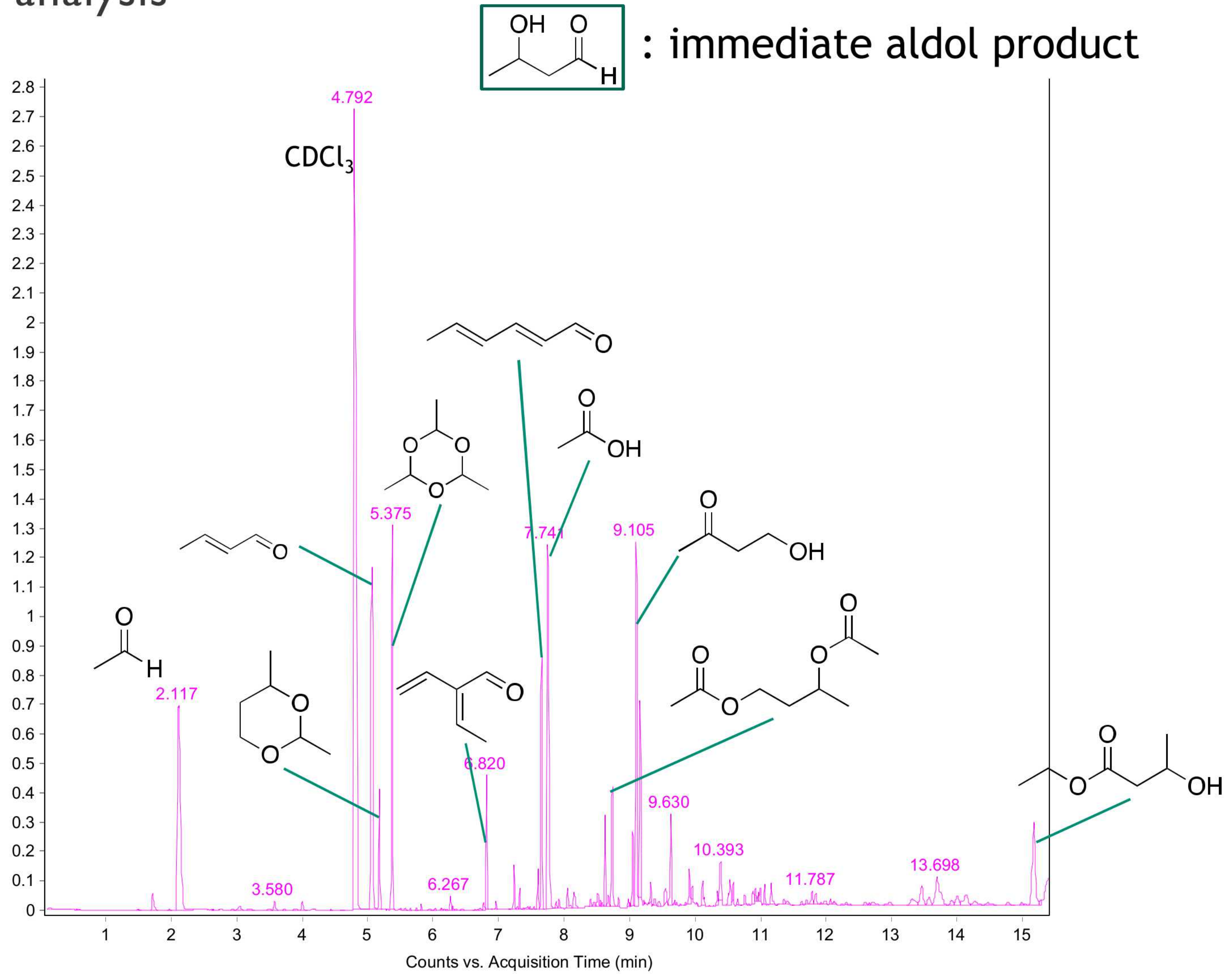


Catalytic Coupling of Acetaldehyde with MOF-808 (Zr)

$$CH_3CHO \xrightarrow[\text{120°C, overnight}]{\text{MOF-808 (Zr)}}$$



GC-MS analysis

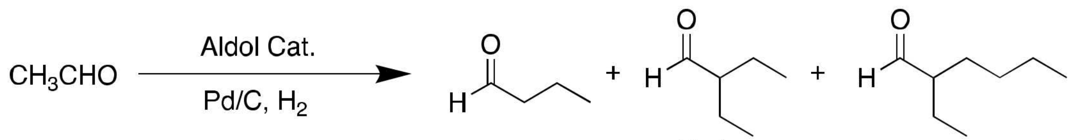


Many products from secondary reaction are identified.

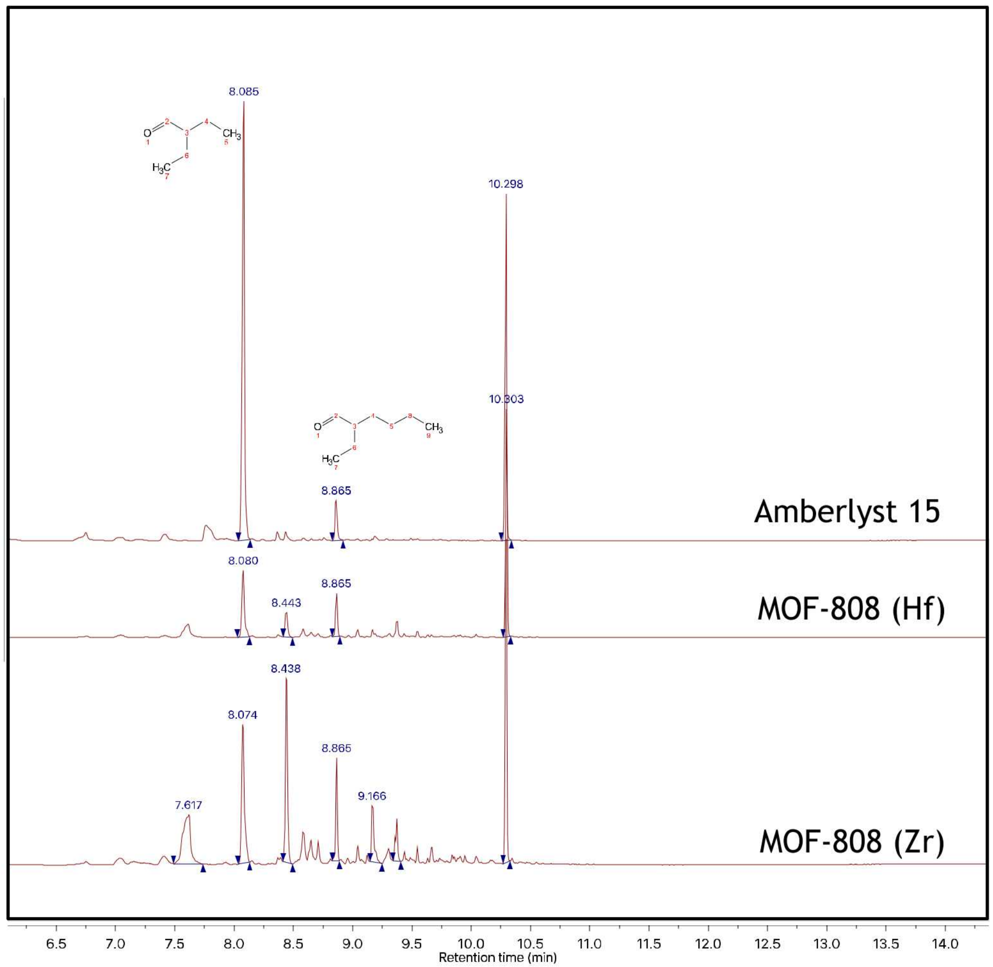
Second aldol, H-transfer reaction, oxidation, esterification

—Better control of secondary reaction is needed

2-Ethylhexyl Aldehyde Synthesis



Major

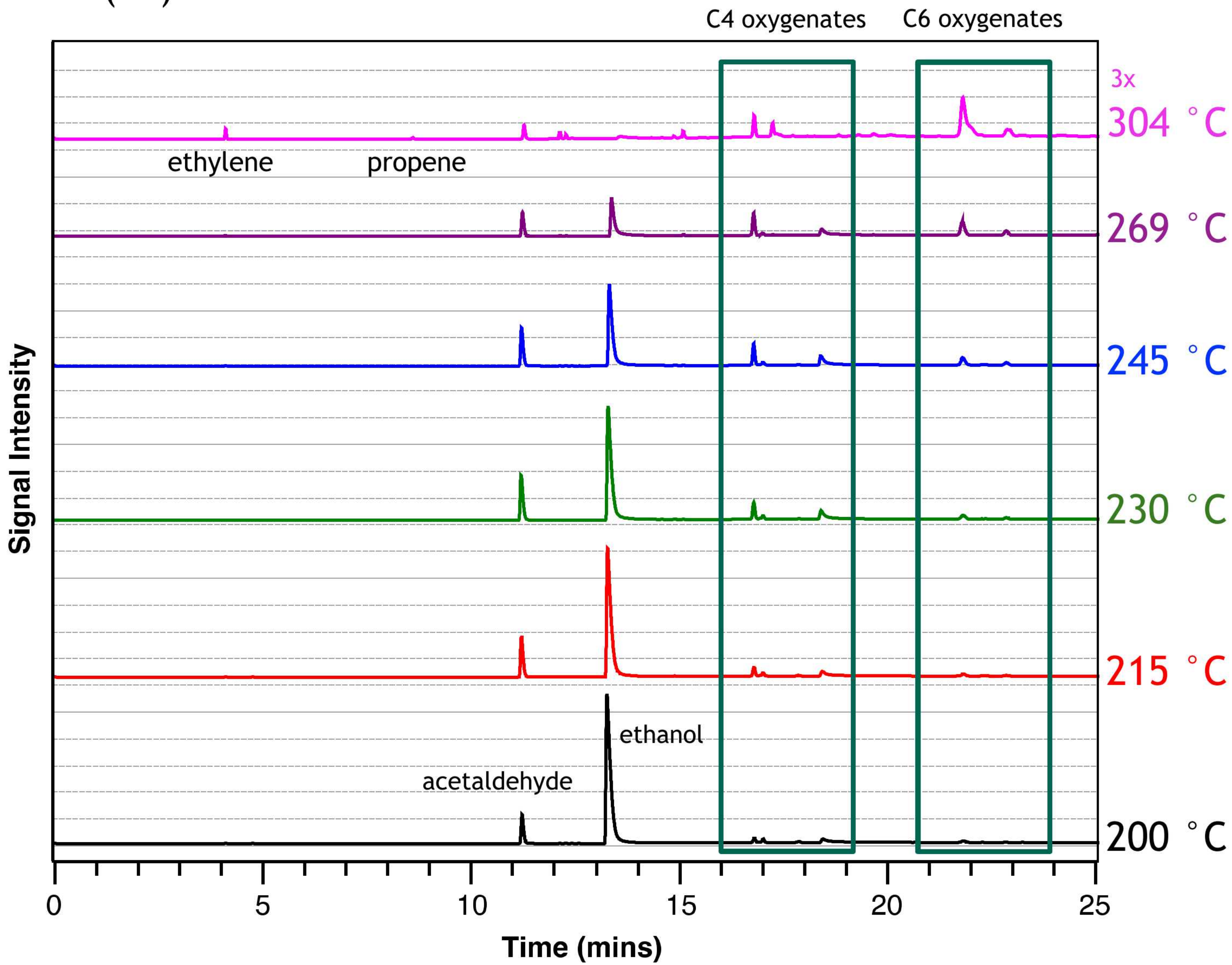


- MOF catalysts have higher C8/C6 selectivity.
- The reaction rate might be lower.
- More side products are synthesized with MOF catalysts: more possible secondary reaction pathway

** In collaboration with Dr. Andy Sutton (LANL)*

Flow Reaction with Ethanol/Acetaldehyde (3:1 mol ratio)

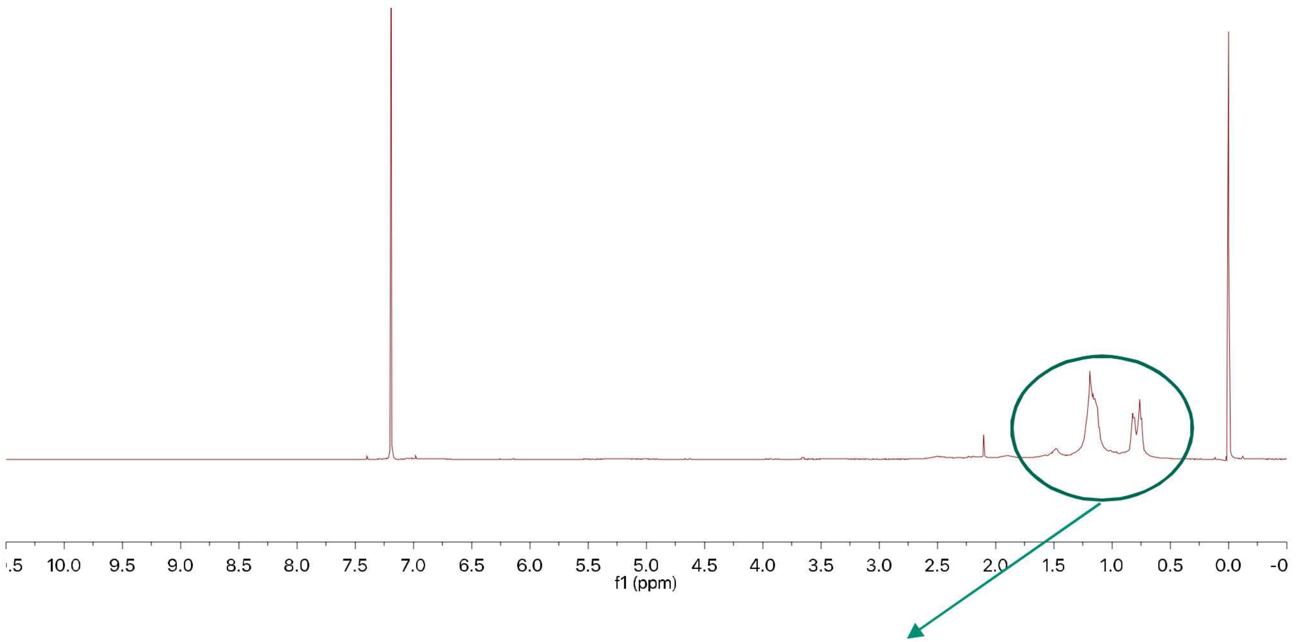
MOF-808 (Hf)



Stability Test on the Post Catalysis MOF-808 (Hf)

- PXRD did not show loss in crystallinity
- Sample lost all N_2 accessible porosity

Washed with $CDCl_3$, NMR taken:



Likely polymer formation in the pores

Summary

- Zr(Hf)-MOFs are active for aldol condensation, key C—C coupling reaction for upgrading acetaldehyde.
- The activity of the MOF catalysts for aldol reaction can be tuned by the density of acidic sites on the metal nodes.
- In addition to aldol condensation, hydrogen transfer reactions, esterification, etc. can be carried out by Zr-MOFs, which can be further utilized to upgrade platform molecules from bio-refinery.
- Control of reaction pathway in the MOFs needs to be investigated.

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