Development of tandem catalysts by surface organometallic chemistry for chemical recycling of polyethylene to α-olefins
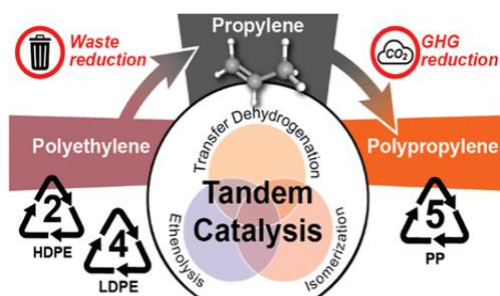
Développement de catalyseurs tandem par chimie organométallique de surface pour le recyclage chimique de polyèthylène en α-olèfines

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Introduction

Polymers are very common everyday life products with a worldwide production of more than 367 million metric tons in 2020 from unsustainable sources.[1] Polymers used for the packaging or in the manufacture of tires, represent more than 40% of the worldwide production. Although the invention of such polymers has provided a series of advantages, it has simultaneously generated a huge plastic pollution problem. Even if thermoplastic may be melted and remoulded, there are only marginally reused due to industry quality standard requirements. Due to the lack of a flexible technology to recycle such polymers, a main part of the produced plastics is discarded without any kind of reuse.[2] The most versatile route to direct recycling is by thermal or chemical treatment of the plastics for the production of monomers (such as ethylene and propylene) or heavier α-olefins, that can be re-polymerised through matured technologies. Current proposal targets to recycle polyethylene (PE) to propylene and α-olefins over heterogeneous catalysts under continuous flow. Propylene and α-olefins are a highly used monomer and the demand is forecasted to increase in the coming years.[3] Preliminary LCA analysis suggests that if 20% of the world's polyethylene was recovered and converted to propylene via the mentioned route, it could lead to a potential saving of 13 MT/year in CO_2 equivalent GHG emissions.[2]

Positioning versus the state of the art

Matured technology to degrade PE, for example by pyrolysis, inevitably results in a mixture of different products and consequently requires additional separation technology. Current approach is based on a tandem dehydrogenation/metathesis reaction on PE in a single reactor that will lead to very high selectivity of the targeted propylene and α-olefins.[2] As PE can be regarded as a macromolecule comprised of (approximately) infinite saturated hydrocarbon chains, the initial step involves dehydrogenation of the saturated hydrocarbon. Once at least one internal C=C double bond is created, metathesis reaction, with for example ethylene (called ethenolysis), can occur, giving shorter α-olefins. Proof-of-principle experiments of this reaction scheme to degrade PE have been reported by Huang and Beckham,[4,5] using the alkane metathesis pathway (combining a separate dehydrogenation and olefin metathesis catalyst) to produce lighter alkanes. A more recent work by Guironnet and co-workers has successfully demonstrated the selective degradation of monounsaturated PE to propylene (up to 95% selectivity) over a mechanical mixture of isomerisation and ethenolysis catalysts.[2] However, using the same approach the depolymerisation of saturated polyethylene remains a challenge due to the low efficiency of the dehydrogenation catalyst used under the given working temperature (200 °C).

The present proposal employs dehydrogenation and olefin metathesis catalysts synthesized by surface organometallic chemistry to degrade PE to propylene and α-olefins. Advantages with this methodology is to access single-site catalysts (surface organometallic chemistry on oxide) and promotion of metallic nanoparticle-based catalysts by selective poisoning (surface organometallic chemistry on metal). In general, all the metals immobilized as single site catalysts are active and thereby maximise the atom economy. It has also been demonstrated, for instance in olefin metathesis, that higher activity can be obtained by single site catalysts even with lower metal loading.[6] This work intents to operate at higher temperature in order to increase the conversion and addressing the mentioned issue about the inefficient dehydrogenation process. Hence, thermally stable dehydrogenation and metathesis catalysts are required. Other novelty is to develop bifunctional catalysts where the same support contains both active sites for dehydrogenation and olefin metathesis in proximity. Moreover, the catalytic degradation of PE will be executed under continuous flow, which remains to date unpublished. Finally, a reactive distillation set-up will be employed in order to control the selectivity of the products. To further boost

the conversion, a H_2 permeable membrane reactor[7] is envisaged to use in order to remove the formed H_2 and shift the equilibrium towards unsaturated PE intermediate for the production of propylene and α-olefins via ethenolysis.

Description

The research program is can be divided into three parts: synthesis, characterisation and catalysis. Taking the advantages of reported alkane dehydrogenation and olefin metathesis catalysts in CP2M, improved systems based on single site or

Removing Hydrogen by PdAg membrane

bimetallic nanoparticles can be further developed through judicious choice of the organometallic precursors and adjustment of the formulation of the catalyst. All catalysts will be prepared by the surface organometallic chemistry approach, involving grafting of suitable organometallic precursors (for example alkyl, aryl, alkoxide) onto a pre-treated conventional support (for example silica, alumina, meso-porous zeolite). The most promising nanoparticle-based dehydrogenation catalyst relies on promoted Pt system and will be optimised through surface organometallic chemistry on metal with different promotor (for example based on Sn, Ga, Ge). Regarding non-noble metal system, single site catalysts based on Ga, V and Cr have been proved to be active and will be investigated. Considering the metathesis catalyst, the focus lies on single site Mo and W systems due to the thermal robustness. The innovative bi-functional catalyst can be obtained through successive grafting.[8] The synthesised materials will be characterised by elemental analysis, spectroscopic methods (IR, NMR, EPR, XAS) and HRTEM/STEM for structure determination. Finally, the catalysts will be investigated in batch and continuous flow reactors, with or without PdAg membrane. A reactive distillation setup will be employed in order to tune the selectivity of the desired product. This can be done by adjusting the reactor length and temperature gradient where heavier molecules will condense and return to the reaction zone for further reaction.

Impact, risk and expectation

The impact of this proposal is extremely high, as it deals with recycling of plastics that has recently become an urgent challenge to address. It will provide an important demonstration for the industry that recycling of plastics can be conducted non-stop in a continuous flow reactor. The risk of this proposal is fairly low, as CP2M has about 30 years of experience in surface organometallic chemistry and catalysis. CP2M is holding the know-how technology for dehydrogenation[9–12] and olefin metathesis[13–17] catalysts, as well as reactive distillation,[18] as justified by numerous published articles. The laboratory is equipped with the necessary equipment to conduct this research. Several publishable manuscripts are expected from this work and the candidate will be trained in material synthesis under inert atmosphere, characterisation and catalysis. Supplementary insights of the structure of the catalysts can be obtained through a pursued collaboration partner (UCCS – Université de Lille) using the newly installed 1.2 GHz solid state NMR (^{95}Mo, ^{51}V, ^{71}Ga) which will further lift the scientific quality.[19]

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