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

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Supporting Information

ABSTRACT: Chemical upcycling of waste polyolefins via hydrogenolysis offers unique opportunities for selective depolymerization compared to high temperature thermal deconstruction. Here, we demonstrate the hydrogenolysis of polyethylene into liquid alkanes under mild conditions using ruthenium 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 $C(sp^3)$-$C(sp^3)$ bonds at temperatures ranging from 200-250°C. Under optimal conditions of 200°C in 20 bar H_2, polyethylene (average M_w ~4,000) 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 post-consumer LDPE plastic bottle to produce C_7-C_{45} alkanes was also achieved over Ru/C, demonstrating the feasibility of this reaction for the valorization of realistic post-consumer plastic waste. By identifying Ru-based catalysts as a class of active materials for the hydrogenolysis of polyethene, this study opens new avenues for the valorization of plastic waste under mild conditions.

The development of polyolefins has enabled the production of safe and sturdy single-use plastic packaging for transportation and storage, sterile medical devices, and countless other transformative consumer products. Because the raw materials for producing polyolefins such as polyethylene (PE) and polypropylene (PP) are abundant and inexpensive, the manufacture of these plastics is immense, and continues to grow. Worldwide, approximately 380 million tons of plastics are generated annually, 57% percent of which are polyolefins.[1] Projections estimate that by 2050, plastic production will reach over 1.1 billion tons per year.[2] From a chemistry perspective, the strong sp^3 carbon-carbon bonds in polyolefins that provide desirable material properties also make them highly recalcitrant to degradation. Mechanical recycling is one method of utilizing plastic waste; however, only around 16% of plastic is actually recycled,[3] and usually ends up being "downcycled" into lower-value materials with diminished properties.[4] The majority of single-use plastics end up in landfills or the environment, harming the ecosystem and effecting the natural enviornment.[1, 3, 5]

Thermochemical pathways, such as pyrolysis and thermal cracking, enable polyolefin depolymerization by breaking the strong C-C bonds in PE to produce small molecules that could be used as fuel or integrated into chemical refineries. However, these processes are energy intensive and suffer from low control over product selectivity.[6,7,8] Alternatively, C-C bond cleavage via hydrogenolysis allows for selective depolymerization of polyolefins into liquid alkanes with targeted molecular weight ranges. This reaction has been studied in the context of short-chain alkane[9-14] and lignin[15-16] conversion, but has not been extensively explored for the depolymerization of polyolefins with high molecular weights. Dufaud and Basset studied the degradation of model PE (C_{20}-C_{50}) and PP over a zirconium hydride supported on silica-alumina, and found moderate activity under mild conditions (190 °C).[17] Celik *et al.* investigated hydrogenolysis using well-dispersed Pt nanoparticles supported on $SrTiO_3$ nanocuboids for the depolymerization of PE (M_n = 8,000 – 158,000 Da) at 170 psi H_2 and 300°C for 96 h under solvent free conditions, obtaining high yields of liquid hydrocarbons.[18] The authors argued that this catalyst is superior to Pt/Al_2O_3 because it produced fewer light hydrocarbons and promoted favorable adsorption of PE on Pt sites. Open questions remain whether the higher yield of light hydrocarbons over Pt/Al_2O_3 was due to the acidity of the support, a promotional effect of the isomerization and hydrocracking pathways, or increased 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 processible 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 M_w 4,000) and commercial low-density polyethylene (LDPE). Finally, we demonstrated that the Ru/C catalyst is capable of converting LDPE from a real post-consumer 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 processible 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/CeO_2, Ru/SiO_2, Ru/Al_2O_3, and Ru/TiO_2, have been shown to be active both for the hydrogenolysis of light alkanes[9-14] 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

Table 1: Hydrogenolysis of *n*-octadecane using heterogeneous transition metal catalysts. Reaction conditions: 700 mg *n*-octadecane, 14 h, 30 bar H_2 (entries 1, 10), 50 bar H_2 (entries 2-9, 11-12)

Entry	Catalyst	Temp [°C]	Mass Catalyst [mg]	Conversion, C_{18} [mol%]	Products (Liquid)	Products (Gaseous)
1	Co_3O_4	200	104	0	none	none
2	Co_3O_4	250	109	46	*n*-alkanes (C_{14}-C_{17})	n/a
3	γ-Al_2O_3	250	103	0	none	none
4	1% Pt/γ-Al_2O_3	250	47.0	0	none	none
5	RuO_2	250	43.0	100	none	CH_4
6	RuO_2	200	20.4	9	*n*-alkanes (C_9-C_{17})	CH_4
7	5% Ru/Al_2O_3	200	26.7	65	*n*-alkanes (C_8-C_{17})	light alkanes (C_1-C_4)
8	5% Ru/Al_2O_3	250	26.3	100	none	light alkanes (C_1-C_4)
9	5% Rh/C	250	22.6	21	*n*-alkanes (C_8-C_{17})	light alkanes (C_1-C_6)
10	5% Ru/C	200	25.0	92	*n*-alkanes (C_6-C_{17})	light alkanes (C_1-C_5)
11	5% Ru/C	250	25.0	100	none	CH_4
12	NiO	250	25.0	0	none	none

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 H_2 pressures ranging from 200-300°C and 30-50 bar, respectively (see **Table 1**). Products were identified by gas chromatography mass spectrometry (GC-MS), and quantified by GC equipped with a flame ionization detector (FID) and thermal conductivity detector (TCD). Additional methods, catalyst characterization, and product characterization are provided in the **Supporting Information (Figures S1-S3, Tables S1-S3)**. At 250°C, 1% Pt/γ-Al_2O_3, NiO, and γ-Al_2O_3 were all inactive. Co-based catalysts (entries 1-2) and Rh-based catalysts (entry 9) showed moderate hydrogenolysis activity, converting *n*-octadecane into a range of C_1-C_{17} alkanes. Notably, Ru-based catalysts stood out for their high hydrogenolysis activity (entries 5-8,10-11). 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 CH_4. 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 towards terminal C-C bond cleavage to produce CH_4.

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 C_8-C_{17} *n*-alkanes, and increasing the extent of reaction shifts the product distribution to lower molecular weights, implicating sequential cleavage events of both terminal and non-terminal C-C bonds. After 16 h, 100% of the *n*-octadecane was consumed and the products shifted from liquid-range alkanes to gaseous products in the C_1-C_6 range. Based on these data, we surmised the hydrogenolysis of longer-chain polyethylene over Ru/C would also proceed via both terminal C-C bond cleavage to produce CH_4 and internal C-C bond cleavage to produce shorter chain alkanes.
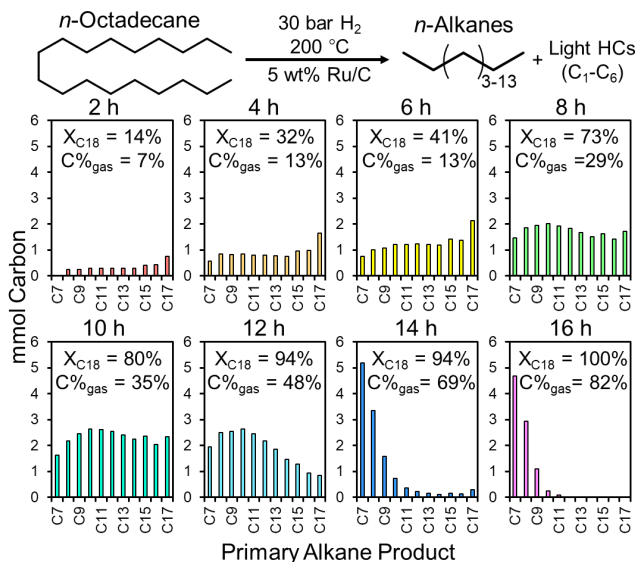

Figure 1: Hydrogenolysis of *n*-octadecane as a function of time over 5 wt% Ru/C. Reaction conditions: 700 mg *n*-octadecane (~50 mmol carbon), 25 mg 5 wt% Ru/C, 33 bar H_2, 200°C.

The effect of temperature and hydrogen pressure on the hydrogenolysis of model polyethylene (Sigma-Aldrich, average M_w 4,000, average M_n 1,700, **Table S1**) was investigated over Ru/C to identify suitable reaction conditions for the hydrogenolysis of realistic post-consumer polyethylene waste (**Figure 2**, **Figure S4-S6**). At all temperatures investigated between 200-250°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 CH_4, ethane, propane, and butane. Upon increasing the temperature to 225°C, only CH_4 and ethane were produced, and at 250°C, the product yield was pure CH_4 in near stoichiometric yields. The effect of hydrogen pressure on polyethylene hydrogenolysis 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 (>C_{45}) to solvated liquid alkanes (C_8-C_{45}), and finally to light alkane gases (C_1-C_7).
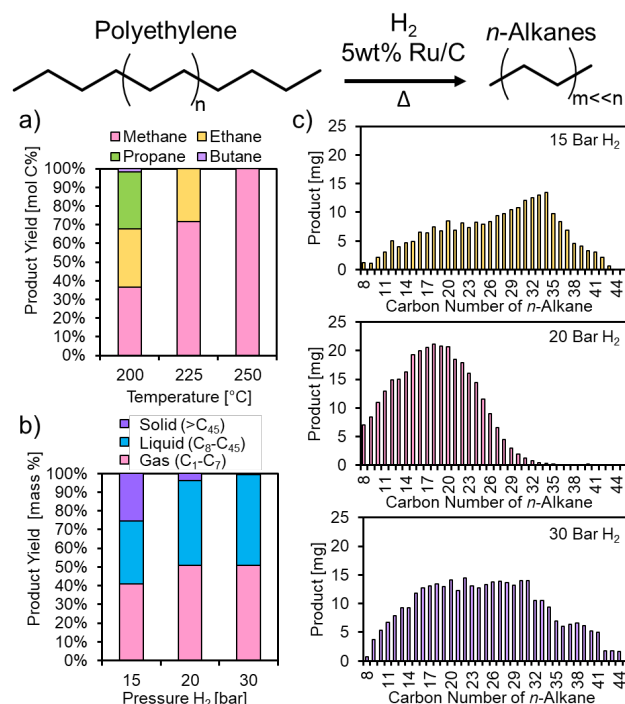
Figure 2: Optimizing reaction conditions for the hydrogenolysis of polyethylene (average M_w 4,000): a) Effect of temperature on overall product yields, 100 mg PE (average M_w 4,000), 16 h, 30 bar H_2, 25 mg 5 wt% Ru/C, 200-250°C, 100% conversion, b) Effect of H_2 pressure on overall product composition, 200°C, 16 h, 700 mg PE (average M_w 4,000), 25 mg 5 wt% Ru/C, c) Liquid composition of C_8-C_{45} products shown in b.

Based on these data, we selected reaction conditions of 20 bar H_2, 200°C as optimal for producing a distribution of *n*-alkanes in the processible liquid range when using 700 mg polyethylene and 25 mg catalyst. 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/CeO_2 also suggested that H_2 pressure had a marked effect on selectivity for C-C bond scission, where high H_2 pressure is necessary to avoid CH_4 formation.[11] These opposing effects explain why an intermediate H_2 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 hydrogenolysis can be tuned by manipulating reaction temperature, H_2 pressure, and residence time.

Implementation of hydrogenolysis technology for the catalytic upcycling of genuine post-consumer 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 (Aldrich, **Table S2**) with a melt index 25 g/10 min (190°C/2.16 kg), denoted here as LDPE MI25, and a post-consumer LDPE plastic bottle. The former is a material commonly used in toys, lids, and closures,[24] and the latter was previously used as a solvent bottle containing water (VWR). The results from these reactions are summarized in **Figure 3** and **Figures S7-S13**. The mass yields of liquid (C_8-C_{45}) and gaseous (C_1-C_7) *n*-alkanes for three 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 M_w 4,000, denoted PE 4K), LDPE MI25, or the LDPE plastic bottle. The gaseous product distributions for the three substrates are shown in **Figure 3b**, and the C_8-C_{45+} products are shown in **Figure 3c-e** for PE 4K, LDPE MI25, and the post-consumer LDPE plastic bottle, respectively. A small number of branched alkanes were also observed (**Figure S10**) 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 polyethene (1,400 mg), the formation of liquid products in spite of the higher complexity of this material and lack of any pre-treatment is promising, and indicates the feasibility of this method for the production of liquid products from post-consumer polyolefins. Furthermore, we observed that at longer reaction times (16 h) at 225°C, the LDPE plastic bottle could be converted into CH_4 with nearly 100% selectivity (**Figure S13**), which represents a promising avenue to produce natural gas from post-consumer plastic waste.
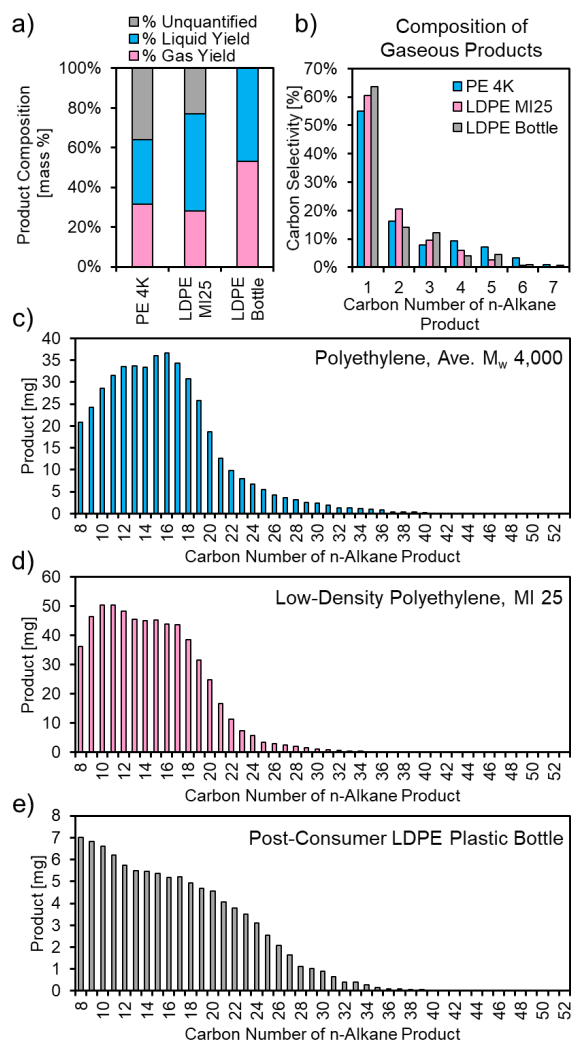

Figure 3: a) Product distributions for polyethylene hydrogenolysis over 5 wt% Ru/C with PE 4K (200°C, 1.4 g PE 4K, 56 mg 5wt% Ru/C, 22 bar H_2, 16 h), LDPE MI25 (225°C, 1.4 g LDPE, 50 mg 5 wt% Ru/C, 22 bar H_2, 16 h), and a post-consumer LDPE plastic bottle (225°C, 200 mg LDPE, 25 mg 5 wt% Ru/C, 22 bar H_2, 2 h); b) gaseous product distribution for PE 4K, LDPE MI25, and LDPE plastic bottle; c) C_8-C_{45+} product distribution for PE 4K; d) C_8-C_{45+} product distribution for LDPE MI25, e) C_8-C_{45+} product distribution for LDPE plastic bottle.

In this work, we have demonstrated that Ru-based catalysts are active for the hydrogenolysis of polyethylene under mild conditions to produce processible 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 CH_4. The identification of Ru-based materials as a class of heterogeneous catalysts for the efficient depolymerization of polyethylene into liquid alkanes, or pure CH_4 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 technoeconomic 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, and the synthesis of bi-metallic 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,[25] as well as engineering creative systems of product removal, 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

Materials and Methods (Fig. S1, Table S1-S2), Catalyst Characterization (Fig. S2-S3, Table S3), Product Characterization (GC-MS, GC-FID, GC-MS, Supporting Images, Fig. S4-S13) (PDF).

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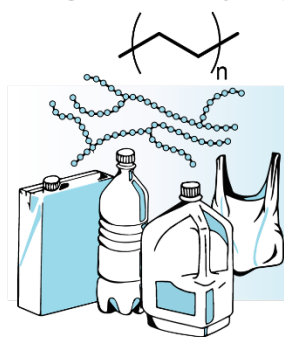
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Single-Use Polyethylene

High-Value Liquid Alkanes

20 bar H$_2$
5 wt% Ru/C
200-225 °C

*Mild Reaction
Conditions*

Mass [mg]

Light HCs
C$_3$H$_8$
C$_7$H$_{16}$
CH$_4$
C$_2$H$_6$

Carbon Number *n*-Alkane