Centre for Sustainable & Circular Technologies

UNIVERSITY OF BATH

Centre for Sustainable and Circular Technologies; University of Bath

Project Title:	Multiscale molecular behaviour in the zeolite catalysed methanol-to-hydrocarbons process
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Industrial Partner:	IChemE (full funding), Johnson Matthey (placement)

Project Summary

The demand for sustainable chemicals and fuels has led to significant research into finding alternative feedstocks to bypass crude oil. Of these, the zeolite catalysed methanol-to-hydrocarbons (MTH) processes is one of the most prominent technologies for the production of olefins in particular,[1] as methanol can be produced from a wide range of carbon-containing sources such as biomass, plastic waste or even carbon dioxide.

While MTH mechanism is one of the most disputed processes in heterogeneous catalysis,[2] other important components such as the mobility of the initial active species (i.e. methanol and dimethylether (DME)) remain mostly unstudied. In part, this is because of the changing nature of the zeolite catalyst as the reaction progresses. It is widely believed that reaction proceeds via a 'pool' of hydrocarbons (consisting mainly of alkenes/aromatics) within the zeolite pores. How this pool is formed and its role in the catalyst deactivation are not so well understood. This is mainly due to the difficulty of determining which species are present, or indeed mobile during the reaction.

Despite numerous in-depth mechanistic studies, fundamental knowledge of molecular mobility as a function of zeolite framework topology, composition (Si/Al ratio), the presence of other important species, the presence of defects due to framework destruction, and pore blockage due to 'coking' remains poorly understood. This is particularly true in terms of multiscale studies, where the local/molecular scale (i.e. < 10 Å from the active site), the nanoscale (probing mobility through the framework structure) and the microscale (measuring mass transport across entire particles) can present significant challenges.

The studentship aims to answer the following questions:

1) How does methanol and DME mobility on the molecular, nano- and microscale change across a variety of zeolite catalyst frameworks and Si/Al ratios? Can any of these changes be correlated and linked with catalytic activity?

2) How does the presence of aromatic compounds, featuring in the hydrocarbon pool affect multiscale methanol/DME mobility, and do the differing framework topologies change the significance of their presence?

3) How does catalyst deactivation due to framework damage and pore blockage affect the mobility of the initiation species, and can this be correlated directly with the loss in catalytic activity?

The aforementioned scales will be probed as follows:

- Motions local to the zeolite Brønsted acid site will be probed with vibrational spectroscopy (both based on IR and neutrons) paired with static DFT and quantum mechanical molecular dynamics (DFT-MD).

- Molecular mobility through each different zeolite framework on the *nanoscale* will be studied with quasielastic neutron scattering and classical molecular dynamics (CMD) simulations.
- Mass transport and inter-/intracrystalline diffusion studies on the microscale would employ pulsed field gradient NMR and gravimetric sorption.

[1] M. Stöcker, *Microporous Mesoporous Mater*. **1999,** 29.1-2, 3-48.

[2] U. Olsbye, U., S. Svelle, M. Bjørgen, P. Beato, T. V. Janssens, F. Joensen., S. Bordiga, K. Lillerud, . *Angew. Chem. Int. Ed*, **2012** *51*(24), 5810-5831.

[3] P. Tian, Y. Wei, M. Ye, Z. Liu, *ACS Catal.* **2015**, *5*, 1922–1938.

[4] I. Yarulina, A. D. Chowdhury, F. Meirer, B. M. Weckhuysen, J. Gascon, *Nat. Catal.* **2018**, *1*, 398–411.

Sustainability issues addressed

Methanol can be produced from a wide range of carbon-containing sources,[4] of particular interest from a sustainability point of view are biomass, waste or even carbon dioxide. Recent policy briefings from the Royal Society [5,6] point to the importance of methanol as a platform molecule for future synthetic fuels and chemicals with its synthesis through CO_2 and green hydrogen. This suggests that methanol along with immediate products such as dimethylether, and technologies for its conversion to higher value chemicals will remain hugely relevant long after current fossil fuel based sources are diminished.

[7] Royal Society (Great Britain), *The Potential and Limitations of Using Carbon Dioxide*, **2017**, Retrieved from https://royalsociety.org/-/media/policy/projects/carbon-dioxide/policy-briefing-potential-and-limitations-of-using-carbon-dioxide.pdf

[8] Royal Society (Great Britain), *Sustainable Synthetic Fuels for Transport*, **2019**, Retrieved from https://royalsociety.org/-/media/policy/projects/synthetic-fuels/synthetic-fuels-briefing.pdf