Chemical Recycling of Polyethylene by Tandem Catalytic Monomerization to Propylene

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ABSTRACT: Although polyethylene (PE) and polypropylene (PP) are by far the world's largest volume plastics, only a tiny fraction of these energy-rich polyolefins is currently recycled. Depolymerization of PE to its constituent monomer, ethylene, is highly endothermic and conventionally accessible only through unselective, high temperature pyrolysis. Instead, a tandem catalysis strategy serves to convert PE to propylene, the commodity monomer used to make PP. The approach combines rapid olefin metathesis with rate-limiting isomerization. Mono-unsaturated PE is progressively disassembled at modest temperatures via many consecutive ethenolysis events, resulting ultimately in propylene. Fully saturated PE can be converted to unsaturated PE starting with a single transfer dehydrogenation to ethylene, which produces a small amount of ethane (one equiv. per dehydrogenation event). These principles are demonstrated using both homogeneous and heterogeneous catalysts. While selectivity under batch conditions is limited at high conversion by formation of an equilibrium mixture of olefins, high selectivity to propylene (greater than 90 %) is possible a semi-continuous process due to the continuous removal of propylene from the reaction mixture.

Plastic pollution is one of the most pressing and difficult environmental challenges of our time. Only 30 % of all plastic ever produced is currently in active use; the vast majority of the discarded plastic (79 %, or nearly 6.3 billion metric tons) has accumulated in landfills or the natural environment.[1] This enormous quantity of largely non-biodegradable material is having visibly detrimental effects on the health of humans, ecosystems, and wildlife at all levels of the food chain.[2,3] The projected increase in the rate of plastic production between 2020 and 2050 will generate another 12 billion metric tons of waste.[1] Consequently, the world urgently needs to develop and implement new effective strategies to reduce the amount of discarded plastic. At the same time, the world must address an even more pressing environmental challenge: climate change. The energy-intensive manufacturing of large volume chemicals could become more circular by recycling carbon, thereby dramatically reducing the need for new inputs of fossil carbon feedstock and energy.

Polyethylene (PE) accounts for almost 29 % of all synthetic polymer production worldwide (109 million metric tons in 2021)[1]. As a strong, lightweight, chemically inert, low-cost material, PE in its many forms (including the three major commercial grades: HDPE, LDPE, and LLDPE) finds extensive application in single-use products and packaging, making it the single largest contributor to the plastic waste problem.[4] PE has a high embodied energy of 72 MJ/kg, and embedded carbon of 1.6 kg/kg.[5] Due to the enormous scale of its production, PE manufacturing alone is responsible for 2.5 % of annual global energy use and almost 1% of annual global carbon emissions.[6]

Recycling strategies for plastics are broadly classified as mechanical, chemical, and energy recovery (including direct combustion and conversion to liquid fuels via pyrolysis.[7,8] Mechanical recycling inevitably leads to polymer degradation, and due to contamination issues, precludes all but low value reuses.[9] Furthermore, even sorted postconsumer PE waste necessarily consists of many different PE grades, as well as a significant amount of residual polypropylene (PP),[10] which make mechanically recycled PE unsuitable as a substitute for virgin PE in most uses. As currently practiced, energy recovery from polyolefins is wasteful since a large fraction of the embodied energy cannot be recovered due to thermodynamic limitations. Consequently, polyolefins are mostly manufactured and discarded without any kind of reuse, **Figure 1**.
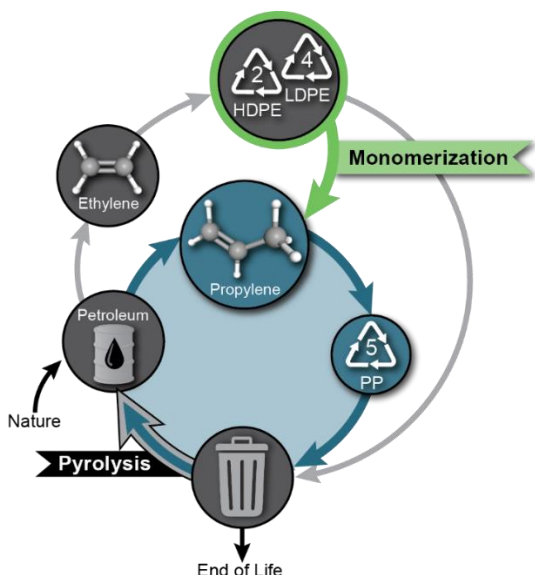
Figure 1. Typical origin and fate of the polyolefins PE (larger grey circle) and PP (smaller blue circle), as well the proposed PE monomerization shortcut between the two (green arrow).

In recent years, chemical recycling of PE has become a goal of intense interest to researchers.[11–16] While some of the proposed approaches may help to address the plastic waste problem, many of the current targets (e.g., lubricants, surfactants) have market sizes much smaller than that of PE itself. Furthermore, converting polyolefins into new materials and chemicals will not reduce the world's production of virgin polyolefins. Moving towards net-zero greenhouse gas (GHG) emissions for plastics will likely require a combination of renewable carbon, decarbonization of the energy supply, carbon capture and storage, and circular technologies for recycling plastics.[17]

Feedstock recovery is the depolymerization of polymers back to their constituent monomers. One key advantage of this strategy is that subsequent repolymerization can create new polyolefins with any desired physical properties, and with the purity necessary for use in any application, including the most demanding food and medical grade uses. This type of polymer circularity would simultaneously decrease the use of non-renewable feedstocks and create a large potential market for plastic waste. Some success in feedstock recovery has been reported in the monomerization at low-to-moderate temperatures of polymers made by step-growth condensation (such as polyethylene terephthalate, PET),[18] and the radical depolymerization of polymers with low ceiling temperatures (such as polystyrene, PS).[19,20] However, such strategies are not viable for PE and PP due to the high strength and chemical inertness of the σ-bonds in their all-carbon backbones. As a result, feedstock recovery is the currently the fate of less than 1 % of polyolefins.[21] Nevertheless, catalytic upgrading of PE-derived pyrolysis oil to mostly light olefins (ethylene, propylene, and butenes) was recently demonstrated using a P-modified, steam-stabilized HZSM-5 zeolite with appreciable selectivity to propylene (up to 51 wt%), but at temperatures of 500-700 °C.[22]

Recently, we proposed a different chemical conversion strategy for PE, and explored its viability via simulation.[23] It involves "monomerization" of PE via its ethenolysis to propylene, and it has a much lower energy requirement than direct thermal or catalytic

depolymerization to ethylene. An efficient and selective conversion of PE to propylene (already produced at a global rate of 90 million metric tons in 2021)[24] would generate the feedstock for manufacturing PP, another commodity polyolefin (global production 76 million metric tons in 2021).[25] This strategy could contribute to a new circular economy for polyolefins (**Figure 1**). In this contribution, we provide key experimental verification for the approach.

Two key steps alternate in the monomerization reaction sequence: (1) ethenolysis of a mono-unsaturated PE chain to achieve C=C bond scission; and (2) isomerization of the resulting vinyl-terminated polymer fragments to internal olefins (**Figure 2A**). Using a large excess of ethylene will serve to drive the metathesis equilibria towards propylene, but will necessitate a final separation of the propylene in order to recycle the unused ethylene. Fortunately, this separation is well-known and already widely practiced, due to its use in naphtha cracking.[24] The 2-step tandem reaction sequence requires PE that initially contains at least one C=C bond per chain. Such mono-unsaturated chains are generated by the Phillips ethylene polymerization catalyst (Cr/SiO$_2$), which operates in the absence of H$_2$ to form chains that are vinyl-terminated at one end.[26] This highly successful commercial process generates up to half of all PE currently manufactured worldwide.[26] Recently, tandem ethenolysis-isomerization was reported in the conversion of much smaller monounsaturated hydrocarbon chains. Two linear α-olefins (C$_6$ and C$_{18}$) were partially converted to propylene, using a combination of heterogeneous catalysts (MoO$_3$/γ-Al$_2$O$_3$ and H-BEA)[27] or homogeneous Ru-based catalysts.[28]
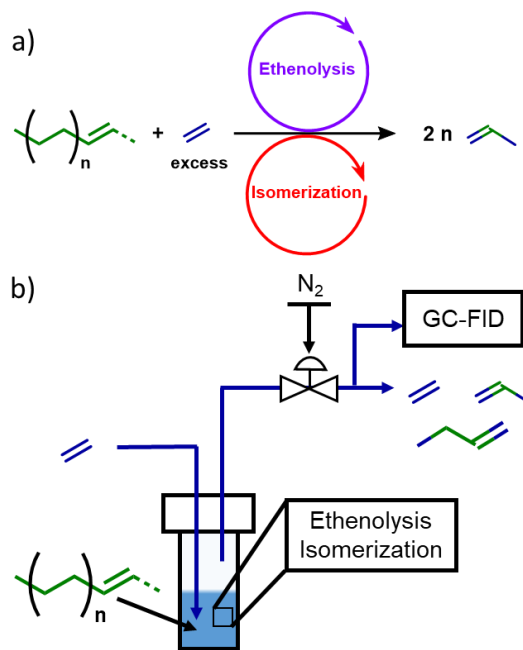

Figure 2. (a) Tandem ethenolysis/isomerization reactions for the conversion of unsaturated PE to propylene. (b) Semi-continuous flow reactor set-up used in this study.
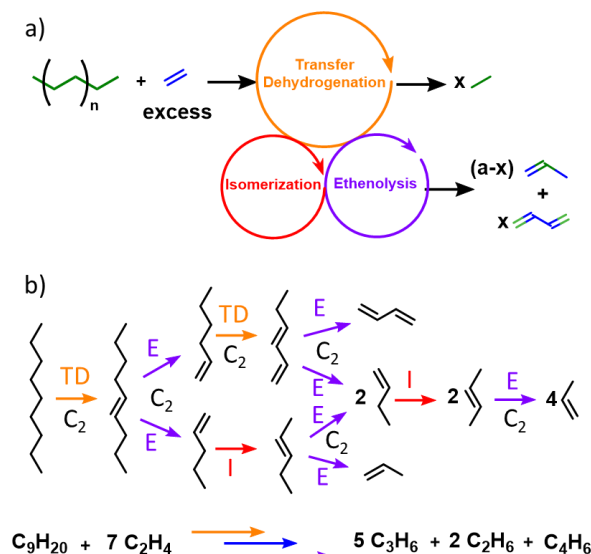
Figure 3. (a)Tandem dehydrogenation/ethenolysis/isomerization reactions for the conversion of saturated PE to propylene and butadiene. (b) Example of the complete monomerization of *n*-nonane into five molecules of propylene, two molecules of ethane and one molecule of butadiene following 2 transfer dehydrogenations (TD), 2 isomerizations (I) and 8 ethenolyses (E).

In contrast to mono-unsaturated Phillips PE, commercial Ziegler-Natta and metallocene catalysts are used in the presence of H_2 to make fully saturated PEs.[29] For such materials, monomerization via the proposed chemistry requires an initial dehydrogenation step to introduce at least one C=C bond into the polymer backbone. However, the presence of excess ethylene (required for the ethenolysis step) allows for occasional transfer dehydrogenation to generate the necessary unsaturation. For each polymer chain, the occurrence of *n* transfer dehydrogenation events (at least one per chain) produces *n* equiv. ethane, as well as (*n*-1) equiv. α,ω-dienes (such as butadiene) associated with multiple dehydrogenation events on the same chain, **Figure 3A-B**. Most important, all reactions in the cascade starting from either unsaturated or saturated PE are near-thermoneutral, and therefore require only enough energy to overcome their intrinsic activation barriers.

To achieve tandem isomerization/ethenolysis of PE, with or without prior transfer dehydrogenation, the catalysts required for each of the two (or three) steps must be mutually compatible. Due to the poor solubility of semicrystalline PE, the catalysts must also be active and stable at a common temperature near the melting point of the polymer (which can be up to 140 °C, depending on the polymer architecture and molecular weight distribution). To simplify the search for compatible catalysts, we initially studied tandem PE isomerization/ethenolysis, without the transfer dehydrogenation step. The reaction was explored using a semi-crystalline, low molecular weight, linear PE (M_n = 3,000 g/mol). Based on its synthesis method,[30] it bears a single olefinic termination per chain. A large excess of ethylene is required to (1) achieve many ethenolysis events per polymer chain, (2) shift the reaction equilibrium towards propylene, and (3) suppress the metathesis of higher α-olefins. However, excess ethylene can also inhibit the rate of ethenolysis due to the occurrence of unproductive ethylene self-metathesis. The latter was minimized by supplying ethylene as the feed to a continuous stirred tank reactor (CSTR, **Figure 2B**).

First, the effectiveness of a homogeneous Ru-based ethenolysis catalyst, Ultracat,[31] was investigated for PE monomerization in the presence of a homogeneous isomerization catalyst (**Figure 4** and **SI**). To counteract relatively rapid catalyst deactivation at the reaction temperature (70 °C), a solution of the two catalysts ([Ultracat] = 10 mM and [isomerization catalyst] = 4.2 mM in toluene) was co-fed to the reactor (pre-loaded with 250 mg PE) over the course of 5 h. Ethylene (≥99.95%) was fed continuously to the reactor at atmospheric pressure (10 mL/min). The gas product mixture exiting the reactor was sampled and analyzed by online GC over the next 10 h to obtain the instantaneous rate of olefin formation.
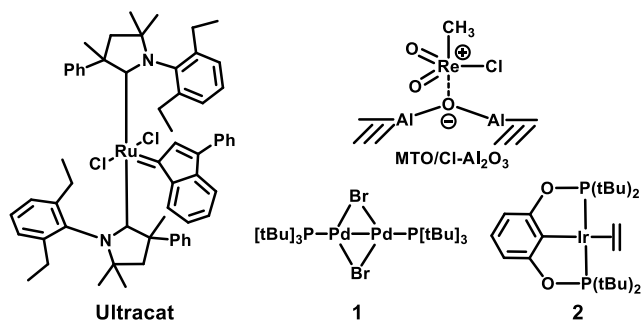

Figure 4. Structures of the two metathesis catalysts (Ultracat, MTO/Cl-Al$_2$O$_3$), the isomerization catalyst **1**, and the transfer dehydrogenation catalyst **2**, used to achieve tandem PE monomerization to propylene.

Among all the isomerization catalysts tested (**Figure 4 and SI**), the combination of Ultracat and **1** gave the highest PE conversion and propylene formation rate (**Figure 5A**). A very high average propylene selectivity was observed (94 mol%, **Figure 5B**). The cumulative mass of non-ethylene olefins detected at the reactor outlet (corresponding to 24 wt% of the PE) was in good agreement with the mass loss of PE, measured at the end of the experiment (27 wt%), further validating the selectivity of the process for light olefin formation. The high propylene selectivity observed throughout the experiment establishes that ethenolysis is considerably faster than isomerization, and therefore that depolymerization proceeds in a truly processive manner from the chain-end.[12,32] ^{1}H NMR analysis of the PE recovered after the reaction reveals a decrease in the number of olefinic protons (i.e., < 2 olefinic protons per polymer chain, **Figure S7**). This observation suggests either that trisubstituted olefins are formed during the reaction (e.g., via skeletal isomerization of the linear PE to generate methyl branches along the backbone) and/or that the olefins undergo a side-reaction (e.g., hydrogen transfer or oligomerization). The nature of this process is currently under investigation.
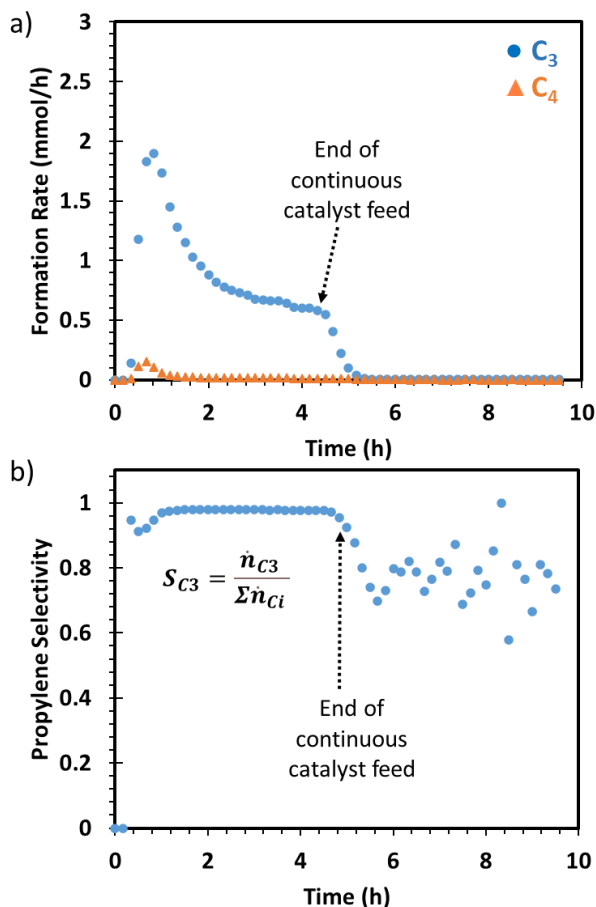
Figure 5. (a) Instantaneous propylene and butene formation rates, and (b) propylene selectivity, recorded during the monomerization of mono-unsaturated PE to propylene via tandem ethenolysis/isomerization. Reaction conditions: 250 mg PE (M_n = 3,000 g/mol), 5 mL of a toluene solution of Ultracat (10 mM) and **1** (2.1 mM), fed to the reactor over the course of 5 h, 70 °C.

Although catalyst separation from the gas-phase reaction products (largely propylene, in this case) is obviously not an issue for the process shown in **Figure 2B**, the high cost and low thermal stability of the homogeneous catalysts led us to investigate heterogeneous catalysts. Screening was accomplished in a batch reactor using a model substrate (1-octadecene) whose discrete molecular mass and facile analysis by GC allow for more precise characterization of the non-volatile hydrocarbon products generated under batch conditions. Three well-known heterogeneous metathesis catalysts (containing Re_2O_7, MoO_3, or CoO-MoO_3, each dispersed on γ-Al_2O_3) were quickly ruled out, due to their tendency to promote ethylene dimerization under the reaction conditions. However, methyltrioxorhenium (MTO, **Figure 4**) supported on and activated by chlorinated alumina (Cl-Al_2O_3), which we previously reported to be highly productive in propene self-metathesis near room temperature,[33] was effective as the ethenolysis catalyst. In the presence of excess ethylene (99.9%, 22.5 mol/mol C_{18}), MTO/Cl-Al_2O_3 (100 mg, 2.5 wt% Re, 4.0 wt% Cl) converted 98 % of the 1-octadecene (0.80 mmol) to a mixture of linear olefins (C_{3+}, including 55 mol% propylene) in just 1 h at 100 °C (olefin products $C_{>18}$ arise due to C_{18} homo-metathesis). The predominance of propylene in the gas-phase products demonstrates that MTO/Cl-Al_2O_3 also catalyzes olefin isomerization at an appropriate rate for the

tandem reaction. The active sites are presumably the acidic sites of the chlorinated support.[34] However, the propylene formation rate still decreased considerably over the 1 h reaction time, due to catalyst deactivation.

The tandem ethenolysis/isomerization mechanism for monomerization of 1-octadecene predicts that both the terminal carbons of propylene arise from ethylene, while the internal (methine) carbon originates from the 1-octadecene. The origin of each carbon atom in the propylene was investigated using $^{13}C_2H_4$ in combination with GC-MS and *in situ* ^{13}C MAS NMR spectroscopy.[35] The reaction was conducted with excess $^{13}C_2H_4$ (22 mol/mol C_{18}) and MTO/Cl-Al_2O_3 as the catalyst. GC-MS analysis of the propylene (m/z = 44, **Figure S30**) reveals that 70 % of the isotopomers contain two ^{13}C atoms (derived from $^{13}C_2H_4$) and one ^{12}C atom (derived from unlabeled 1-octadecene). The ^{13}C MAS NMR spectrum shows intense peaks in the ranges 116-118 ppm and 19-21 ppm, corresponding to propylene's terminal olefinic carbons and methyl carbons, respectively, **Figure S29**. In contrast, the intensity at 135 ppm (characteristic of the methine group of propylene) is four times lower than for either of the terminal carbons (**Figure S28**).

Next, the performance of MTO/Cl-Al_2O_3 was evaluated in selective monomerization of mono-unsaturated PE. In the semi-continuous reactor at 100 °C over the course of 5 h, PE (250 mg) was converted (19%) to light olefins, with 71 % average selectivity for propylene (**Figure S35**). The catalyst (150 mg) was fully deactivated by the end of the experiment. The modest average reaction rates observed here reflect this deactivation and emphasize the need for development of more robust catalysts for the tandem reaction.

To achieve monomerization of saturated PE, it is necessary to identify a PE dehydrogenation catalyst effective in the moderate temperature range required for stability of ethenolysis catalyst. We first explored the (transfer) dehydrogenation of saturated PE in the absence of a metathesis catalyst. Homogeneous Ir-based pincer catalysts are known to perform alkane dehydrogenations at temperatures below 200 °C.[36] Dehydrogenation of saturated PE (M_n = 1700 g/mol, Đ = 24, 400 mg) was catalyzed by **2** (34 μmol) in refluxing mesitylene. After 20 h, the polymer was recovered, dissolved in $C_2Cl_4D_2$ at 100 °C, and characterized by ^1H NMR. The presence of unsaturation in the polymer was confirmed via the appearance of a characteristic olefinic signal at 5.5 ppm (on average, 1 olefin group per 14 polymer chains, **Figure S2**). A higher extent of olefin incorporation was obtained via transfer dehydrogenation using a heterogeneous dehydrogenation catalyst (Pt/γ-Al_2O_3, 1.5 wt% Pt, 300 mg). In the presence of 52 bar ethylene, it gave 1 olefin group per 6 polymer chains, **Figure S4**. Furthermore, the expected product of transfer dehydrogenation, ethane, was detected by GC-TCD in the reactor headspace.

The partially dehydrogenated polymer (250 mg, made with Pt/γ-Al_2O_3, 1.5 wt% Pt) was subjected to tandem ethenolysis/isomerization catalyzed by MTO/Cl-Al_2O_3 (75 mg) in the CSTR (100 °C, atmospheric C_2H_4). A stable rate of propylene formation (0.01 mmol/h) was sustained for the next 10 h, although the total conversion was only ca. 1 wt%. The low rate is a consequence of the small extent of PE dehydrogenation and the low solubility of high molecular fraction of the polymer.

Next, the possibility of performing all three catalytic reactions in tandem was explored. Dehydrogenation catalyst **2** (40 μmol) and MTO/Cl-Al_2O_3 (150 mg) were combined with mono-unsaturated

PE (250 mg) at 100 °C in the semi-continuous reactor. The appearance of traces of butadiene at early times on-stream suggests that additional dehydrogenation did indeed occur (**Figure S69**). The presence of **2** slowed the rate of ethenolysis, resulting in a lower initial rate of propylene formation (0.85 vs. 1.40 mmol/h). Intriguingly, it also resulted in better stability of the metathesis catalyst (which deactivated only after 15 h in the presence of **2**, compared to 5 h in its absence).[37] This sustained catalytic activity led ultimately to 30 wt% conversion of mono-unsaturated PE after 15 h. Overall, this experiment demonstrates that performing dehydrogenation, isomerization and ethenolysis simultaneously in a flow reactor is a promising strategy for the conversion of the waste plastic with the largest volume (PE) into the commodity olefin monomer with the second-largest demand (propylene).

Finally, we conducted a preliminary assessment of the potential carbon footprint of the PE monomerization process, using a comparative life cycle assessment (LCA) approach. The basis for comparison is fossil-fuel-derived propylene produced by conventional steam cracking of naphtha (see the SI for details). In the new approach, saturated PE is assumed to be completely converted to propylene via its reaction with ethylene, in a fully continuous process that includes ethylene/propylene separation. The small amount of ethane produced by transfer dehydrogenation is neglected. Including polymer collection, sorting, the manufacture of propylene by PE monomerization would result in a reduction of ca. 13 % in greenhouse gas (GHG) emissions, relative to conventional propylene production (**Figure S71**). The largest contributor by far to GHG emissions in the PE monomerization process is ethylene production. The modest overall reduction is comparable to that reported for PE pyrolysis followed by upgrading of the pyrolysis oil to light olefins and aromatics by steam cracking using natural gas heating.[22] Furthermore, a selective monomerization process, like the competing two-step pyrolysis-cracking process,[22] is expected to have a much lower carbon footprint than traditional incineration.

The preliminary LCA analysis further suggests that if even 20% of the world's PE were recovered and converted to propylene via monomerization, it could represent a potential savings of 13 MT/yr in CO_2-equiv. GHG emissions, comparable to the impact of taking 3 million cars with internal combustion engines off the road.[38] This prospect motivates further investigation and development of PE monomerization for at-scale production of propylene. In particular, there is tremendous potential for much larger GHG reductions, either by replacing the fossil energy-derived heat used to dehydrogenate ethane by renewable electricity,[22] and/or by substituting the fossil-derived ethylene itself with a sustainable source of ethylene (e.g., from bio-ethanol dehydration).

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