

Conversion of polyolefin waste to valuable base chemicals using steamed and phosphorus-modified mesoporous HZSM-5 zeolites

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Introduction

At present, limited technologies exist to recycle polyolefin waste streams and as a consequence, they are mostly incinerated or landfilled. Mechanical recycling, involving melting and reshaping of plastic, is successfully applied for PET bottles, but for polyolefin waste streams it leads to a steep reduction in product quality. Chemical recycling processes are a more 'thorough' means of recycling, wherein the molecular structures of polymers are broken up, thereby forming various hydrocarbon products. By the catalysed pyrolysis of waste polyolefins, valuable base chemicals such as light olefins (C₂-C₄) and aromatics are formed, that can subsequently be used for the production of new plastics. Enhancing the selectivity towards these desired products and increasing catalyst stability and are therefore important challenges to enable a circular economy for polyolefins.[1]

In this study, catalytic pyrolysis of polyolefinic (waste) feeds was performed, wherein the feed was first thermally decomposed by fast pyrolysis whereafter it was transported by a carrier gas to a second reactor for catalytic cracking aiming to maximize the yields of light olefins (C₂-C₄) and aromatics. HZSM-5 catalysts with different properties (Si/Al ratios, mesoporosity, phosphorus content and steaming) were used in combination with virgin polyolefins or a mixed polyolefin waste (MPO).[2] This MPO feed was obtained from a real-life waste stream collected from Belgian households and was sorted out and washed with cold water in an industrial sorting facility. This MPO feed contained several organic and inorganic impurities.[3] A micropyrolysis reactor coupled to two-dimensional gas chromatography was used for ex-situ pyrolysis experiments to study the performance of the catalysts.

Results & Discussion

Thermal pyrolysis of polyethylene (PE) at 600 °C yielded 8 wt.% of C₂-C₄ olefins and 2 wt.% of aromatics, while the other formed products consisted mostly of linear long-chain α-olefins and paraffins (64 wt.%). Similar high yields to long chain hydrocarbons were observed when thermally pyrolyzing the MPO feed. At the same temperature, pressure and carrier gas flowrate, while loading the reactor with a steamed and phosphorus-stabilized microporous HZSM-5 catalyst, resulted in yields of 75% C₂-C₄ olefins and 6% of aromatics. Increasing the reaction temperature in the range of 500 to 700 °C, increased the aromatics and C₂-C₄ olefins yield, showing increased yields of ethylene and 1,3-butadiene at the expense of propylene, C₄ mono-olefins and C₅₊ paraffins (Figure 1). Using the MPO feed at 600 °C resulted in yields of 73% and 9% to light olefins and aromatics, respectively, whereby the higher selectivity to aromatics was attributed to presence of polystyrene and PET in the MPO feed (±2%).

The catalyst stability was studied by repeated pulses of pyrolysis vapours of the MPO feed over the catalyst bed. During a total of 130 catalytic runs, the parent HZSM-5 displayed quick deactivation, which was apparent by decreased yields of C₂-C₄ olefins and increased yields of C₅₊ aliphatics (Figure 2). A phosphorus-modified and steamed HZSM-5 displayed a stable activity over >120 runs and showed high yields towards C₂-C₄ olefins, aromatics and C₅₊ aliphatics. Mesoporosity that was introduced by a post-synthesis desilication method, did not result in enhanced catalyst stability within the studied range of run numbers. Catalyst deactivation was attributed to coke formation on the catalyst surface and could be quantified with TGA and elemental analysis. The coking propensity of the parent ZSM-5 zeolite was significantly higher than the phosphorus-modified and steamed ZSM-5 catalyst, as was apparent by the surface coke concentrations of 32 µg/m² and 8 µg/m², respectively. Further studies proved that phosphorus-modified and steamed ZSM-5 catalyst displayed similar activity and selectivity after six regeneration cycles in an oxidizing environment at 700 °C.



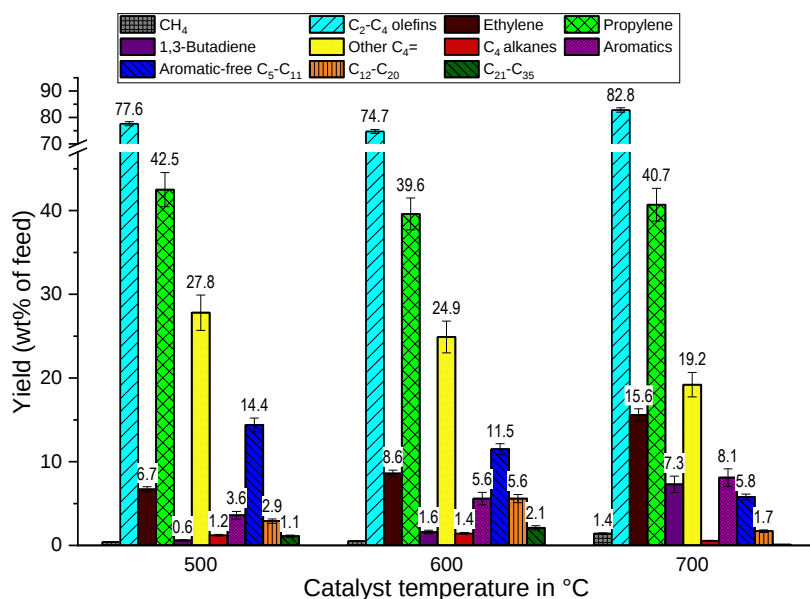


Figure 1. Yields obtained for a single reaction using LDPE as feed and *P/meso*Z55-ss as catalyst at different catalyst temperatures. Catalyst loading was 32 mg and catalyst/feed ratio = 80.

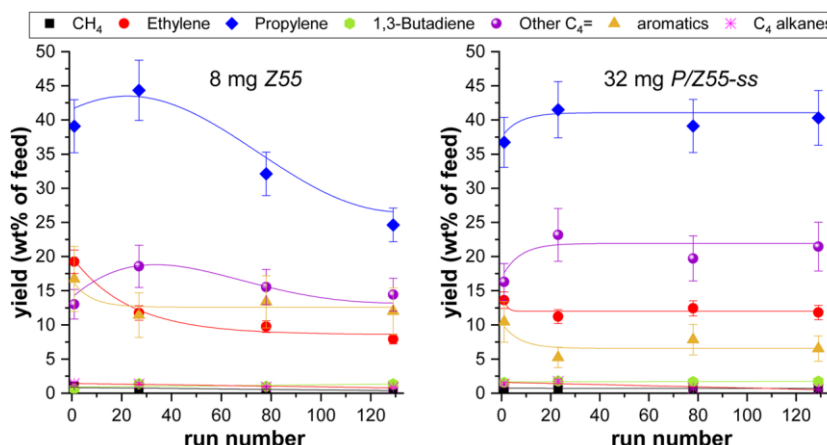


Figure 2. Product yields as function of run number for 8 mg of a parent ZSM-5 catalyst (left) and a phosphorus modified and steamed ZSM-5 catalyst (right). (ZSM-5 Si/Al = 30, Catalyst temperature = 600 °C)

Conclusions

Modified ZSM-5 catalysts employed for catalytic pyrolysis were demonstrated to be suitable catalysts for producing high yields of valuable base chemicals from virgin and waste polyolefins. The results of this study are highly relevant in order to improve the circularity of current chemical recycling processes.

References

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