Hydrogenolysis of Polypropylene and Mixed Polyolefin Plastic Waste over Ru/C to Produce Liquid Alkanes
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ABSTRACT: Catalytic depolymerization of polyolefins is a promising chemical recycling strategy to create value-added products from waste plastics, which are accumulating in landfills and the natural environment at unsustainable rates. The cleavage of strong C–C bonds in polyolefins can be performed using a noble metal and hydrogen via a hydrogenolysis mechanism. Previously, we identified ruthenium nanoparticles supported on carbon (Ru/C) as a highly active heterogeneous catalyst for the conversion of polyethylene into liquid and gaseous n-alkanes under mild conditions. In the present study, we investigated the catalytic depolymerization of polypropylene (PP) under mild conditions (200–250 °C, 20–50 bar H2). We demonstrate that Ru/C produces C5−C15 iso-alkane yields above 68% in the absence of solvent and identify trade-offs between product yield and temperature, hydrogen pressure, and reaction time. We apply a rigorous analytical method to quantify all liquid and gaseous alkane products. The characterized catalyst was found to be recyclable after the complete depolymerization of high molecular weight PP (Mw ~ 340,000 Da) to liquid and gaseous hydrocarbons and after depolymerization of a postconsumer PP centrifuge tube. Further, the catalyst was shown to be effective in depolymerizing a mixture of high-density polyethylene and PP to produce a mixture of linear and branched liquid alkanes, demonstrating feasibility for the depolymerization of streams of mixed polyolefin waste.

KEYWORDS: Plastic upcycling, Hydrogenolysis, Polypropylene, Polyethylene, Mixed plastics, Depolymerization, Ruthenium

INTRODUCTION

The global consumption of single-use plastic has caused massive accumulation of plastic waste in landfills and the environment, adversely affecting the ecosystem and human health. Each year, approximately 380 million tons of plastics are generated,1 and projections estimate that plastic production will reach over 1.1 billion tons per year by 2050.2 In the U.S. alone, plastics consumption accounts for 3.2 quads of annual energy use and 104 MMT of CO2e in annual greenhouse gas emissions.3 Globally, plastics consume 6% of today’s fossil carbon use.4 Polyolefins are the most widely produced plastic, as polyethylene (PE) and polypropylene (PP) make up 36% and 21% of global plastics production, respectively.3 Mechanical recycling can offer a second life to waste plastics, but only around 16% of plastic is actually recycled.5 These recycled materials often exhibit inferior properties such as lower mechanical stability and contamination from dyes and additives.6

Chemical recycling offers an opportunity for plastic waste streams to be converted into higher value chemicals which could be used as drop-in fuel additives, integrated into chemical refineries, or used as synthons to produce the next generation of recyclable-by-design polymers.7–11 Existing pathways such as pyrolysis and thermal cracking can enable the conversion of polyolefin waste into fuel-range chemicals, but they require high operating temperatures (400–900 °C) and suffer from low product selectivity.12–14 Recent efforts in chemical recycling have identified methods of activating the strong C–C bonds of PE at lower temperatures (200–300 °C) through both thermochemical and electrochemical routes.15–18 Platinum-based catalysts have been shown to be effective for PE depolymerization via hydrogenolysis19,20 and hydrocracking21 and through tandem dehydrogenation/metathesis with a SnPt/γ-Al2O3 and Re2O7/γ-Al2O3 catalyst system.22 Recently, our group identified ruthenium nanoparticles supported on carbon (Ru/C) as a highly active catalyst for PE depolymerization into liquid n-alkanes via hydrogenolysis under mild conditions (200–225 °C, 20–30 bar H2).16 This reaction was performed in the absence of solvent, and the catalyst was shown to be recyclable for multiple cycles. Ruthenium-based heterogeneous catalysts are attracting growing interest as materials for the hydrogenolysis of aromatic plastic waste.23

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Polypolyethylene (Mn ~12 kDa) and model alkanes. The high activity and stability of Ru-based heterogeneous catalysts in various catalytic systems make them excellent candidates for the hydrogenolysis of realistic waste plastic streams. In addition to being recyclable, carbon supports can be sourced sustainably from biogenic carbon or even from the pyrolysis of waste plastics themselves. Mixed polyolefin (MPO) streams are considered a low-value feedstock for mechanical recycling, as the difference in melting points and processing temperatures between the different polymers present technical challenges concerning the degradation of lower-molecular weight components. Further, blends of PE/PP have different mechanical and thermal properties than their constituent parts. While the tertiary carbon–carbon bonds in PP have lower bond dissociation energies than secondary carbon–carbon bonds in PE, PP generally also exhibits a higher Tm3,4,5 and thus, the effect of carbon chain branches on hydrogenolysis activity is unclear. To utilize hydrogenolysis for the chemical upcycling of waste plastic, we must understand how the reaction proceeds over polymers with varying molecular weights and carbon chain branches. To this end, challenges include quantifying products and identifying product distributions obtained from varying feeds and optimizing conditions and feed stream compositions to achieve targeted product distributions and properties. In this study, we demonstrate PP hydrogenolysis to iso-alkanes over Ru/C by identifying suitable reaction conditions for PP depolymerization and performing rigorous quantification of liquid and gaseous products. We then demonstrate the proof of concept for catalyst recoverability and recyclability, as well as the hydrogenolysis of mixed streams of PE and PP waste.

RESULTS AND DISCUSSION

The first goal of this study was to identify suitable reaction conditions for PP hydrogenolysis to maximize the yield of liquid hydrocarbons, defined here as C5−C32 iso-alkanes. We started by investigating the hydrogenolysis of model PP (isotactic, Mw 12,000 Da) using the optimal conditions identified in our previous study for the hydrogenolysis of linear low-density polyethylene (i.e., using a 5 wt % Ru/C at temperatures and pressures ranging from 200 to 225 °C and 20–30 bar H2, respectively, with substrate to catalyst ratios ranging from 8:1 to 28:1).19 PP beads were added directly to a 25 mL Parr reactor along with the catalyst and pressurized with hydrogen gas. The reactor was placed in an insulated aluminum block with a temperature-controlled heater. After the specified reaction time, the reactor was cooled to room temperature by quenching in an ice bath. Gaseous products were collected from the headspace and analyzed with GC-FID and GC-TCD, (c) picture of initial substrate, and (d) GC-MS spectra of liquid iso-alkane products dissolved in toluene. Reaction conditions: 225 °C, 16 h, 20 bar H2, 400 rpm, 700 mg of isotactic PP, and 100 mg of catalyst. Raw data and the detailed quantification scheme are provided in the SI, as well as additional reaction conditions screened.

Figure 1. Hydrogenolysis of PP (Mw ~ 12,000 Da, Mn ~ 5000 Da) over ruthenium nanoparticles (5 wt %) supported on carbon: (a) liquid products quantified by GC-FID, (b) gaseous products quantified by GC-FID and GC-TCD, (c) picture of initial substrate, and (d) GC-MS spectra of liquid iso-alkane products dissolved in toluene. Reaction conditions: 225 °C, 16 h, 20 bar H2, 400 rpm, 700 mg of isotactic PP, and 100 mg of catalyst. Raw data and the detailed quantification scheme are provided in the SI, as well as additional reaction conditions screened.

The gaseous product distribution is similar to that observed for PE hydrogenolysis over Ru/C18; however, the liquid products comprised a range of alkanes with varying degrees of branching (Figure S1). Depending on the application, PP is used in vastly different molecular weight ranges; thus, we turned our investigation to the hydrogenolysis of isotactic PP with an average molecular weight (Mw) of 340,000 Da. To investigate the hydrogenolysis of this substrate over Ru/C, a series of reactions were performed with varying reaction time, temperature, and hydrogen pressure. Figure 2 shows the product distributions as a function of time between 4 to 16 h for the hydrogenolysis of 340,000 Da PP beads (700 mg) under reaction conditions of 250 °C, 40 bar H2, and 600 rpm. The liquid product distributions are shown in Figure 2a. At early reaction times (4 h), the product distribution is very broad, ranging from C5−C24 alkanes, with a significant fraction (62%) of insoluble iso-alkanes in the lubricant/wax range (C33+). As the reaction time is increased, the solid fraction is consumed, and the product distribution shifts to shorter alkanes. Eventually, between 8 and 12 h, the product distribution reaches a maximum yield of liquid products centered around C12−C15, past which the C=C bonds continue to cleave, and the fraction of gaseous hydrocarbons increases (Figure 2c). The gaseous hydrocarbons are primarily composed of methane, which results from the cleavage of terminal C=C bonds. As shown in Figure 2d, the masses of methane, ethane, propane, and butane produced increase with increasing extent of reaction. Indeed, under harsher reaction conditions (250 °C, 24 h, 50 bar H2, 100 mg of 5 wt % Ru/C, 700 mg of PP, 600
rpm), the PP substrate is completely converted to methane, ethane, and propane (Figure S2). Under slightly milder conditions for the complete conversion of PP into gaseous hydrocarbons (225 °C, 48 h, 50 mg of 5 wt % Ru/C, 40 bar H₂, 700 mg of polypropylene, 600 rpm), the selectivity toward ethane and propane relative to methane can be increased (Figure S2).

Comparable liquid hydrocarbon yields from PP (Mₙ 340,000 Da) can be achieved by operating at lower reaction temperatures and extended reaction times. As shown in Figure 3a, the liquid product distribution for PP (340,000 Da, 225 °C, 48 h, 50 mg of 5 wt % Ru/C, 40 bar H₂, 700 mg of polypropylene, 600 rpm) resembles the distribution at 250 °C for 8 h in Figure 2. The liquid yield at 225 °C was further increased by optimizing the H₂ pressure. As shown in Figure 3a and b, the liquid yield increases as the pressure is increased from 40 to 50 bar H₂, then decreases slightly from 50 to 60 bar H₂. The gaseous product distribution shown in Figure 3c shows that methane production is minimized at an intermediate pressure of 50 bar. In our previous study, we found 20 bar to be the ideal pressure for PE hydrogenolysis at 225 °C, 16 h, 600 rpm, 700 mg of PP, and 50 mg of 5 wt % Ru/C. Raw data are presented in the SI.

With these optimized reaction conditions for the depolymerization of high molecular weight (340,000 Da) PP (225 °C, 24 h, 600 rpm, 700 mg of PP, 50 mg of 5 wt % Ru/C), we investigated the recyclability of the catalyst for PP depolymerization. To account for some loss of catalyst during the reaction workup, spent catalysts from identical reactions were separated from the products via centrifugation, collected, and dried overnight to evaporate the acetone solvent. This spent catalyst was then combined to perform replicate reactions with a recycled catalyst. As shown in Figure S3, Ru/C could be recycled and reused, yielding similar liquid product distributions with minimal reduction in activity. We note that while acetone was used in the workup to quantify products, solvents are not necessary to recover the catalyst, as the catalyst can be separated directly from the liquid products and reused.

Figure 3. Effect of hydrogen pressure on the hydrogenolysis of PP (Mₙ ~ 340,000 Da, Mₘ ~ 97,000 Da). Reaction conditions: 225 °C, 24 h, 600 rpm, 700 mg of PP, and 50 mg of 5 wt % Ru/C: (a) liquid product distribution at 40, 50, and 60 bar H₂, (b) mass liquid produced, and (c) gaseous product distribution. Raw data are presented in the SI.
To demonstrate the proof of concept for the hydrogenolysis of realistic PP feedstocks, we used a plastic centrifuge tube as a waste PP substrate (Figure 4a). The clear sections of the tube were cut into squares of approximately 3 mm by 3 mm and placed in the reactor with no pretreatment or solvent (Figure 4b). The resulting liquid products after performing hydrogenolysis over Ru/C (reaction conditions: 225 °C, 24 h, 50 bar H₂, 600 rpm, 700 mg of PP, and 50 mg of 5 wt % Ru/C) are shown in Figure 4c, with the quantified products shown in Figure 4d. As shown in Figure 4e, the catalyst could be recovered from the reaction and used again with minimal change in product distribution. A slight shift to higher molecular weight hydrocarbons over the spent catalyst is likely due to nanoparticle sintering during the reaction, as evidenced by transmission electron microscopy of the fresh and spent catalysts, which shows a shift in the average Ru particle diameter from 1.23 ± 0.61 to 1.78 ± 0.64 nm (Figure S4). The fact that the substrate could be used without any pretreatment or solvent, and that the catalyst could be recovered and recycled, is a promising step toward utilizing waste plastic streams.

To demonstrate the utilization of Ru/C for the hydrogenolysis of mixed plastic feeds, a mixture of PP (Mₓ 340,000 Da) and HDPE was prepared and used as a model mixture for hydrogenolysis at 225 °C for 24 h under 40 bar H₂. The resulting product was a clear liquid, which is characterized in Figure 5. From the raw chromatogram in Figure 5a, it is evident that the products contain a mixture of linear and branched alkanes. The linear n-alkanes are denoted by the asterisks and are centered around lower retention times, whereas the branched alkanes are more distributed throughout the chromatogram. Quantification of the linear and branched alkanes in Figure 5b reveals that the n-alkanes are centered around a carbon chain length of around 8 (n-octane), whereas the branched alkanes range from C₇–C₃₂. This difference in product distribution suggests that the rate of hydrogenolysis was faster over the HDPE compared to the PP. The differences in reactivity of the substrates is an important consideration for developing product streams from mixed waste feedstocks with desired liquid properties. For example, for fuel applications, the ratio of branched alkanes will affect the cetane number. This promising result highlights opportunities for producing tunable product streams by adjusting polyolefin feedstock composition, residence time, temperature, and additional reaction conditions.

## CONCLUSIONS AND OUTLOOK

In this study, ruthenium nanoparticles supported on carbon (5 wt % Ru/C) were shown to be effective heterogeneous catalysts for the depolymerization of PP plastic via hydrogenolysis under relatively low temperatures (225–250 °C) and hydrogen pressures (20–50 bar). Unlike PE hydrogenolysis, which produces linear n-alkanes, PP hydrogenolysis produces a range of iso-alkanes in both the liquid (C₃–C₁₂) and gas (C₁–C₃) ranges. Liquid iso-alkane yields of over 68% were achieved for the depolymerization of PP (Mₓ 12,000 Da) under mild conditions (225 °C, 20 bar H₂, 16 h) over 5 wt % Ru/C in the absence of solvent. Under slightly elevated conditions (225–250 °C, 50 bar H₂, 6–24 h), higher molecular weight PP (Mₓ 340,000 Da) could also be completely depolymerized into liquid and gaseous hydrocarbons. Through rigorous quantification of gaseous and liquid products, this study identified trade-offs between reaction time, temperature, and hydrogen pressure for PP depolymerization and demonstrated the feasibility and recyclability of Ru/C for the hydrogenolysis of genuine PP plastic waste and mixtures of PE and PP.

Challenges moving forward will include characterizing the mass transport of the system on both micro- and macro-molecular scales (e.g., diffusion of substrate to and from the active site, diffusion and activation of H₂, solvation effects, viscosity, entanglement) and developing methods to increase...
carbon selectivity toward central C–C bond cleavage to avoid loss of carbon and hydrogen to methane formation. Modification of nanoparticle size as well as investigation into acidic and confined supports (e.g., tandem hydrogenolysis/hydrocracking, shape selectivity) to suppress methane formation, improve light alkane yields, and lower hydrogen pressure requirements are currently underway. Ongoing work also includes conducting techno-economic analyses to compare hydrogenolysis to other methods of chemical recycling such as pyrolysis. Beyond ruthenium-based catalysts, investigation into earth-abundant alternatives to noble metals will be a critical step toward the economical chemical upcycling of waste polyolefins. By enabling targeted C–C bond cleavage of polyolefins, hydrogenolysis has the potential to give new value to waste plastics, producing tunable and high-quality liquid products that could replace fossil-derived resources to enable a circular plastic economy.

**REFERENCES**


