Conversion of Polyolefin Waste to Liquid Alkanes with Ru-Based Catalysts under Mild Conditions

Julie E. Rorrer, Gregg T. Beckham, and Yurii Román-Leshkov*

ABSTRACT: Chemical upcycling of waste polyolefins via hydrogenolysis offers unique opportunities for selective depolymerization compared to high temperature thermal deconstruction. Here, we present the hydrogenolysis of polyethylene into liquid alkanes under mild conditions using rhenium nanoparticles supported on carbon (Ru/C). Reactivity studies on a model \( n \)-octadecane substrate showed that Ru/C catalysts are highly active and selective for the hydrogenolysis of (sp\(^3\))\(\text{C} \rightarrow \text{C}(\text{sp}^3)\) bonds at temperatures ranging from 200 to 250 °C. Under optimal conditions of 200 °C in 20 bar H\(_2\), polyethylene (average \( M_n \sim 4000 \) Da) was converted into liquid \( n \)-alkanes with yields of up to 45% by mass after 16 h using a 5 wt % Ru/C catalyst with the remaining products comprising light alkane gases (\( C_1 - C_6 \)). At 250 °C, nearly stoichiometric yields of CH\(_4\) were obtained from polyethylene over the catalyst. The hydrogenolysis of long chain, low-density polyethylene (LDPE) and a postconsumer LDPE plastic bottle to produce \( \text{C}_n \rightarrow \text{C}_{45} \) alkanes was also achieved over Ru/C, demonstrating the feasibility of this reaction for the valorization of realistic postconsumer plastic waste. By identifying Ru-based catalysts as a class of active materials for the hydrogenolysis of polyethylene, this study elucidates promising avenues for the valorization of plastic waste under mild conditions.

KEYWORDS: plastic upcycling, hydrogenolysis, ruthenium, depolymerization, polyethylene, polyolefins, heterogeneous catalysis, alkanes
activity for terminal C–C bond cleavage, and whether similar activity could be obtained at lower temperatures. Indeed, further investigation of other supported noble metals for hydrogenolysis at even milder conditions is needed.

Here, we demonstrate the selective depolymerization of polyethylene to processable liquid hydrocarbons under mild conditions in the absence of solvent using Ru nanoparticles supported on carbon. First, we screened a series of noble metal catalysts using n-octadecane—a model compound for linear polyethylene—and identified Ru nanoparticles supported on carbon as the most active. Next, we investigated the C–C bond cleavage selectivity as a function of conversion to understand how product distributions change as a function of extent of reaction. We then implemented optimized reaction conditions for the hydrogenolysis of a model PE substrate (average Mₙ 4000 Da) and commercial low-density polyethylene (LDPE). Finally, we demonstrated that the Ru/C catalyst is capable of converting LDPE from a real postconsumer plastic bottle. The identification of Ru-based catalysts as a class of materials for highly active hydrogenolysis is important for developing effective depolymerization processes of waste plastics to produce processable and transportable liquid that could be used as fuels, chemicals, or synthons for the next generation of infinitely recyclable polymers.¹⁹

Ruthenium-based catalysts such as Ru/CoOₓ, Ru/SiO₂, Ru/Al₂O₃, and Ru/TiO₂ have been shown to be active both for the hydrogenolysis of light alkanes and lignin.²⁰,²¹ Our group has also shown that cobalt-based catalysts have tunable activity for C–O vs C–C bond hydrogenolysis of oxygenated arenes.²² These previous observations prompted us to test a series of noble metal catalysts including Ru- and Co-based catalysts, as well as other transition metals, for the hydrogenolysis of n-octadecane in 25 mL Parr stainless steel pressurized reaction vessels under temperatures and H₂ pressures ranging from 200 to 250 °C and 30–50 bar, respectively (see Table 1). Products were identified by gas chromatography mass spectrometry (GC-MS) and quantified using a GC equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). Additional methods, catalyst characterization, and product characterization are provided in the Supporting Information (Figures S1–S4, Tables S1–S5). At 250 °C, 1% Pt/γ-Al₂O₃, NiO, 5 wt % Ni on carbon, and γ-Al₂O₃ showed little to no activity. Co-based catalysts (entries 1 and 2) and Rh-based catalysts (entry 9) showed moderate hydrogenolysis activity, converting n-octadecane into a range of C₁–C₁₇ alkanes. Notably, Ru-based catalysts stood out for their high hydrogenolysis activity (entries 5–8, 10, and 11). Specifically, the 5 wt % Ru/C catalyst (entry 10) reached an n-octadecane conversion of 92% at 200 °C, generating a mixture of liquid and gaseous alkanes, while at 250 °C, 100% of the n-octadecane was converted into CH₄. Due to the high activity at low temperatures and relatively low catalyst loadings, the 5 wt % Ru/C catalyst was selected for further investigation. Using a catalyst that is active at low temperatures decreases both the energy requirements for polyethylene processing and the thermodynamic driving force toward terminal C–C bond cleavage to produce CH₄.

Based on these preliminary results, the hydrogenolysis of n-octadecane over 5 wt % Ru/C at 200 °C was investigated as a function of time to track changes in the product distribution of n-alkanes with increasing conversion. As shown in Figure 1, the product distribution after 2 h includes C₆–C₁₇ n-alkanes, and increasing the extent of reaction shifts the product distribution to lower molecular weights, implicating sequential cleavage events of both terminal and nonterminal C–C bonds. After 16

![Figure 1. Hydrogenolysis of n-octadecane as a function of time over 5 wt % Ru/C. Reaction conditions: 700 mg n-octadecane (~50 mmol carbon), 25 mg 5 wt % Ru/C, 30 bar H₂, 200 °C.](https://dx.doi.org/10.1021/jacsau.0c00041)

<table>
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<th>catalyst</th>
<th>temp (°C)</th>
<th>mass catalyst (mg)</th>
<th>conversion, C₁₄ (mol %)</th>
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<th>products (gaseous)</th>
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*Reaction conditions: 700 mg of n-octadecane, 14 h, 30 bar H₂ (entries 1, 10), 50 bar H₂ (entries 2–9, 11–13).*
between 200 and 250 °C and using a 4:1 PE:catalyst mass ratio, polyethylene conversion reached 100% and generated exclusively gaseous products. At 200 °C, the head space contained mainly CH₄, ethane, propane, and butane. Upon increasing the temperature to 225 °C, only CH₄ and ethane were produced, and at 250 °C, the product yield was pure CH₄ in near stoichiometric yields. The effect of hydrogen pressure on polyethylene hydrolysis products over Ru/C at 200 °C (using a 28:1 PE:catalyst mass ratio) is shown in Figure 2b, with a more detailed compositional analysis shown in Figure 2c. At increasing hydrogen pressures, the yield of gas relative to liquid and solid increases, suggesting a sequence shifting from solid alkanes (>C₄₅) to solvated liquid alkanes (C₄−C₄₅), and finally to light alkane gases (C₁−C₄).

Based on these data, we selected reaction conditions of 20 bar H₂, 200 °C as optimal for producing a distribution of n-alkanes in the processable liquid range when using 700 mg of catalyst and 25 mg of Ru/C catalyst samples. Investigations of hydrogenolysis of Ir-based catalysts with both experiment and density functional theory (DFT) calculations have suggested that hydrogen inhibits hydrogenolysis rates, the extent of which is affected by the structure of the alkane due to changes in enthalpy and entropy of the transition state.23 A study of the mechanism of hydrogenolysis of light alkanes over Ru/C and iridium-based catalysts has also suggested that H₂ pressure has a marked effect on the selectivity of C-C bond scission, where high H₂ pressure is necessary to avoid CH₄ formation.24 These opposing effects explain why an intermediate H₂ pressure of 20 bar was ideal for achieving high selectivity to liquid-range n-alkanes in our experiments. As observed from both the model compound studies with n-octadecane and with polyethylene, the product distribution and selectivity for hydrogenation can be tuned by manipulating reaction temperature, H₂ pressure, and residence time.

Implementation of hydrogenolysis technology for the catalytic upcycling of genuine postconsumer polyolefin waste will require flexibility in the molecular weight and composition of the feedstock, including extent of branching, moisture, and contaminants. To this end, we demonstrated the hydrogenolysis of two additional sources of polyethylene: low-density polyethylene (Alrich, Table S2) with a melt index 25 g/10 min (190 °C/2.16 kg), denoted here as LDPE MI25, and a postconsumer LDPE plastic bottle. The former is a material commonly used in toys, lids, and closures,25 and the latter was previously used as a solvent bottle containing water (VWR) and Figures S8–S14. The mass yields of liquid (C₈−C₄₅) and gaseous (C₁−C₄) n-alkanes for these substrates are shown in Figure 3a. For each of these substrates, both liquid and gaseous products are obtained, while the gray represents the unaccounted products in the mass balance. Only gaseous and liquid products were observed for the reactions over polyethylene (average Mₙ 4000 Da, denoted PE 4K), LDPE MI25, and the LDPE plastic bottle. The gaseous product distributions for the three substrates are shown in Figure 3b, and the C₄−C₄₅, products are shown in Figure 3c–e for PE 4K, LDPE MI25, and the postconsumer LDPE plastic bottle, respectively. A small number of branched alkanes was also observed (Figure S11) over LDPE MI25, likely due to carbon chain branches in the substrate. While less substrate was used for the hydrogenolysis of the LDPE plastic bottle (200 mg) compared to the model polyethylene (1400 mg), the formation of liquid products in spite of the higher complexity of this material and lack of any pretreatment is promising and indicates the feasibility of this method for the production of liquid products from postconsumer polyolefins. Furthermore, we observed that at longer reaction times (16 h) at 225 °C, the LDPE plastic bottle could be converted into CH₄ with nearly 100% selectivity (Figure S14), which represents a promising avenue to produce natural gas from postconsumer plastic waste.

The depolymerization of a well-characterized NIST linear polyethylene Standard Reference Material (SRM 1475, avg Mₙ ~ 52 000 Da, avg Mₘ ~ 18 310 Da) was also investigated over 5 wt % Ru/C and was found to undergo complete conversion to liquid and gaseous alkanes under similar reaction conditions (Figures S15–S17). In addition, polyethylene hydrogenolysis experiments over recycled catalyst also demonstrated that the catalyst can be reused with minimal change in activity (Figure S18, Table S6). Characterization of...
polyolefin plastics under mild conditions to produce processable liquid alkanes. Temperature, hydrogen pressure, and reaction time can all be manipulated to control product distribution and selectivity, enabling the production of liquid products or complete hydrogenolysis to pure CH₄. The identification of Ru-based materials as a class of heterogeneous catalysts for the efficient depolymerization of polyethylene into liquid alkanes, or pure CH₄ compatible with existing natural-gas infrastructure, opens doors for future investigations into improving reactivity, understanding selectivity, and exploration of a variety of feedstocks and compositions. Further studies involving the effects of substrate branching, reactivity, and characterization of other hydrocarbon polymers such as polypropylene and polystyrene, mechanistic interrogation of active site requirements for selective internal C–C bond cleavage, models for predicting distributions of C–C bond cleavage, utilization of experimentally determined kinetic parameters to inform cleavage probability at various locations along the carbon chain, characterization of the Ru catalyst surface and mass transfer in the polymer melt, and techno-economic analysis of the process are currently underway in our laboratory.

With heterogeneous catalysts, additional parameters for exploration include utilizing tailored acid or acid–base supports to promote tandem isomerization and hydrogenolysis, zeolites and microporous materials to impose confinement effects, Raney-type catalysts to improve catalytic activity, and the synthesis of bimetallic catalysts to improve selectivity, activity, and stability, and to control C–O, C–C, and C≡C bond scission in mixed plastics feeds. Exhaustive studies into the effects of moisture and contaminants as well as engineering product removal strategies to decrease the formation of light alkanes will be critical for the industrialization of this reaction, enabling the integration of polyolefin upcycling technology into the global economy and ultimately providing an economic incentive for the removal of waste plastics from the landfill and environment.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.0c00041.

Materials and methods (Figure S1, Table S1–S3), catalyst characterization (Figure S2–S3, Tables S4–S5), product characterization (GC-MS, GC-FID, GC-MS, supporting images, Figures S5–S17), recyclability studies (Figure S18, Table S6), catalyst stability studies in flow reactor, and TON calculation (Figure S19) (PDF)

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