

Chemical recycling of polymers with novel dual function catalysts.

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In 2017 a shocking report highlighted the scale of the plastic problem. It reported that by 2015, 8.3 billion metric tonnes of virgin plastics had been produced, but only 2 billion tonnes of which remained in active service. Of the 6.3 billion tonnes of resultant plastic waste, only 9% of that material had been recycled.¹ The general challenge in recycling polymers lies in the dominance of polyolefins.² These polymers have saturated back bones which are exceptionally robust and difficult to degrade. Even with new biodegradable polymers growing in production volume, there will always be a great need for strategies to deal with the legacy polyolefin plastics that have been produced to date.

Zeolites – microporous, aluminosilicate, acidic materials with shape selective catalytic properties – revolutionized the catalytic cracking of crude oil when introduced into refinery operations. The high thermal stability, high Brønsted and Lewis acidity, and synthesis from earth abundant elements (O, Si, Al only) have resulted in zeolites becoming the principal cracking component in Fluidized Catalytic Cracking (FCC). The FCC reaction selectively cracks the saturated alkane chains in heavy gas oil into shorter chain olefins (with aromatics, alkanes and carbonaceous material as by-products). Therefore, it is no surprise that zeolites have been shown to have great potential in the chemical recycling of polyolefins to useful chemicals and fuels (Figure 1).^{3,4}

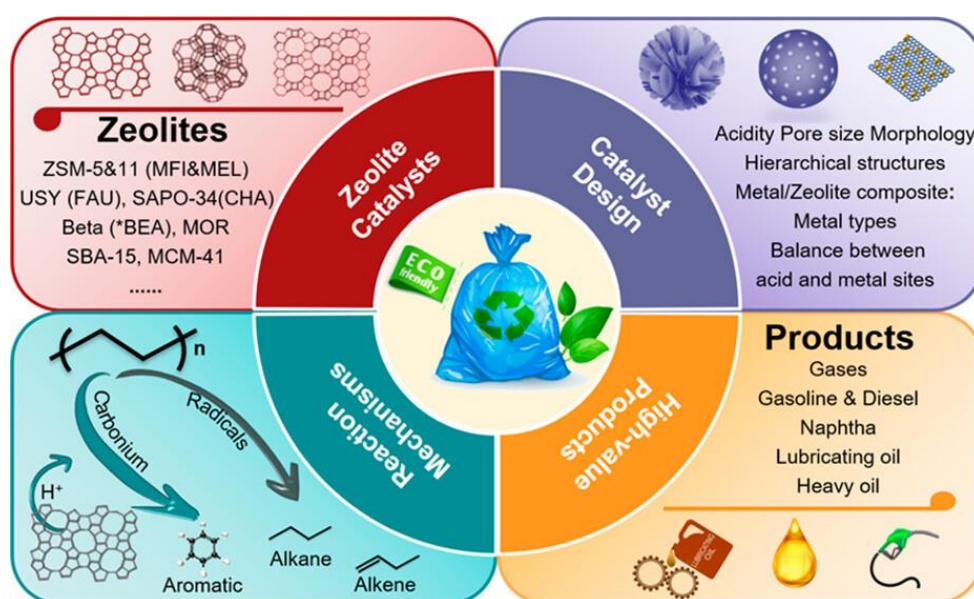


Figure 1 Structure-activity relationships in the conversion of polyolefins by zeolites Reprinted with permission from reference 3 (*ACS Catal.*, **2022**, *12*, 14882). Copyright 2022 American Chemical Society.

However, one of the main drawbacks in using solid zeolites to convert heavy oil or polyolefins is the very poor contact between the two components. In the FCC process, catalyst composites are utilized which have a hierarchical porosity, but this embeds the zeolite within a solid matrix which still restricts accessibility to the zeolite. Recent work has reported that zeolites can be fully dispersed in bulky ionic liquids, forming porous liquid zeolites, and the zeolites remain active acid catalysts.^{5,6} Moreover, it has been shown very recently that chloroaluminate ionic liquids (ILs) enable full conversion of polyethylene (PE) and

polypropylene (PP) to liquid isoalkanes (C6 to C10) at temperatures below 100 °C through Lewis acidic aluminium sites.⁷

The aim of this proposal is to **develop new porous, liquid phase catalysts** that are effective for the conversion of **polyolefins to useful chemicals and fuels** through the combination of Lewis and Brønsted acid catalysis. Dispersing zeolites in an ionic liquid medium will greatly **enhance the catalytic effectiveness** of these materials and provide **shape selective catalysis to tune the cracking products**. The Lewis acidic ILs will provide initial low temperature cracking ability. The combination of ionic liquid and zeolite enables a vast parameter space through which to optimise the target chemistry. Initial efforts will explore the difference between all-inorganic ILs and inorganic/organic ILs with zeolite additives for the conversion of PP and PE. Stability of the zeolites in the different media and the activity for PE and PP conversion will be key initial learning outcomes. **Tailoring of the IL and zeolite to optimize the production of monomer alkenes for the circular polymer economy is the ultimate target for this timely project.**

1 *Science Advances*, 19 Jul 2017: Vol. 3, no. 7, e1700782. DOI: 10.1126/sciadv.1700782

2 *Green Chem.*, **2022**, 24, 8899. DOI: 10.1039/D2GC02588D

3 *ACS Catal.*, **2022**, 12, 14882. DOI: 10.1021/acscatal.2c04915

4 *Angew. Chem. Int. Ed.*, **2021**, 60, 16101. DOI: 10.1002/anie.202104110

5 *Nanoscale*, **2019**, 11, 1515. DOI: 10.1039/C8NR07337F

6 *Chem*, **2021**, 7, 3340. DOI: 10.1016/j.chempr.2021.08.022

7 *Science*, **2023**, 379, 807. DOI: 10.1126/science.ade7485