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Multicatalysis enables turning plastic waste into chemical commodities

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ABSTRACT:

Recent studies by the laboratories of Hartwig, and Scott and Guironnet demonstrated that ingenious cascades of reactions driven by catalysts operating in concert enable converting ethylene and polyethylene (PE) materials, the largest plastic waste contributor, into propylene, the valuable olefin used in the synthesis of various chemicals and commodity materials.

KEYWORDS: multicatalysis, plastic waste recycling, polyethylene, commodity chemistry, sustainability

MAIN TEXT:

Over 6.3 billion metric tons of plastic materials have already accumulated in the environment, and additional 12 billion metric tons are expected to be discarded by 2050.[1] Valorization of plastic waste to produce common chemical feedstocks represents an attractive strategy to address these issues that threaten our society from environmental, economic, and social viewpoints (Figure 1a). [2] Polyethylene (PE) is the single major contributor to the plastic waste generated (29%).[1,3] However, the mechanical and chemical stability of PE, which is, on the one hand, attractive for the use of the material, on the other hand, hinders recycling and retards (bio)degradation when released into the environment. The current recycling strategies, employing mechanical, pyrolytic, and energy recovery processes, are burdened with severe drawbacks, including the low value of recycled materials, complex mixtures of products, and inefficient energy recovery, respectively, resulting in modest recycling rates of PE (~14% in 2015).[4,5] Therefore, new innovative methodologies for recycling are urgently needed.[6,7]

The breakdown of PE waste with ethylene to produce propylene, a high-volume raw material used in the synthesis of a wide variety of polymers and chemical commodities,[8] represents an attractive approach to plastic waste valorization, as envisioned previously in a theoretical work by Peter and Guironnet.[9] The envisioned strategy employs a cascade of dehydrogenation–isomerizing ethenolysis (DIE) reactions operating in concert in the presence of two or three catalysts (Figure 1b). While the theoretical background[9] and initial systems[10] for low-molecular-weight models of PE were reported before, only recently were the multicatalytic systems operating with authentic high-molecular-weight PE materials independently disclosed by the laboratories of Hartwig (Figure 1c), [11] and Scott and Guironnet (Figure 1d),[12] demonstrating the feasibility of the approach toward real-life scenarios.

Hartwig[11] and co-workers reported a multicatalytic system that promotes the chemical breakdown of both virgin PE and post-consumer PE to propylene with high yields in a two-step sequence (Figure 1c). More specifically, the DIE process was promoted by combining three catalysts, iridium hydride complex **D1**, Hoveyda-Grubbs metathesis catalyst **M1**, and dimeric Pd(I) bromide isomerization catalyst **I1**. Dehydrogenation of high-molecular-weight HDPE (high-density PE) or LDPE (low-density PE) with *tert*-butyl ethylene (TBE) as a hydrogen acceptor was achieved with a homogeneous catalyst **D1** or heterogeneously supported Pt/Sn[13] and Pt/Zn[14] catalysts. The earlier yielded higher levels of unsaturation required for the efficient polymer breakdown. Importantly, varying levels of unsaturation can be introduced (within the range of 0.6% - 3.2% of olefins) with **D1** by simply modulating the loading of TBE. The subsequent degradation of unsaturated PE samples under ethylene in the presence of **I1** and **M1** furnished propylene in high yields. The performance of the overall degradation process depended on the level of unsaturation introduced in the preceding dehydrogenation step. An outstanding 87% yield of propylene was obtained with the HDPE sample bearing 1.9% of unsaturation. In turn, the unsaturated LDPE samples degraded to propylene with yields up to 70%. Most remarkably, post-consumer PE materials, such as HDPE from a milk jug and LDPE from food packaging, generated propylene in >50% yields, demonstrating the approach in real-case scenarios.

Noteworthy, in some cases, additives and impurities present in post-consumer PE materials disturbed the performance of the DIE process. However, a simple pre-treatment of the PE material through dissolution-precipitation was sufficient to recover the reactivity, proving the robustness of the catalytic strategy.

Mechanistic experiments with ^{13}C -labeled HDPE and non-labeled ethylene confirmed that most of the propylene formed arose from polymer degradation rather than from the background conversion of ethylene to propylene. The authors also gained insights into the challenges that need to be addressed to establish the practical processes for PE recycling. For instance, they noted that the degradation of LDPE consistently delivered lower yields of propylene than the reactions with HDPE. The reduced efficacy was attributed to a significant degree of branching present in LDPE that would lead to the formation of trisubstituted alkenes during the process, which are more resistant to degradation, in line with the control experiments. Additionally, the degree of unsaturation introduced into the polymer needs to be precisely controlled. Its low level prohibits efficient polymer breakdown, while its high level promotes the formation of 1,3-dienes that tend to poison the catalysts, lowering the yield of propylene. Lastly, the requirement of the large excess of ethylene and the modest activity and stability of the homogeneous catalysts need to be overcome. The authors envisioned that the use of continuous flow reactors with heterogeneous catalysts for metathesis and isomerization processes, which are routinely used in the industrial processes performed on commodity scales, would facilitate the implementation of the DIE strategy in large-scale.

In parallel studies, Scott, Guironnet,[12] and co-workers investigated breaking virgin PE materials employing different homogeneous and heterogeneous catalysts in a continuous stirred tank reactor (CSTR; Figure 1d), providing a highly valuable set-up that mimics large scale operation conditions. Specifically, the authors showed that heterogeneous $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalyst introduced one unsaturation (i.e., C=C bond) per 6 polymer chains of saturated PE, while homogeneous Ir-based pincer catalyst **D2** promoted dehydrogenation to a lower extent, with one olefin group introduced per 14 polymer chains. In turn, a mixture of homogeneous catalysts **I1** and **M2** and heterogeneous catalyst $\text{MTO}/\text{Cl-Al}_2\text{O}_3$ were shown to be effective for the isomerization/ethenolysis steps. More specifically, starting with monounsaturated PE and a combination of **I1** and **M2**, under a continuous ethylene flow that suppresses unproductive self-metathesis, the process produced propylene with 94 mol% selectivity and 24% yield. In turn, the use of heterogeneous catalyst $\text{MTO}/\text{Cl-Al}_2\text{O}_3$, in place of **I1** and **M2**, produced propylene with similar selectivity and with higher initial activity. Both processes, however, suffered from the deactivation of the catalysts; **I1** and **M2** were required to be continuously fed to the reactor to maintain the propylene formation, while the activity of $\text{MTO}/\text{Cl-Al}_2\text{O}_3$ ceased within 7 h. Notably, the use of CSTR proved crucial to gain insights into the catalysts deactivation processes, which is the most challenging aspect to be resolved for future studies and applications. Experiments using ^{13}C -labeled ethylene and non-labeled 1-octadecene, demonstrated that degradation of the substrate is the source of carbon atoms present in the propylene product, alongside with ^{13}C from ethylene. Finally, the authors perform a preliminary assessment of the potential carbon footprint by using a comparative life cycle assessment (LCA), which showed that converting 20% of world's waste PE to propylene via this multicatalytic approach could lead to significant saving of CO_2 -equiv. GHG emissions, commensurable to removing from the streets 3 million cars running with internal combustion engines.

Both studies uncovered several cross-disciplinary challenges that must be tackled in order to bring the strategy into real-world recycling scenarios. In this context, research efforts should focus on the development of significantly robust catalytic systems able to perform in the presence of contaminants, to ideally avoid the need of pre-treatments of the waste samples that could compromise large scale processes. Moreover, special attention should be devoted to the development of novel dehydrogenation catalysts that can operate in milder conditions, to ensure the success of the initial step in a wider variety of conditions and sample-types. At last, the abovementioned processes should ideally evolve into a one-step flow system employing heterogeneous catalysts that mimic settings used currently in industry, to target economically feasible processes.

In conclusion, although challenges related to the activity, compatibility, and stability remain to be addressed for the development of commercially viable industrial-scale processes, these benchmark studies set the blueprints to enable converting PE containing materials, the largest plastic waste contributor, into propylene, the commodity olefin of the second-largest demand. In a broader context, the studies demonstrate the unique opportunities offered by multicatalytic systems that are beyond classic monocatalytic systems.[15]

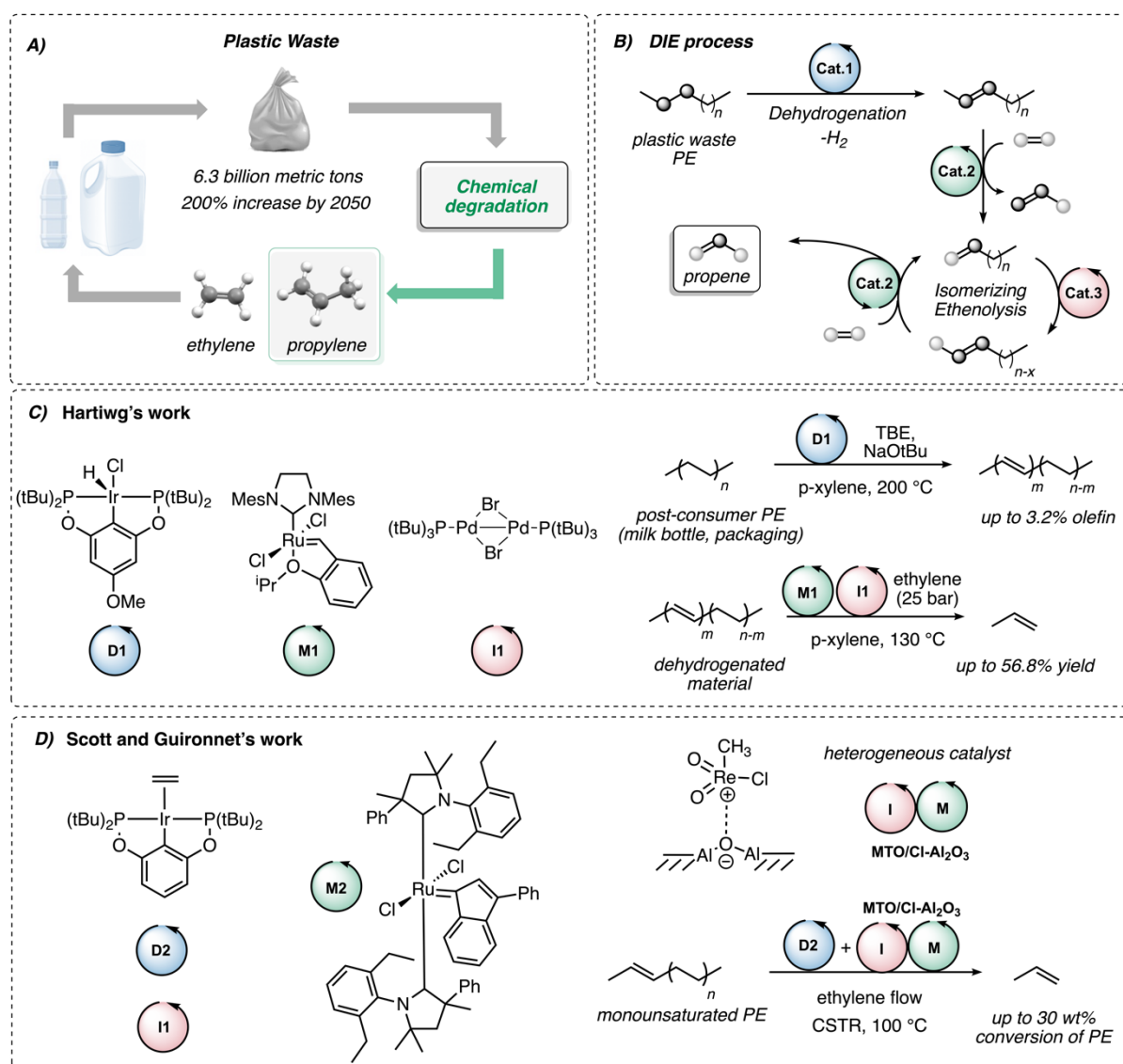


Figure 1. Multicatalytic strategy for the degradation of plastic waste. A) Valorization of plastic waste. B) Dehydrogenation – Isomerization/Ethenolysis process scheme (DIE). C) Summary of Hartwig's work. D) Summary of Scott and Guironnet's work.

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