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Relevant design parameters for catalytic conversion of model polyolefin waste to aromatics

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PURPOSE OF THE ABSTRACT

More than a century of polymer engineering has led to the development of plastics that are durable, lightweight and extremely versatile. However, the release of plastic waste into the environment is harmful. A drastic increase in recycling rates could slow this leakage of plastic waste and create economic opportunities. However, current recycling techniques, i.e. by melting and re-extrusion yield plastic of degraded quality and require sorted waste streams. Plastic waste it is essentially a, sometimes even cleaner, version of crude oil and can be used to replace it as carbon source for the refining industry. Simple thermal pyrolysis is used to convert plastic waste to a low value feedstock for e.g. naphtha crackers [1]. However, this work explores the use of different catalysts to obtain a more valuable stream of aromatics.

As a model waste stream, we investigated the conversion of polypropylene (PP), predominantly used in packaging making up 19.4 % of European polymer resin demand [2]. The fluid catalytic cracking catalyst (FCC-cat) and the equilibrium catalyst (ECAT), discarded from FCC operation as a waste product showed to be promising candidates for polymer conversion due to their open hierarchical pore system. The FCC-cat consists of zeolite Y with a pore size of about 7 Å and a high density of Brønsted acid sites (BAS) as well as alumina and silica components that pre-crack larger molecules. Lastly, clay is used as filler to shape the catalyst body [3]. During industrial FCC operation, metals, mostly Fe, Ni and V originating from the VGO feedstock and reactor fouling, deposit on the catalyst particles making a large fraction of the zeolite domains inaccessible and causing changes in the overall morphology of the catalyst [4]. In the regenerator of the FCC unit, catalysts are also subjected to steaming leading to dealumination and further deactivation of the zeolite domains [3]. In addition to FCC-cat and ECAT, model catalyst consisting of varying levels of metal poisoning and an FCC-cat without zeolite Y as well as zeolite Y were used for the catalytic conversion of PP.The product distribution was similar for ECAT and FCC-cat, most notably consisting of about 20 wt.% aromatics. With the discarded catalyst, however, the coke content was significantly lower [5] (Figure 1). A detailed analysis of the evolution of reaction products and coke showed that the FCC matrix plays a role in aromatization and that the presence of zeolite Y domains significantly increases coke formation.

Although the cracking of PP proceeds similar to cracking of vacuum gas oil, the traditional input to the FCC operation, the significantly larger size of polymer molecules limits penetration into the smaller pores of the catalyst (Figure 2A). In addition, the viscosity of the molten polymer make initial contact of polymer and solid catalyst inefficient. Varying the ratio between catalyst and polymer weight significantly affected the onset temperature of reaction (Figure 2B), showing that an increased available outer surface area of catalyst increases the rate of polymer cleavage. Testing various PP model polymers of molecular weights between 10,000 and 250,000 g/mol and PP waste materials also showed that lower molecular weight polymers lead to a lower onset temperature for cleavage, because of easier penetration of the polymer chains into the catalyst pores. Furthermore, the extent to which the reaction proceed throughout the catalyst was investigated by confocal fluorescence microscopy (CFM) of catalyst particles, recovered at relevant time points of the reaction, cut open by microtomy (Figure 2C). CFM visualizes fluorescent reaction intermediates throughout the catalyst particle.

These results suggest two main handles for further catalyst design: 1) high accessibility for the polymer chains and 2) moderate acidity in the matrix of the catalyst composite which were further explored with targeted synthesis of large pore materials like SBA-15.

FIGURES

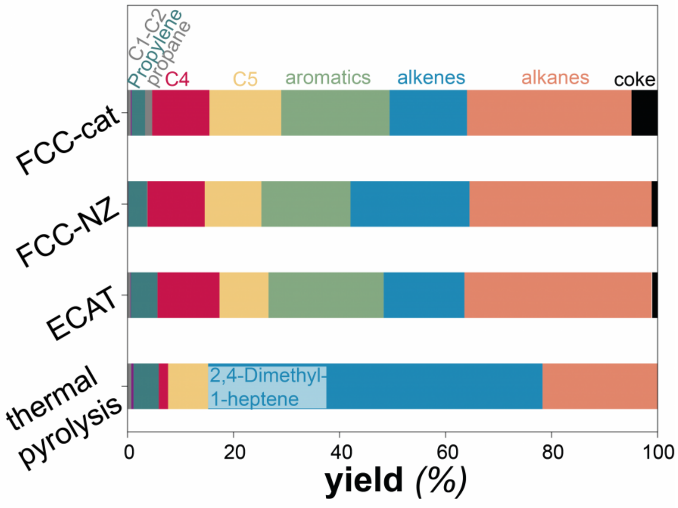

FIGURE 1

Product composition

Yields of products obtained from reaction at standard reaction conditions. C1-5 products were integrated from online GC analysis and >C5 products were identified and classified offline via GC-MS and quantified via GC-FID.

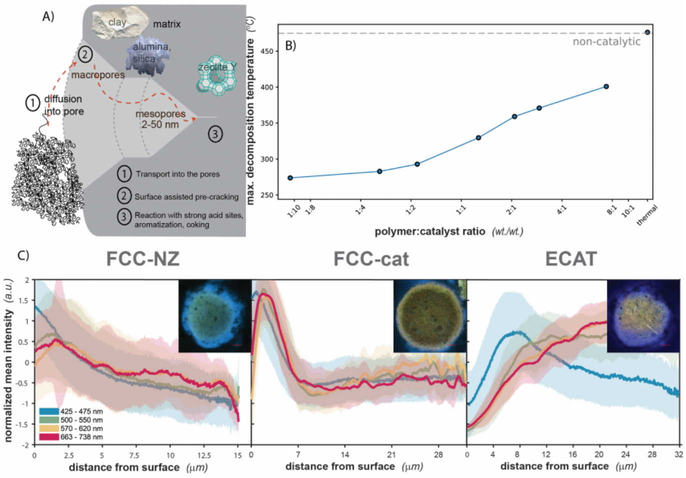

FIGURE 2

Transport limitations

Maximum decomposition temperature of PP (Mw=12,000 g/mol) over ECAT at different catalyst to polymer ratios, determined with thermogravimetric analysis under nitrogen A). A simplified depiction of the pore network of a FCC-cat and the interaction of the

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KEYWORDS

plastic waste | upcycling | catalytic cracking | transport limitations

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BIBLIOGRAPHY

[1] Tsuchiya, Y.; Sumi, K. J. Polym. Sci. Part A-1 Polym. Chem., 7, 1599–1607 (1969).

[2] Plastics - the Facts 2020. https://plasticseurope.org/wp-content/uploads/2021/09/Plastics_the_facts-WEB-2020_versionJun21_final.pdf (2020).

[3] Vogt, E. T. C.; Weckhuysen, B. M.. Chem. Soc. Rev., 44 (20), 7342–7370 (2015).

[4] F. Meirer, S. Kalirai, D. Morris, S. Soparawalla, Y. Liu, G. Mesu, J. C. Andrews, B. M. Weckhuysen, Sci. Adv., 1, e1400199 (2015).

[5] I. Vollmer, M.J.F. Jenks, R. Mayorga Gonzalez, F. Meirer, B. M. Weckhuysen, Angew. Chem. - Int. Ed., 60 (29), 16101-16108, (2021)