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Short communication

Non-thermal plasma-assisted hydrogenolysis of polyethylene to light hydrocarbons

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ABSTRACT

Upcycling is an attractive approach for valorization of waste plastics to valuable chemicals. Here we report the first case study of non-thermal plasma-assisted hydrogenolysis of high-density polyethylene (HDPE) to C_1-C_3 hydrocarbons. Light alkanes, predominately CH_4, C_2H_6 and C_3H_8 with >95% selectivity, were obtained under ambient condition as result of favorable thermodynamics and fast reaction kinetics. The findings demonstrated that hydrogenolysis that typically demands above 300 °C with thermal catalysis can occur at room temperature in assistance of non-thermal plasma. This proof-of-concept study showcases a novel strategy for upcycling of plastics to valuable hydrocarbons under ambient condition.

1. Introduction

While the wide application of plastic materials has significantly improved the convenience and quality of human life, the processing and recycling of waste plastics (WP) have become an ever-growing challenge [1–3]. In US only, over 35 million tons WP are generated annually and most of them are processed by landfill or incineration, with less than 10% being recycled [4]. The inability to recycle WP has not only caused huge pressure to the environment, but also wasted tremendous amount of carbon resource.

"Upcycling" involves conversion of waste materials to more valuable chemicals and fuels, which is an attractive approach to recover hydrocarbon resource from its polymeric structure [5–7]. Currently, pyrolysis and gasification are the most intensively investigated methods for plastic upcycling [8–12]. Aiming at producing liquid fuels and hydrogen-rich gases that have relatively high commercial values, the research in terms of reaction parameters, catalyst and process design of pyrolysis and gasification has been well developed in the past few decades [9,13–16]. However, the inevitable high energy input (400–1000 °C reaction temperature), with or without catalysts, demanded by highly endothermic feature of depolymerization process makes it less preferred from energy cost-effectiveness point of view [17,18]. In addition, the complex product distribution (syngas, gasoline and diesel fuels, pyrolysis oil and char, etc.) is another factor that limits application of this approach. Thermodynamically, the endothermic deficiency of plastic depolymerization can be effectively reversed by adding H_2 to the reaction [19]. Via hydrogenolysis/hydrocracking, the upcycling of plastics turns into exothermic and significantly reduces the reaction temperature to about 300 °C and a narrower product distribution (light alkanes, diesel fuel and wax) compared with typical pyrolysis process was also witnessed [20,21]. But the temperature was still not low enough to claim a good energy advantage. Hereby, we report the use of non-thermal H_2 plasma for initiating ambient-condition hydrogenolysis of high-density polyethylene (HDPE) to produce light hydrocarbons (C_1–C_3). By means of plasma-activated H_2, the hydrogenolysis of polyethylene can effectively take place at room temperature, resulting in highly selective production of light alkanes (C_1–C_3, >95% selectivity). The employment of Pt/C and SAPO-34 zeolites, two routinely used catalysts in hydrogenation and pyrolysis of plastics [9,20,21], shows limited improvement in gas production but pronounced enhancement in energy efficiency. The proof-of-concept study provides a novel approach for energy efficient upcycling of plastics.

2. Experiments

2.1. Materials

High density polyethylene (HDPE, Sigma Aldrich, Merck KGaA, Darmstaht. Stock No. 427985), 20% platinum on Vulcan XC-72R carbon (20 wt% Pt/C, Fuel Cell Store, College Station, TX, USA. Product Code

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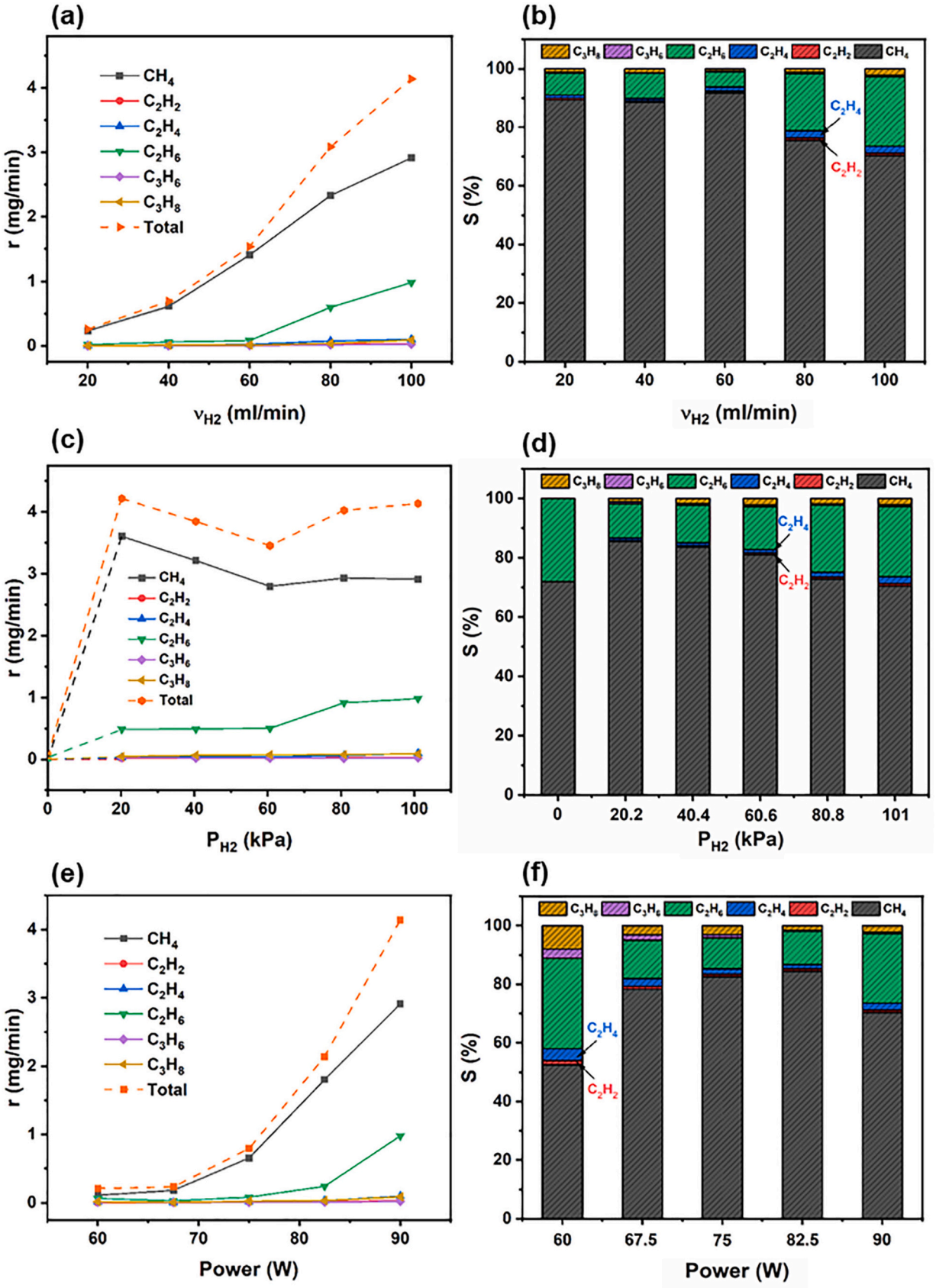

Fig. 1. Effects of (a–b) H_2 flow rate, (c–d) H_2 partial pressure (balanced by Ar with 100 ml/min total flow rate) and (e–f) plasma power on the HDPE hydrogenolysis rate and product selectivity.

3151721), SAPO-34 zeolite (ACS material, Pasadena, CA, USA) were used. H_2 (99.999%) and Ar (99.999%) gases were purchased from Praxair, Linde.

2.2. Plasma hydrogenolysis of HDPE

Non-thermal plasma-assisted HDPE hydrogenolysis experiments were conducted in a quartz tube reactor equipped with a dielectric barrier discharge (DBD) plasma generator, where cold hydrogen plasma was generated (Fig. S1). In a typical experiment, 200 mg HDPE pellets sieved to 125–250 μm was mixed in the center of plasma generation zone (5 wt% catalyst when introduced), with standard reaction condition of 100 ml/min H_2 flow rate, 101 kPa H_2 partial pressure and 90 W plasma power unless being stated otherwise. The HDPE pellets take up 0.47 ml of the reactor, which equals to 12,900 h^{-1} gas hourly space velocity (GHSV, Eq. (1)) at 100 ml/min H_2 flow rate. The gas effluent products were analyzed with an online Agilent 6890 GC–MS equipped with automatic gas injector. The gas chromatography is equipped with a 0.33 mm (internal diameter) silica column. Influences of various reaction parameters, including H_2 flow rate (20–100 ml/min), H_2 partial pressure (0–101 kPa), plasma power (60–90 W), as well as catalyst (Pt/C and SAPO-34) were examined. Gas products, including CH_4, C_2H_2, C_2H_4, C_3H_6 and C_3H_8, were quantified separately by externally feeding standard calibration gas. Calibration curves at 0–5% v/v% were obtained for each gas. Selectivity was calculated by respective gas production rate divided by the overall production rate (g/min).

$$GHSV = \frac{\nu_{H2}}{V_{HDPE}} = \frac{100\ ml/min}{0.47\ ml} = 12900\ h^{-1} \quad (1)$$

The energy efficiency (η) is represented by total formation rate (mg/min) over input power (W):

$$\text{Energy efficiency}\left(\frac{\text{g}}{\text{kWh}}\right) = \frac{\text{total product}\ \frac{\text{mg}}{\text{min}}}{\frac{\text{P(W)}}{1000}} * 60 = 60\frac{\text{totoal product (mg)}}{\text{P (W)}} \quad (2)$$

2.3. FT-IR characterization

The HDPE, Pt/C + HPDE and SAPO + HPDE samples before and after reaction were characterized by an FTIR spectrometer (Nicolet 6700, Thermo Scientific) in the diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) mode at 25 °C. The SAPO-34 and Pt/C catalysts were heated in situ from 25 °C to 150 °C under an argon flow rate of 40 ml/min for analysis of surface hydroxyl in an effort to determine possible active sites for the reaction.

3. Results and discussions

3.1. Evaluation of HDPE hydrogenolysis

Non-thermal plasma-assisted hydrogenolysis of HDPE leads to a total of six gas products, including methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), propene (C_3H_6) and propane (C_3H_8), were detected (Fig. S2), suggesting successful demonstration of the plasma-assisted plastic hydrogenolysis concept (Fig. S3a). No liquid product was observed in the retrieved samples from the flow reactor (Fig. S4). An increase of ν_{H2} leads to an enhanced generation rate of all gas products (Fig. 1a), indicating an improved hydrogenolysis efficiency that could be attributed to more available H_2 plasma for reaction. CH_4 accounts for a majority of the gas products (>70% in selectivity), with a higher ν_{H2} resulting in a decrease in S_{CH4} that produces more fractions of C_2H_6 and C_3H_8 (Fig. 1b). Despite of the intriguing phenomenon of unsaturated hydrocarbons formation, their overall selectivity is smaller than 5%, likely due to unfavorable thermodynamics. The study on effect of H_2 partial pressure found negligible gas product formation in pure Ar atmosphere (Fig. 1c) although intense Ar plasma was generated in the reactor (Fig. S3b). The little reaction can be attributed to endothermic characteristic of HDPE decomposition in Ar plasma atmosphere. The addition of H_2 is evidently critical to drive exothermic HDPE hydrogenolysis, with plasma H_2 to overcome the activation barrier for

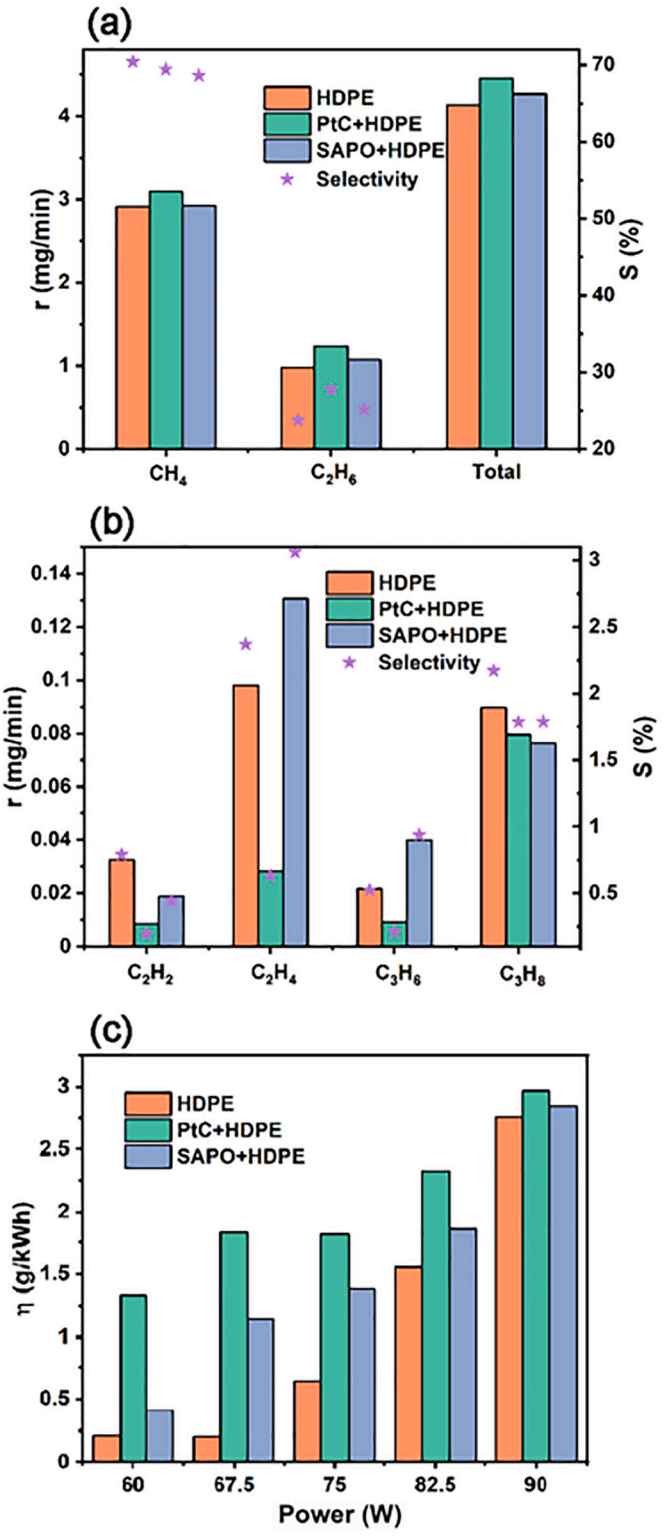

Fig. 2. Influence of catalysts on plasma-assisted HDPE hydrogenolysis: (a, b) formation rate and selectivity of individual products and total gas products. Reaction condition: 100 ml/min H_2, 101 kPa, 90 W. (c) energy efficiency as a function of plasma power input. Reaction condition: 100 ml/min H_2, 101 kPa.

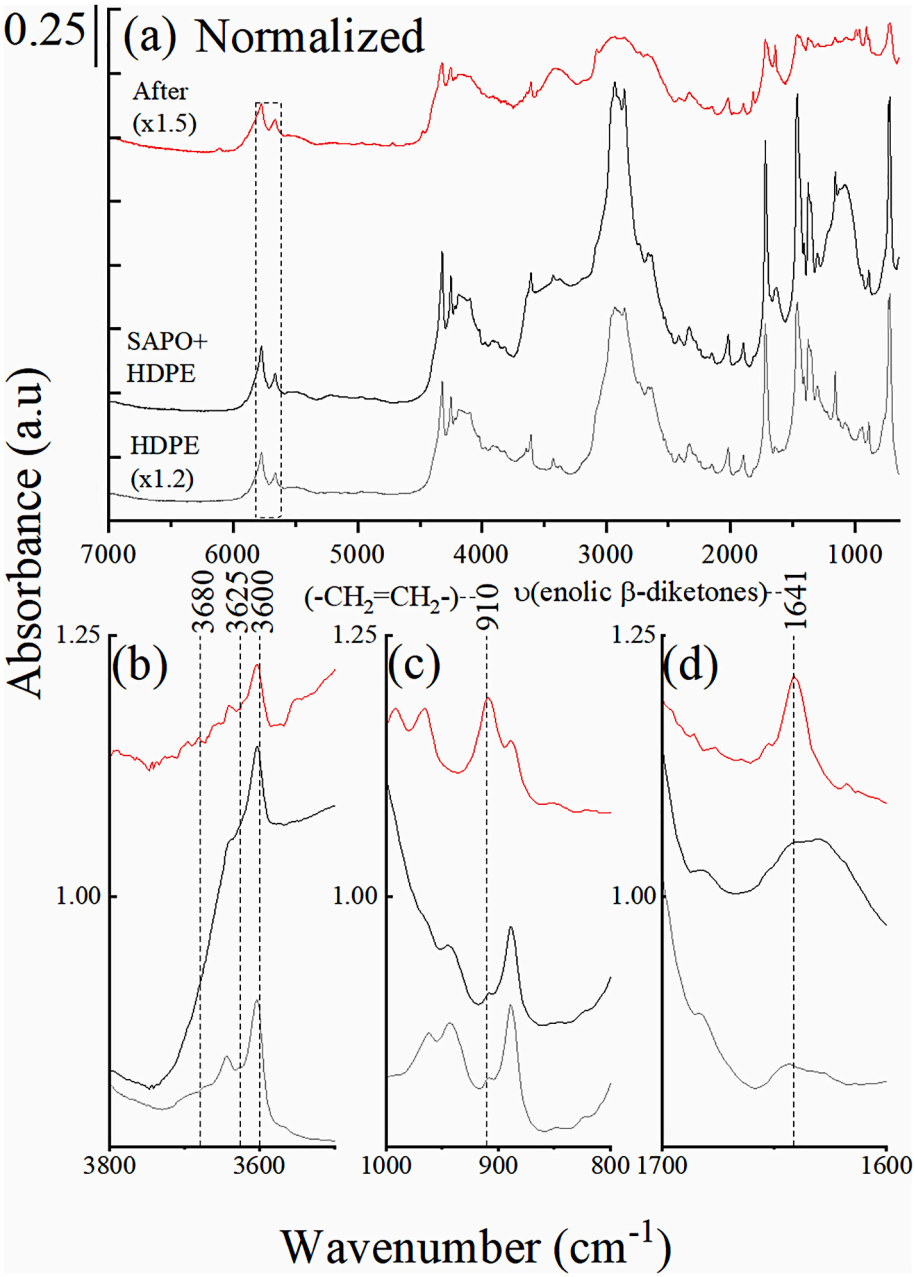

Fig. 3. Normalized absorbance spectra of the SAPO + HDPE reactant before and after plasma hydrogenolysis. (a) IR and near IR spectra, (b) absorbance spectra of the surface hydroxyls, and (c)-(d) absorbance spectra of the samples after reaction indicate the formation of vinyl groups and enolic β-diketone.

reaction under ambient condition. Less methane but more other gas products were produced with an increase of P_{H2}, resulting in a lower S_{CH4} and a higher S_{C2H6} (Fig. 1d). With stepwise increase of the plasma power from 60 W to 90 W, all products exhibited a monotonous increase in the formation rate that could be associated with more intense H_2 generation and thus faster reaction kinetics (Fig. 1e–f).

The catalyst effect on plasma hydrogenolysis of HDPE was investigated by mixing HDPE with Pt/C and SAPO-34 zeolite (denoted as PtC + HDPE and SAPO + HDPE, 5 wt% catalyst loading) respectively and examining the influences on the reaction properties. Overall, the PtC + HDPE and SAPO + HDPE experiments exhibit a similar trend of hydrogenolysis rate dependency on the examined reaction parameters as those without catalyst employment (Figs. S5 and S6). Fig. 2a–b compares the reaction properties achieved with and without catalyst under 100 ml/min H_2, 101 kPa, 90 W condition. The total gas production rate was improved to only a limited extent (<10%) in presence of catalyst under this specific testing condition (Fig. 2a), suggesting hydrogen plasma still plays a dominant role in controlling the overall hydrogenolysis kinetics. One major difference caused by the catalyst is the products selectivity. The production of alkanes (CH_4 and C_2H_6) was moderately enhanced and meanwhile the formation of unsaturated products (C_2H_2, C_2H_4 and C_3H_6) was significantly suppressed when the Pt catalyst was used. In contrast, significantly improvement of unsaturated products generation was observed when the SAPO-34 catalyst was in use, with 1.3 and 4.9 times higher S_{C2H4}, and 1.8 and 4.5 times higher S_{C3H6} compared with the HDPE and PtC + HDPE experiments, respectively. The results suggest the Pt/C and SAPO-34 play a role in affecting the distribution of different product formation reactions. Likely, the presence of Pt is beneficial for generating adsorbed hydrogen due to efficient H_2 dissociative adsorption, which consequently boosts hydrogenation of produced unsaturated hydrocarbons to alkanes. As a common methanol-to-olefin (MTO) catalyst, the acid sites on SAPO-34 are

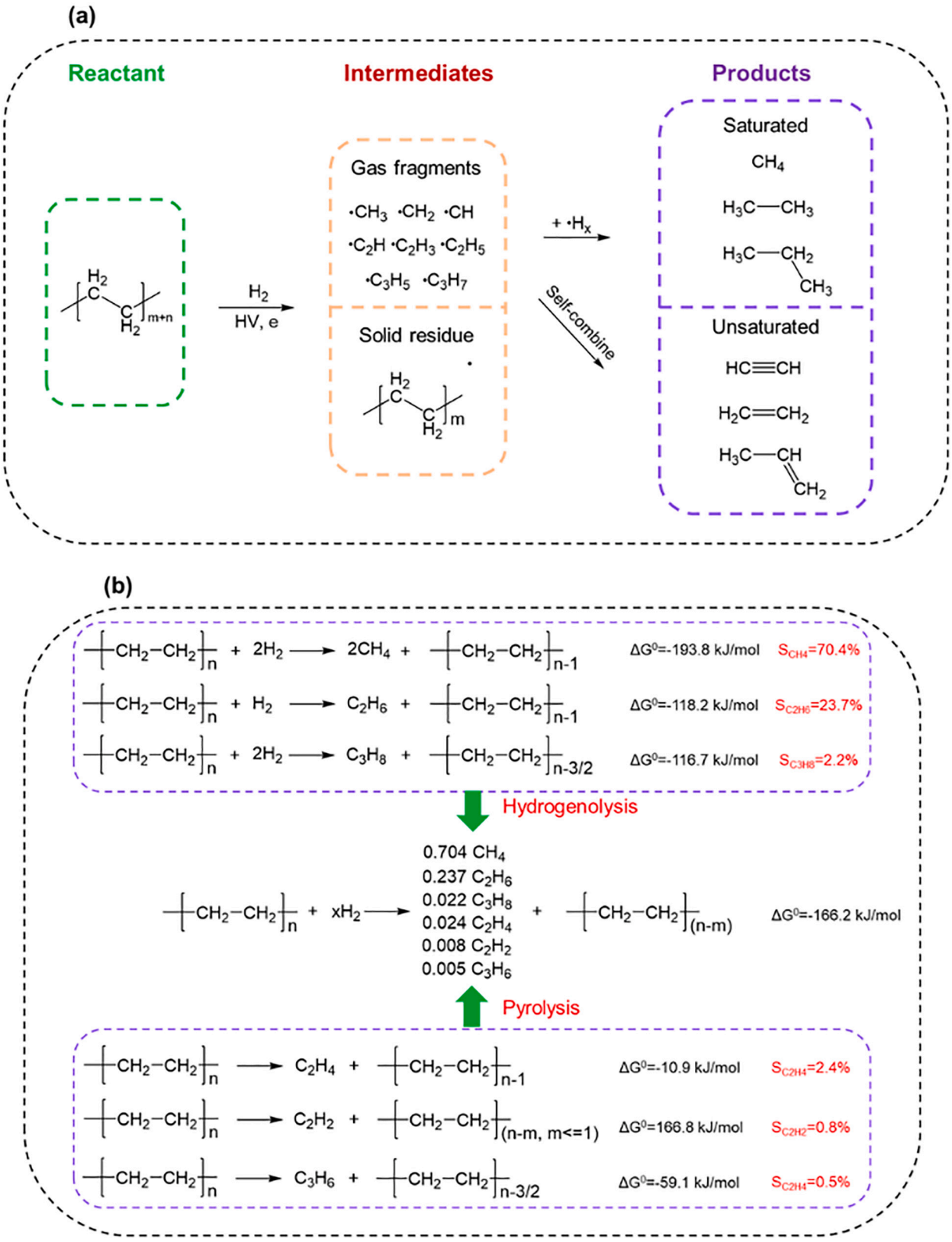

Fig. 4. (a) Proposed reaction pathway. (b) Reaction formula and Gibbs free energies (ΔG^0) under standard condition. Product selectivity value obtained from HDPE hydrogenolysis reaction. Reaction condition: 100 ml/min H_2, 101 kPa, 90 W.

capable of catalyzing low carbon number olefin formation via coupling of C—C bond, which could explain a higher olefin selectivity in this study. It needs noted, despite the improvement, the production of olefin still accounts for a low fraction of all products, as restricted by reaction thermodynamics (Fig. 2a, Figs. S7 and S8). Energy efficiency (η) was calculated for evaluating the utilization of plasma in assisting HDPE hydrogenolysis (Fig. 2c). A generic trend of higher η with an increase in the plasma power was observed, regardless of catalyst in use or not. Interestingly, the influence of catalyst on η was found to be plasma power dependent. At a high power of 90 W, the efficiency improvement was very limited. However, in a lower power range the catalyst can dramatically improve the η value to be as high as nine times. This indicates the catalyst plays a more dominant role in improving the HDPE hydrogenolysis kinetics under a lower plasma intensity condition.

3.2. Solid product analysis by FTIR

The solid mixture of SAPO + HDPE after 4.5 min plasma reaction was analyzed by FTIR. Fig. S9 revealed infrared spectra of hydroxyls at 3600, 3625 and 3680 cm^{-1} by in situ heating SAPO-34 from 25 °C to 150 °C. Hydroxyls at 3600 and 3625 cm^{-1} are assigned to Si-OH-Al bonding while the hydroxyl at 3680 cm^{-1} is indicative of P-OH bonding [22]. The hydroxyls at 3600 and 3625 cm^{-1} in SAPO-34 have been shown to be acidic active sites for solid acid catalysis [22]. The absorbance spectra of the SAPO + HDPE and PtC + HDPE were taken before and after plasma hydrogenolysis. Fig. 3 shows the absorbance spectra of HDPE, SAPO + HDPE before and after reaction. All the IR features of HDPE stay intact after mixing with SAPO. Plasma hydrogenolysis decreases the IR intensity of C—H stretching bands in 2700–3100 cm^{-1} and C—H bending bands in the finger print region as well as C—C bonds in 1065–1080 cm^{-1} region [23], suggesting that solid products produced from plasma hydrogenolysis was resulted from C—H and C—C bond breaking of HDPE. Fig. 3a also shows the reaction decreased the intensity of CH_2 at 5661 and 5775 cm^{-1} in the near IR, further indicating the long chain HDPE had been fragmented and shortened since the intensity of these near IR bands is proportional to the chain length of polyethylene [24]. These fragmented species may reside on the acidic site of SAPO, decreasing the intensity of surface hydroxyl in Fig. 3b. Fig. 3c and d show peaks at 910 cm^{-1} and 1641 cm^{-1} indicating the formation of a vinyl (-CH=CH_2-) and the possible formation of enolic β-diketones, respectively [25]. Similar features can be observed on HDPE (Fig. S14), but not on Pt + HDPE (Fig. S10–13). Although IR was not able to determine the structure of HDPE, the results of IR do provide an indirect evidence to show plasma hydrogenolysis is effective in breaking C—H and C—C bonds in HDPE.

3.3. Reaction mechanism and thermodynamic discussions

Plausible reaction pathway was proposed based on the experimental findings (Fig. 4a). The plasma-assisted HDPE hydrogenolysis would initiate from breakage of the polymeric structure by the bombardment of high energy H_2 plasma ($\bullet H_x$). This generates intermediates that can be categorized to small gas fragments ($\bullet C_xH_y$, not limited to the presented ones) and solid residues. The production of gas products would follow either hydrogenation reaction between $\bullet C_xH_y$ and $\bullet H_x$ or recombination reaction between $\bullet C_xH_y$ intermediates. Under an abundant hydrogen atmosphere, majority of the reaction goes through the first route to form alkanes, as evidenced by >90% alkane selectivity in the experiments and indicating its faster hydrogenation kinetics compared with the recombination process. Fig. 4b summarizes Gibbs free energies (ΔG^0) for various reactions based on the thermodynamic properties tabulated in Table S2. The hydrogenolysis of HDPE to alkanes is highly spontaneous as indicated by Fig. 4b. The production of unsaturated products, however, shows slightly negative/positive free energies. This explains the observed low olefin products selectivity, because their formation is restricted by the thermodynamics. When taking the product selectivity into account, the ΔG^0 for the overall reaction is −166.2 kJ/mol as calculated by summation of selectivity-weighted free energy. This confirmed the plasma-assisted HDPE hydrogenolysis is favorable in terms of reaction thermodynamics.

4. Conclusions

In this study, we successfully demonstrated a proof-of-concept method for polyethylene upcycling by means of non-thermal plasma-assisted hydrogenolysis which produces over 95% selectivity of light alkanes (C_1-C_3) and low fractions of unsaturated hydrocarbons (<5%) with promising reaction rate under ambient condition. The fast reaction kinetics was attributed to the cold H_2 plasma that can effectively break polymeric structure to generate fragment intermediates for further hydrogenation and recombination into the final products. The shrinkage of hydrocarbon chains as well as detection of unsaturated bonds observed by FTIR spectra of solid residue of reacted samples indicate effectiveness of bond cleavage by plasma hydrogenolysis. Introduction of Pt/C and SAPO-34 shows limited influence on production formation rate (<10%), but its effect on energy efficiency is significant, exhibiting as high as nine times improvement at lower plasma power. The highly spontaneous thermodynamic feature (ΔG ~ -166 kJ/mol) and fast kinetics induced by energy-intensive H_2 plasma collectively drive the efficient hydrogenolysis reaction. This novel strategy provides a simple approach in upcycling of not only polyethylene but also many other polymeric materials, which we will conduct more careful investigations in our future study.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2020.106274.

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