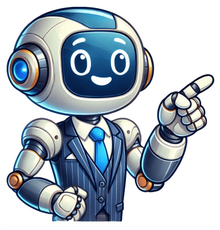
Continue



COMPOUND: C19503 Entry Name Formula(C2H4)n Structure Commentpolymer of Ethylene [CPD:C06547] Other DBs LinkDB KCF dataATOM21C2a C18.6900-15.40002C2a C20.0900-15.4000BOND1112 2BRACKET116.5900-16.520016.5900-14.2100122.1900-14.210022.1900-16.52001n ORIGINAL112 REPEAT1 2022 Apr 15;27(8):2557. doi: 10.3390/molecules27082557Metakaolin-based geopolymer microspheres (MGM) with hierarchical pore structures were prepared by suspension dispersion method in dimethicone at 80 C. The hydrothermal modification of MGM was carried out at a lower temperature of 80 C, and a NaA molecular sieve converted from metakaolin-based geopolymer (NMGM) with good crystal structure was prepared and applied in thermal catalytic cracking of low-density polyethylene (LDPE) reaction. The one-pot two-stage thermal catalytic cracking of LDPE was carried out in a 100 mL micro-autoclave under normal pressure. In this work, the optimal proportions and optimal reaction conditions of catalysts for NMGM thermal catalytic cracking of LDPE waste to fuel oil were investigated. The NMGM catalyst showed high selectivity to the liquid product of thermal catalytic cracking of waste LDPE. Under the reaction conditions of reaction time of 1 h and reaction temperature of 400 C, the liquid-phase yield of thermal catalytic cracking of LDPE reached a high of 88.45%, of which the content of gasoline components was 10.14% and the content of diesel components was 80.97%.Keywords: geopolymers, NaA molecular sieve, catalysts, plastic waste, fuel oilPlastics are durable and cheap, so they have become a common item in thousands of households, which greatly facilitates human life. It was once hailed as one of the greatest inventions of the 20th century. Over time, plastic has gone from a lauded invention to one of the biggest enemies of environmental pollution. Although the pace of technological development continues to advance, the problem of plastic pollution has not yet been fundamentally solved. Microplastics, which have been widely criticized in recent years, refer to plastic particles smaller than 5 mm that cannot be degraded in a short period of time and thus remain in the environment, and are difficult to be detected by the naked eye [1,2]. Microplastics have been detected in the sparsely populated Arctic [3,4]. Microplastics enter the diet of marine organisms, accumulate in the biological chain, and then enter the human table, endangering human health [5].Landfilling plastics in traditional plastic-disposal methods will bring about secondary pollution problems. Plastics have a high calorific value (CV) that matches conventional fuels such as gasoline, kerosene, diesel, etc., so incinerating plastics to generate electricity, steam and heat is also a major way of recycling. However, its economic value has been questioned and the issues of unstable combustion and the emission of toxic pollutants such as dioxins and furans have not been resolved [6,7]. The above two methods will bring about the problem of secondary pollution, but most developing countries are still using these two types of traditional treatment solutions [8]. At present, researchers focus on two solutions to plastic pollution: one is research on degradable plastics, and the other is research on cracking plastics into high-value-added products [9,10,11,12]. The research and development of degradable plastics is considered to solve the problem of plastic pollution from the root cause, but degradable plastics are still inferior to traditional plastics in terms of finished-product quality and performance. Degradable plastics have a large gap compared with traditional plastics, with good performance in terms of tensile strength and elongation at break, and the cost is much higher than traditional plastics [13]. As a degradable plastic as a packaging material, its biodegradability needs to be improved, and it cannot degrade quickly and completely after completing the mission of packaging, and the residue is difficult to degrade, causing land pollution [14]. Therefore, there are a series of scientific and technological problems in the process of optimizing the performance of degradable plastics, which cannot fully replace traditional plastic products.It is currently popular to recycle plastics into gaseous and liquid products with high added value [15,16,17]. Methods of gasifying plastic waste into syngas have been studied, but their recycling is expensive [18]. Cracking plastic wastes into fuel (gasoline, diesel) is convenient for transportation and has practical significance in rapidly rising oil prices. The cracking method can be divided into pyrolysis, catalytic cracking, and a method combining pyrolysis and catalytic cracking [19]. The pyrolysis reaction needs to be carried out at a high temperature of 500 to 900 C; the operating temperature is high, and the heat demand increases sharply because the pyrolysis is an endothermic reaction [20]. The carbon-number distribution of the product after pyrolysis is wide, and further processing is required to improve the quality of the oil in the product. The catalytic-cracking method uses a catalyst, which can reduce the activation energy required for the reaction, so that the plastic is cracked at a lower reaction temperature [21]. The use of suitable catalysts can narrow the distribution of reaction products, improve the selectivity of target products, and reduce subsequent separation and processing procedures.The combined method of thermal cracking and catalytic cracking can be divided into catalytic pyrolysis, thermal cracking-catalytic cracking, and catalytic cracking-catalytic upgrading [22]. The catalyst in the catalytic-pyrolysis process is mixed with a plastic sample in a batch reactor. The disadvantage of this process is the high tendency to form coke on the catalyst surface, which reduces catalyst efficiency over time and results in high residue yields. In addition to this, the separation of the residue from the catalyst at the end of the experiment was difficult. Catalytic cracking-catalytic upgrading means adding a small amount of catalyst in the pyrolysis stage of the two-step method, thereby shortening the cracking time and reducing the cracking temperature [23]. However, its shortcomings are also more obvious, the amount of catalyst is increased, and there is no economic benefit. The difference between the thermal cracking-catalytic cracking upgrading conversion method and the catalytic cracking-catalytic upgrading conversion method is that there is no catalyst involved in the thermal cracking process [24].Molten plastics have high viscosity and low thermal conductivity, which will cause a series of heat- and mass-transfer problems. Therefore, many scholars have carried out research on the selection of plastic-cracking reactors, so as to improve the mass transfer and heat transfer of the reaction process. Kaminsky et al. [25] developed a process consisting mainly of a fluidized-bed reactor, ensuring a uniform temperature throughout the reactor. Fluidized beds can be operated with a continuous plastic feed, which is beneficial for scaling up the process, but when operating conditions are out of range, molten plastic-coated particles can agglomerate and bed deflow occurs [26]. The helical kiln consists of a tubular reactor and a screw conveyor. The residence time of the polymer can be controlled by changing the speed of the screw, and the heat-transfer rate and pyrolysis temperature can be well controlled [27]. The gas-solid contact in the spouted-bed reactor is violent, and it can be used to treat irregular particles, fine particles, and other materials that are difficult to deal with by other methods of gas-solid contact [28]. Fixed-bed reactors are usually operated in batch mode during the pyrolysis of waste plastics [29]. Due to the poor heat- and mass-transfer efficiency of the molten plastic, the pyrolysis products initially formed from the plastic in the fixed-bed reactor are usually passed into another reactor for further cracking under the purging of an inert gas stream. Because batch or semi-batch reactor parameters are easy to control, they are the best reactors for obtaining high liquid yields, and their main disadvantage is the tendency to form coke on the outer surface of the catalyst, thereby reducing the overall yield of liquid product [30].In this work, the method of separating the catalyst from the cracking raw materials is adopted, and the low-density polyethylene at the bottom is heated to vaporize it through the catalyst in the upper layer, and the thermal cracking and catalytic cracking are combined: A one-pot two-stage reaction. Compared with the traditional thermal cracking-catalytic upgrading method, this method is more convenient and saves on equipment and equipment cost. This is referred to herein simply as thermal catalytic cracking.The key to the thermal catalytic cracking-catalytic pyrolysis process is the catalyst. Due to the high activity of solid acid catalysts in the cracking of plastic wastes into fuel oil, researchers are currently focusing on this type of catalysts [31,32]. However, its high-strength acidity can easily lead to the deactivation of the catalyst. Zeolite molecular sieves with high Si/Al ratio, such as ZSM-5 [33,34], HZSM-5 [24] and H [35], are all high-strength acid catalysts, which are expensive to prepare and require high-precision preparation technology. The degradation effect of different catalysts on plastics has been investigated by many researchers and examined using kinetic parameters determined by different models. Khan et al. [36] used a commercial LZ-Y52 molecular-sieve catalyst to react at 370 C for 60 min, and the oil yield exceeded 40%. Nisar et al. [37] calculated the kinetic parameters and found that the use of catalysts can reduce the activation energy of the reaction. Aguado et al. [38] found that mesoporous catalysts with high accessibility of plastic molecules and catalysts with small crystal size (high specific surface area) are expected to improve the catalytic activity of plastic cracking.Geopolymer is a three-dimensional network gel with amorphous and quasi-crystalline characteristics, which is formed by the polymerization of silicon-oxygen tetrahedron and aluminum-oxygen tetrahedron, which is similar to zeolite in chemical composition [39,40,41]. The production-energy consumption of geopolymer is low, equivalent to only 30% of the energy consumption of cement production. Geopolymer properties and formation methods are similar to natural zeolites. The zeolite molecular-sieve microspheres prepared from geopolymers have suitable acidity and controllable acidity. Microspheres with a hierarchical pore structure can be prepared by adding a suitable foaming agent, which provides abundant acidic reaction sites and channels for the catalytic cracking of plastics [42]. Alkali-excited geopolymers have high mechanical strength, so recovery after the reaction is complete is convenient.At present, commercial catalysts still have problems such as low selectivity of oil products and low quality of oil products, high cost of catalyst preparation and easy deactivation, and high energy consumption caused by high cracking temperature. The problem of environmental pollution caused by plastics is becoming more and more serious, and the price of crude oil is rising. Therefore, it is of practical significance to develop an inexpensive plastic-cracking catalyst with high catalytic activity, so as to produce high value-added oil products with high selectivity.In this work, metakaolin was used as raw material, sodium hydroxide was used as alkaline activator, and 0.1wt% H2O2 and 0.05wt% K12 were added to prepare geopolymer microspheres with hierarchical pore structure and low Si/Al ratio. It was hydrothermally treated and successfully converted into a metakaolin-based NaA molecular sieve (NMGM), which was used in the thermal catalytic cracking of urban solid plastic LDPE to make fuel oil. The changes of NMGM catalyst-preparation conditions and reaction conditions on the yield and hydrocarbon composition of liquid-phase products from thermal catalytic cracking of waste LDPE were investigated.The Na2O/SiO2 of the catalyst was varied by varying the amount of NaOH added during the preparation of the NMGM catalyst. The prepared microspheres were all hydrothermally heated at 80 C for 1 d. From the SEM test at 100 m, the microspheres remained spherical after hydrothermal treatment (Figure 1b,d,f,h). When Na2O/SiO2 was 0.2, the molecular-sieve grains obtained by the transformation of geopolymers could not be found (Figure 1a). When the dosage of NaOH was increased to Na2O/SiO2 of 0.4, a few polyhedral grains with a diameter of about 1 m were observed on the surface of the microspheres (Figure 1c). When the Na2O/SiO2 ratio was 0.8, a large number of cubic molecular-sieve grains with side lengths of about 0.68 m were formed on the surface of the microspheres, and many macropores could be observed on the surface (Figure 1e). When Na2O/SiO2 was 1.2, the amount of alkali activator reached its peak, and the surface of the microspheres was denser than the first three groups. It could be observed that the molecular sieves have different grain sizes and rough edges (Figure 1g). SEM and XRD tests of NMGM with different NaOH additions: (a,c,e,g) are the SEM tests of NMGM with Na2O/SiO2 of 0.2, 0.4, 0.8, 1.2, respectively; (b,d,f,h) SEM of NMGM with Na2O/SiO2 of 0.2, 0.4, 0.8, 1.2, respectively; (i) is the XRD pattern of different Na2O/SiO2 ratios (*: characteristic peaks of NaA molecular sieves).From Figure 1i, there were ten main characteristic peaks in the standard card spectrum of the NaA molecular sieve. The 2 of ten main characteristic peaks were the diffraction peaks at 7.18, 10.16, 12.45, 16.09, 21.65, 23.96, 26.09, 27.09, 29.92, and 34.17, respectively. With the increase in alkali activator, the crystallinity of NMGM first increased and then decreased. The NaA molecular sieve with higher crystallinity could be obtained by adding an appropriate amount of NaOH. When the amount of alkali activator was insufficient, the metakaolin could not be fully excited, and it mainly presented an amorphous dispersion peak between 20 and 30 of 2. If the alkali activator was used in excess, due to the influence of the high-alkaline environment, the formed NaA molecular-sieve crystal grained with complete crystal form would be dissolved again [43]. In this work, a Na2O/SiO2 ratio of 0.8 was chosen as the base activator dosage for the preparation of NMGM catalysts.The XRD test showed that the crystallinity of metakaolin-based geopolymer converted into NaA molecular sieve was affected by hydrothermal time. When the hydrothermal time was 1 d, the XRD diffraction peaks would be transformed from the initial amorphous diffraction peaks to the crystalline diffraction peaks of NaA molecular sieves. Among them, when the hydrothermal time was 2 d, the diffraction peak intensity was the strongest and the crystallinity was the highest. When the hydrothermal time was extended to 3 d, the intensity of diffraction peaks decreased instead (Figure 2a). The in situ transformation of geopolymers into molecular sieves could be divided into nucleation and growth stages. The alkalinity in the hydrothermal solvent reached the maximum when the conversion rate of molecular sieves reached the maximum. At this time, if the hydrothermal treatment was not stopped, part of the formed molecular sieve would dissolve and collapse. Therefore, the long-term hydrothermal treatment would cause the intensity of the diffraction peak to weaken. XRD test and BET test of NMGM catalyst with Na2O/SiO2 of 0.8 at hydrothermal time of 0 d, 1 d, 2 d, 3 d: (a) XRD (*: characteristic peaks of NaA molecular sieves), (b) pore-size distribution, (c) specific surface area.The BET test of the microspheres subjected to different hydrothermal times clearly showed that the NMGM catalyst was a porous structure dominated by mesopores and macropores from the pore-size-distribution map (Figure 2b). The presence of catalyst mesopores plays a positive role in plastic cracking, and Sakata et al. [44] claim that KFS-16 is a pure silica mesoporous material without acid sites. However, it can crack polyethylene as quickly as silica-alumina, thereby producing more liquid. This is because mesopores act as sites for long-term storage of free-radical species, so abundant free radicals may accelerate plastic degradation. When the hydrothermal time was 1 d, the specific surface area of NMGM reached the maximum, which was 38.49 m2/g (Figure 2c). At this time, the NaA molecular sieve had experienced a period of growth, and the larger NaA molecular-sieve crystals grew in a staggered manner, resulting in numerous pores. The hydrothermal time continued to extend to 2 d, and the specific surface area decreased to 23.11 m2/g. At this time, the growth of NaA molecular-sieve crystals reached saturation, and the formation of excessive molecular-sieve crystals blocked some of the pores, resulting in a decrease in the specific surface area. When the hydrothermal time was 3 d, some of the formed NaA molecular-sieve grains were dissolved and collapsed under strong alkaline conditions, resulting in blockage and collapse of some of the pores of NMGM, and the specific surface area and pore size were reduced. The increase in specific surface area and the existence of mesopores had a positive effect on the thermal catalytic cracking of LDPE. The NMGM catalyst prepared in this work selects 1 d as the optimal hydrothermal modification time for the conversion of metakaolin-based geopolymers into NaA molecular sieves.NH3-TPD tests were performed on NMGM that were not hydrothermally and hydrothermally modified for 1 d at 80 C (Figure 3). The changes in acid properties of NMGM after hydrothermal modification were significant, and the total acid content increased from 45.01 mol/g to 951.09 mol/g. The total acid content and pore structure of the catalyst determine its catalytic activity in acid-catalyzed reactions [31]. After hydrothermal treatment for 1 d, the NMGM catalyst was converted from an amorphous structure to a NaA molecular sieve, resulting in a significant increase in the total acid content and abundant pores, thereby improving the reactivity of the catalyst. The total acid content of the catalyst was related to the specific surface area of the catalyst and the density of acid sites on the catalyst surface. NH3-TPD tests of NMGM before and after hydrothermal 1 d.After hydrothermal treatment for 1 d, NMGM had three desorption peaks: the low-temperature peak corresponded to the weak acid site, the high-temperature peak corresponded to the strong-acid site, and the middle peak was the medium strong-acid site. After hydrothermal modification, the strong-acid center of NMGM did not shift greatly compared with that before hydrothermal modification, and the overall acidic-reaction site was composed of weak acid and medium strong acid, which is a catalyst of non-high-strength acid type. Sakata et al. [44] explored the effect of catalyst acidity on the distribution of HDPE pyrolysis products. The results of the acidity-strength test of the catalyst showed that SA-1 > ZSM-5 > SA-2. The results showed that SA-2 catalyst with lower acidity was observed to produce the highest amount of liquid oil, and ZSM-5 with strong-acid sites tended to produce more gaseous products with very low liquid yield. Appropriate acidity is beneficial to inhibit excessive cracking of liquid products and prepare liquid products with high selectivity. The molten LDPE has strong viscosity. If the waste LDPE plastic was directly mixed with the catalyst, it would easily adhere to the surface and block the catalyst pores, increasing the occurrence of coking reaction. In this experiment, the solid-plastic waste LDPE raw materials were first pyrolyzed and vaporized at the bottom of the quartz cup glass, and then catalytically cracked with the NMGM catalyst on the upper layer of quartz wool under the purging of N2.Used NMGM before and after hydrothermal modification at 80 C for 1 d, the results of catalytic thermal cracking of waste LDPE at 400 C for 1 h are shown in Figure 4. The yield of liquid oil in the cracked product increased from 23.51 wt% to 88.45 wt%, and the solid yield decreased from 38.59 wt% to 3.48 wt% (Figure 4a). The yield of aromatic products in the liquid fraction increased from 1.18% to 6.79%. After hydrothermal treatment, the content of hydroxyl groups in the pores of the NMGM microspheres and on the surface of the microspheres decreased, so the hydroxyl groups involved in the replacement reaction decreased, and the yield of alcohol products decreased significantly, from 47.88% to 20.33% (Figure 4b). Product test of NMGM before and after hydrothermal thermal catalytic cracking of waste LDPE for 1 h (a) yield, (b) hydrocarbon composition distribution of liquid product, (c) liquid product composition distribution, (d) FTIR test.Figure 4d shows the FTIR test results of the liquid-phase products after NMGM cracking waste LDPE before and after hydrothermal treatment. The stretching vibration peaks of the C-H bond at 2925.51 cm1 and the shear and bending vibration peaks of the C-H bond at 1469.87 cm1 confirmed the existence of alkanes in the liquid product, and their peak intensity was enhanced. In the infrared test results of the liquid-phase product after hydrothermal NMGM-cracking waste LDPE, the strength of the stretching vibration peak of the C=C bond at 1639.46 cm1 and the C-H bending vibration peak at 967.74 cm1 of the olefin were weakened. The appearance of the C-H bending vibration peak at 721.69 cm1 indicates the presence of olefinic and aromatic compounds in the product.Figure 5 shows when the reaction time of 1 h at 350 C, 400 C and 450 C in a 100 mL micro-autoclave reactor system with a feed/catalyst ratio of 5, the activity test results of NMGM catalyst for thermal catalytic cracking of LDPE plastic into fuel oil. Product tests after thermal catalytic cracking of waste LDPE with NMGM at different reaction temperatures for 1 h (a) yield, (b) hydrocarbon composition distribution of liquid products, (c) liquid product-composition distribution, (d) FTIR test.As the reaction temperature increased from 350 C to 450 C, the yield of solid components gradually decreased. The yield of liquid-oil products was the highest at 400 C, the yield of gas-phase components was the lowest at this time, and the yield of gas-phase products reached its highest at 450 C. A low reaction temperature could not fully crack LDPE, and the increase in temperature had a positive effect on the formation of gas-phase products (Figure 5a). Onwudili et al. studied the effect of temperature and residence time on the degradation of LDPE. It has been observed that long residence times and excessively high reaction temperatures provide opportunities for secondary reactions and cracking of oil to produce gas and char [45].The GC-MS test of the liquid oil of NMGM thermal catalytic cracking of LDPE showed that the main hydrocarbons were alkanes and alcohols, and the olefins and aromatics were relatively few. Among them, the octane number of aromatic hydrocarbons was higher, so they were good components of gasoline. If the reaction temperature was too high, it was not conducive to the formation of aromatic hydrocarbon products, and the aromatic hydrocarbon products were the highest at 400 C, reaching 6.79% (Figure 5b). The content of gasoline components (C5-C12) was the highest when the reaction temperature was 450 C, and the total content of gasoline and diesel components (C5-C22) reached the highest value of 91.10% at 400 C. Among them, the decrease in diesel components (C13-C22) at 450 C was presumed to be due to the higher temperature promoting the further cracking of diesel components (Figure 5c).The FTIR test results of the liquid-phase products are shown in Figure 5d. The stretching vibration peak of the alkane C-H bond at 2925.51 cm1 and the shear and bending vibration peak of C-H bond at 1469.87 cm1 increased and then weakened after the reaction temperature increased. This was corroborated with the GC-MS test results in Figure 4b. The olefins in the liquid phase were the stretching vibration peak of C=C bond at 1639.46 cm1 and the C-H bending vibration peak at 967.74 cm1 gradually weakened. The C-H bending vibration peak at 721.69 cm1 indicates the presence of olefin and aromatic compounds in the product. 3440.12 cm1 was the bending vibration peak of alcohols.Figure 6 shows the reaction temperatures of 0.5 h, 1 h, 2 h, and 4 h at 400 C in a 100 mL micro-autoclave reactor system with a feed/catalyst ratio of 5, and the activity test results of the NMGM catalyst for thermal catalytic cracking of waste LDPE plastics into fuel oil. Product tests of NMGM thermal catalytic cracking of waste LDPE at 400 C after different reaction times: (a) yield, (b) hydrocarbon-composition distribution of liquid products, (c) liquid product-composition distribution, (d) FTIR test.The longer the reaction time, the higher yield of gas-phase products. The highest yield of gas-phase products was 48.22% under the reaction time of 4 h, and the highest solid yield was 30.50% under the reaction time of 0.5 h. The yield of liquid oil was up to 88.45% under the reaction conditions of 1 h (Figure 6a).When the reaction time was extended to 4 h, the content of alcohol compounds in the liquid product reached its highest, 61.79%. The reason was deduced that the surface of the base-excited NMGM catalyst prepared by geopolymer contained abundant hydroxyl groups, the reaction time was long, and the reaction products tended to generate relatively stable alcohol compounds in the reaction system. The content of olefins in the liquid oil gradually decreased with the prolongation of the reaction time, and the olefin products were unstable, and tended to generate more stable alcohols and alkanes in the progress of the reaction (Figure 6b). When the reaction time is 1 h, the reaction had the best selectivity to diesel components, and the content of diesel components accounted for 80.97% of the liquid oil (Figure 6c).The preparation of NMGM catalyst can be seen in Figure 7a. First, a certain amount of metakaolin was taken, an appropriate dosage of NaOH solution of 11 mol/L was added according to the required sodium-silicon ratio (Na2O/SiO2), and the amount of distilled water added was controlled according to the water-sodium ratio (H2O/Na2O) of 20. The above slurry was stirred at a speed of 1000 r/min for 5 min under a mechanical stirring paddle to a uniform state. Then, 0.05 wt% H2O2 and 0.1 wt% K12 (sodium dodecyl sulfate) were added; the purpose was to increase the porosity in the geopolymer slurry, and the slurry was stirred at 1000 r/min for 2 min to foam status. Flow chart of NMGM thermal catalytic cracking of waste LDPE: (a) Microsphere preparation process, (b) NMGM thermal catalytic cracking of LDPE waste.In this experiment, the suspension-dispersion polymerization method was used to prepare the geopolymer-catalyst microspheres, and the prepared alkali-excited geopolymer slurry was sheared into small segments by the shearing force during the rotating operation of the stirring paddle, then dispersed into spheres under the action of surface tension of silicone oil. The prepared slurry was put into a 20 mL syringe and injected into simethicone at 80 C. The speed of the stirring paddle was adjusted to 600 r/min, and the microspheres were rapidly solidified and formed. The microspheres were placed in an oven at 60 C for 12 h in dimethyl silicone oil to make them completely cured.The cured microspheres were separated from the silicone oil with a rotary-vane vacuum pump. The filtrate was dimethyl silicone oil, which could be collected for recycling. The separated microspheres were washed three times with hot distilled water to remove the dimethyl silicone oil remaining on the surface of the microspheres and the inner pores. Next, the cleaned microspheres were dried in an oven at 60 C, and then calcined at 450 C for 6 h to remove residual silicone oil. After the temperature of the microspheres dropped to room temperature, the microspheres were placed in a 100 mL conical flask, 50 mL of distilled water was added, and the solution was heated at 80 C for 1 d. Finally, the microspheres were dried in an electric blast-drying oven at 60 C.In this work, a two-stage method was adopted. The reactor was lined with a quartz glass cup (254 mm in height and 21 mm in inner diameter); LDPE was placed at the bottom, the middle layer was quartz wool, and the catalyst was placed on the upper layer of quartz wool. The LDPE was heated and vaporized at 400 C and reacted through the upper catalyst, as shown in Figure 7b.The quartz glass was placed in a programmable and temperature-controlled 100 mL micro-autoclave, and the four knobs were tightened above the reactor in a clockwise direction to ensure that the inside of the reactor was airtight. Before the heating program of the reaction kettle started, N2 was fed with a flow rate of 100 mL/min, and the air was purged for 10 min to remove the air in the reactor. Then, the valves on both sides of the reaction kettle were tightened so that the kettle was in a closed state filled with N2. The K-type WRNT-042 m open-probe thermocouple produced by ELECALL, which was equipped with the reactor, was placed near the center of the reactor to monitor the real-time temperature in the reactor at all times. The heating rate was set as 4 C/min. When the temperature in the reaction kettle reached the reaction temperature, the valves on both sides of the reaction kettle were slowly twisted, and the flow meter was adjusted to control the flow rate of N2 at 50 mL/min. Driven by nitrogen, the product outlet was connected to a U-shaped tube placed in a constant-temperature circulating condensing pool at 0 C, and the condensed-liquid products were recovered. The uncondensed product was connected to the gas outlet, and the gas was collected with a 3L aluminum-foil air bag with single valve from Beekman Bio. After the reaction, the reaction kettle was cooled down to room temperature by natural cooling before the next set of experiments could be carried out.The total yield of LDPE degradation (wt%) and the conversion rate of liquid, gas, coke, or residue (wt%) were calculated as follows:TotalYieled(T)=MpMrMp100%(1)LiquidYieled(L)=MlMp100%(2)GasYieled(G)=MpMlMwMcMp100%(3)SolidYieled(S)=MwMp100%(4)In the above formulas, Mo represents the mass of the MGM catalyst added before the reaction, Mp is the mass of LDPE, Mc is the mass of coke on the catalyst after the reaction, Mw is the mass of solid in the quartz tube after the reaction, and Ml is the mass of the liquid-phase product in the U-shaped tube after the reaction. According to the law of conservation of mass, the gas-product conversion rate was determined by subtracting the yield of the liquid-phase products and coke or residue.The waste LDPE used in this experiment comes from plastic waste bottles, and the results obtained from the test showed that its density is 0.921 g/cm3. The melt mass-flow rate (mass of polymer extruded through a 1 mm die after 10 min use at 190 C with a nominal load of 2.16 kg) was 2.00 g/10 min. The collected waste LDPE plastic bottles were cleaned, cut into small squares of 1 mm 1 mm, and dried in a blast-drying oven at 60 C for 12 h. The metakaolin used in the experiment is the product of kaolin calcined at a high temperature of 800 C for 2 h, and its supplier is Chaopai Company in Inner Mongolia. The main components of metakaolin are SiO2 and Al2O3, of which the mass fraction of SiO2 is 56.91% and the mass fraction of Al2O3 is 42.35%.Various methods were used to characterize the catalyst. Under a voltage of 10 kV, a scanning electron microscope (SEM, Thermo Fisher Scientific, FEI Quattro S, Waltham, MA, USA) was used to observe the morphology of the catalyst.X-ray diffractometer (XRD, Rigaku, MiniFlex 600, Kyoto, Japan) was used to investigate the change in the crystal form of the catalyst. A Cu-K target with a wavelength of 0.154 nm was used for testing at a working voltage of 40 kV and a working current of 15 mA. The scanning range of the test data was 0 to 80, 2 degrees, and the scanning speed was 5/min. Continuous sampling was selected as the sampling method.The pore-size distribution and specific surface area of the catalyst were analyzed on a Brunauer-Emmett-Teller analyzer (BET, Micromeritics, Gemini VII 2390, Norcross, GA, USA). The BET equation was used to calculate the surface area of the sample, and the Barret-Joyner-Halenda (BJH) equation was used to calculate the pore-size distribution.The liquid product was qualitatively and quantitatively analyzed using a gas chromatography-mass spectrometer (GC-MS, Agilent Technologies, 7890A-5975C, Santa Clara, CA, USA). Chromatographic conditions: Chromatographic column is HP-5MS (60 m 250 m 0.25 m); He was selected as carrier gas and the flow rate was 1.5 mL/min; split ratio 20:1, sample injection volume 1 L, inlet temperature 280 C. The test conditions of the mass spectrometry were an EI source; electron energy 70 eV; ion source temperature 230 C; quadrupole 150 C; scan mode was Scan; scan mass range was 50550 u; solvent delay 4.0 min.Ammonia temperature-programmed desorption (NH3-TPD, Altamira Instruments, AMI-300lite, Pittsburgh, PA, USA) experiment was performed to obtain the acidic-site type and concentration information of the catalyst. A total of 100 mg of sample were activated in an Ar flow at 550 C for 0.5 h and then cooled to 100 C. A gaseous ammonia flow (8 vol% in He, 30 mL/min) was introduced for 40 min to saturate the sample adsorption. Then, the sample was flushed with Ar (30 mL/min) for 40 min. The sample was heated from 100 C to 600 C in a He flow (20 mL/min) at a rate of 10 C/min; the absorbed NH3 started to desorb from the sample, and the desorbed NH3 was monitored using a thermal conductivity detector.Fourier transform infrared spectroscopy (FT-IR, Thermo Nicolet, iS50, Waltham, MA, USA) was performed in order to obtain the changes in the hydrocarbon composition of the liquid-phase products. The prepared samples were dried in a blast drying oven at 60 C for 12 h, mixed with KBr powder and ground them into powder, then made it into tablets and tested in the range of 4004000 cm1.In order to investigate the effect of the amount of alkali activator on the properties of the microspheres, metakaolin was used as the raw material; the alkali activator was sodium hydroxide; the molar ratio of H2O/Na2O was 20; the molar ratios of Na2O/SiO2 were 0.2, 0.4, 0.8, and 1.2, respectively. The dosages of sodium oxide were 1.36 g, 2.72 g, 5.43 g, and 8.15 g, respectively. A total of 1 g of microspheres were taken and put in a 100 mL beaker, and 80 mL of deionized water was added. The beaker was sealed with plastic wrap and placed in a constant-temperature water bath; the water-bath temperature was 80 C and the water-bath time was 3 d. The prepared microspheres were tested by XRD, and the optimal dosage of the alkali activator was determined according to the conversion of the molecular sieve of microspheres.In order to explore the effect of hydrothermal modification time on the properties of microspheres, NMGM catalysts were prepared under the optimal dosage of alkali activator. Under the determined optimal water-bath temperature, the hydrothermal conversion times were 0.5 d, 1.0 d, 1.5 d, 2.0 d, and 2.5 d, respectively. The specific surface area and crystal-form changes of NMGM prepared with different hydrothermal times were compared.At present, the plastic-cracking mechanisms that have been widely recognized are mainly the free-chain scission mechanism and the carbocation mechanism [46]. The thermal catalytic-cracking method adopted in this work mainly follows the free-chain scission mechanism, and the catalytic-cracking process mainly follows the carbocation mechanism. The cleavage of plastic was divided into three stages: chain initiation, propagation stage, and chain termination (Figure 8). In the chain-initiation step, the free chains of long-chain LDPE molecules were cleaved into macromolecular fragments with radicals at one or both ends. The macromolecular LDPE fragments underwent a hydrogen-transfer reaction with the SiO2-Al2O3 framework to generate smaller LDPE fragments with carbocations. In the propagation stage of step 2, the free radical-bearing LDPE fragments are brought into contact with acidic sites on the surface and in the pores of the NMGM catalyst. In this step, the LDPE fragments tend to undergo a hydrogen transfer reaction, thereby abstracting hydrogen atoms from the LDPE macromolecular chain to restore the structure. Image of the NMGM thermal catalytic-cracking LDPE mechanism.According to the compounds obtained in this work, it was inferred that the chain termination step in step three can be divided into four categories. NMGM were less acidic and therefore dominated by free-chain scission, in which a large number of LDPE-cracked fragments generated more stable alkanes through hydrogenation ((3-4) in Figure 8). The alkane products further reacted with the abundant hydroxyl groups on the surface of NMGM to generate a large number of alcohols ((3-3) in Figure 8). Fragments containing free radicals in the reaction underwent a hydrogen-transfer reaction to generate alkenes ((3-2) in Figure 8). Conjugated dienes reacted with olefins to undergo a Diels-Alder reaction to form cycloalkenes, and cycloalkenes further underwent a hydrogen-transfer reaction to form aromatic hydrocarbons ((3-1) in Figure 8) [47].In this work, LDPE waste rich in municipal solid-plastic waste was catalytically pyrolyzed using a low-Si/Al-ratio NaA molecular-sieve NMGM catalyst with a SiO2/Al2O3 molar ratio of 1. NMGM was transformed into NaA molecular-sieve microspheres in a water bath at 80 C under normal pressure for 1 d. The acid-enhanced geopolymer-based NaA molecular-sieve porous microspheres NMGM after hydrothermal treatment were confirmed to have potential significance in the thermal catalytic cracking of solid-plastic waste LDPE. The results of this study confirmed this idea, as NMGM catalyst actively participated in the thermal catalytic cracking of waste LDPE into fuel oil, and its liquid-phase yield reached 88.45% at 400 C for 1 h. The total content of gasoline and diesel components accounted for 91.10% of the liquid product after the reaction. NMGM exhibits high catalytic activity and high selectivity for cracking waste LDPE into fuel oil. Given these facts, NMGM is considered as a promising catalyst for the degradation of municipal solid-waste plastics.Conceptualization, X.C.; data curation, S.T.; formal analysis, X.D.; funding acquisition, X.C.; investigation, S.T.; methodology, S.T.; project administration, Y.H.; resources, X.C.; supervision, Y.H. and X.C.; writingoriginal draft, S.T.; writingreview and editing, S.T. and X.D. All authors have read and agreed to the published version of the manuscript.This study was funded by the National Natural Science Foundation of China (Project No. 51772055) and the Key Project of Guangxi Natural Science Foundation (Project No.: 2021JJD120043).Not applicable.Not applicable.Not applicable.The authors declare no conflict of interest.Samples of the compounds are available from the authors.1.Andrady A.L. Microplastics in the marine environment. Mar. Pollut. Bull. 2011;62:15961605. doi: 10.1016/j.marpolbul.2011.05.030. [DOI] [PubMed] [Google Scholar]2.Fendall L.S., Sewell M.A. Contributing to marine pollution by washing your face: Microplastics in facial cleansers. Mar. Pollut. Bull. 2009;58:12251228. doi: 10.1016/j.marpolbul.2009.04.025. [DOI] [PubMed] [Google Scholar]3.Lusher A.L., Tirelli V., OConnor I., Officer R. Microplastics in Arctic polar waters: The first reported values of particles in surface and sub-surface samples. Sci. Rep. 2015;5:14947. doi: 10.1038/srep14947. [DOI] [PMC free article] [PubMed] [Google Scholar]4.Mu J., Qu L., Jin F., Zhang S., Fang C., Ma X., Zhang W., Huo C., Cong Y., Wang J. Abundance and distribution of microplastics in the surface sediments from the northern Bering and Chukchi Seas. Environ. Pollut. 2019;245:122130. doi: 10.1016/j.envpol.2018.10.097. [DOI] [PubMed] [Google Scholar]5.Van Cauwenberghe L., Janssen C.R. Microplastics in bivalves cultured for human consumption. Environ. Pollut. 2014;193:6570. doi: 10.1016/j.envpol.2014.06.010. [DOI] [PubMed] [Google Scholar]6.Fu Z., Zhang S., Li X., Shao J., Wang K., Chen H. MSW oxy-enriched incineration technology applied in China: Combustion temperature, flue gas loss and economic considerations. Waste Manag. 2015;38:149156. doi: 10.1016/j.wasman.2014.12.026. [DOI] [PubMed] [Google Scholar]7.Buekens A.G., Huang H. Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes. Resour. Conserv. Recycl. 1998;23:163181. doi: 10.1016/S0921-3449(98)00025-1. [DOI] [Google Scholar]8.Browning S., Beymer-Farris B., Seay J.R. Addressing the challenges associated with plastic waste disposal and management in developing countries. Curr. Opin. Chem. Eng. 2021;32:100682. doi: 10.1016/j.coche.2021.100682. [DOI] [Google Scholar]9.Lee K.-H., Noh N.-S., Shin D.-H., Seo Y. Comparison of plastic types for catalytic degradation of waste plastics into liquid product with spent FCC catalyst. Polym. Degrad. Stab. 2002;78:539544. doi: 10.1016/S0141-3910(02)00227-6. [DOI] [Google Scholar]10.Nishino J., Itoh M., Ishinomori T., Kubota N., Uemichi Y. Development of a catalytic cracking process for converting waste plastics to petrochemicals. J. Mater. Cycles Waste Manag. 2003;5:8993. doi: 10.1007/s10163-003-0086-6. [DOI] [Google Scholar]11.Suriyamongkol P., Weselake R., Narine S., Moloney M., Shah S. Biotechnological approaches for the production of polyhydroxyalkanoates in microorganisms and plantsA review. Biotechnol. Adv. 2007;25:148175. doi: 10.1016/j.biotechadv.2006.11.007. [DOI] [PubMed] [Google Scholar]12.Meinander K., Niemi M., Hakola J.S., Selin J.-F. Polylactidesdegradable polymers for fibres and films. Macromol. Symp. 1997;123:147153. doi: 10.1002/masy.19971230115. [DOI] [Google Scholar]13.Yang X., Steck J., Yang J., Wang Y., Suo Z. Degradable Plastics Are Vulnerable to Cracks. Engineering. 2021;7:624629. doi: 10.1016/j.eng.2021.02.009. [DOI] [Google Scholar]14.Degradable Plastics Generate Controversy in Solid Waste Issues. Chem. Eng. News Arch. 1990;68:714. doi: 10.1021/cen-v068n026.p007. [DOI] [Google Scholar]15.Bhaskar T., Kaneko J., Muto A., Sakata Y., Jakab E., Matsui T., Uddin M.A. Pyrolysis studies of PP/PE/PS/PVC/HIPS-Br plastics mixed with PET and dehalogenation (Br, Cl) of the liquid products. J. Anal. Appl. Pyrolysis. 2004;72:2733. doi: 10.1016/j.jaap.2004.01.005. [DOI] [Google Scholar]16.Escola J.M., Aguado J., Serrano D.P., Briones L., Daz de Tuesta J.L., Calvo R., Fernandez E. Conversion of Polyethylene into Transportation Fuels by the Combination of Thermal Cracking and Catalytic Hydroreforming over Ni-Supported Hierarchical Beta Zeolite. Energy Fuels. 2012;26:31873195. doi: 10.1021/ef300938r. [DOI] [Google Scholar]17.Arshad H., Sulaiman S.A., Hussain Z., Naz M.Y., Moni M.N.Z. Effect of Input Power and Process Time on Conversion of Pure and Mixed Plastics into Fuels Through Microwave-Metal Interaction Pyrolysis. Waste Biomass Valorization. 2021;12:34433457. doi: 10.1007/s12649-020-01225-9. [DOI] [Google Scholar]18.Kannan P., Al Shoaibi A., Srinivasakannan C. Temperature Effects on the Yield of Gaseous Olefins from Waste Polyethylene via Flash Pyrolysis. Energy Fuels. 2014;28:33633366. doi: 10.1021/ef500516n. [DOI] [Google Scholar]19.Miandad R., Barakat M.A., Aburiazaiza A.S., Rehan M., Nizami A.S. Catalytic pyrolysis of plastic waste: A review. Process Saf. Environ. Prot. 2016;102:822838. doi: 10.1016/j.psep.2016.06.022. [DOI] [Google Scholar]20.Almeida D., de Ftima Marques M. Thermal and catalytic pyrolysis of plastic waste. Polmeros Cincia E Tecnol. 2016;26:4451. doi: 10.1590/0104-1428.2100. [DOI] [Google Scholar]21.Dada T.K., Sheehan M., Murugavelh S., Antunes E. A review on catalytic pyrolysis for high-quality bio-oil production from biomass. Biomass Convers. Biorefinery. 2021:120. doi: 10.1007/s13399-021-01391-3. [DOI] [Google Scholar]22.Lpez A., de Marco I., Caballero B.M., Laresgoiti M.F., Adrados A., Aranzabal A. Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud. Appl. Catal. B Environ. 2011;104:211219. doi: 10.1016/j.apcatb.2011.03.030. [DOI] [Google Scholar]23.Uemichi Y., Nakamura J., Itoh T., Sugioka M., Garforth A.A., Dwyer J. Conversion of Polyethylene into Gasoline-Range Fuels by Two-Stage Catalytic Degradation Using SilicaAlumina and HZSM-5 Zeolite. Ind. Eng. Chem. Res. 1999;38:385390. doi: 10.1021/ie980341+. [DOI] [Google Scholar]24.Aguado J., Serrano D.P., San Miguel G., Castro M.C., Madrid S. Feedstock recycling of polyethylene in a two-step thermo-catalytic reaction system. J. Anal. Appl. Pyrolysis. 2007;79:415423. doi: 10.1016/j.jaap.2006.11.008. [DOI] [Google Scholar]25.Kaminsky W., Predel M., Sadiki A. Feedstock recycling of polymers by pyrolysis in a fluidised bed. Polym. Degrad. Stab. 2004;85:10451050. doi: 10.1016/j.polymdegradstab.2003.05.002. [DOI] [Google Scholar]26.Mastellone M.L., Arena U. Bed defluidisation during the fluidised bed pyrolysis of plastic waste mixtures. Polym. Degrad. Stab. 2004;85:10511058. doi: 10.1016/j.polymdegradstab.2003.04.002. [DOI] [Google Scholar]27.Vasile C., Pakdel H., Mihai B., Onu P., Darie H., Cioclteu S. Thermal and catalytic decomposition of mixed plastics. J. Anal. Appl. Pyrolysis. 2001;57:287303. doi: 10.1016/S0165-2370(00)00151-0. [DOI] [Google Scholar]28.Makibar J., Fernandez-Akarregi A.R., Alava I., Cueva F., Lopez G., Olazar M. Investigations on heat transfer and hydrodynamics under pyrolysis conditions of a pilot-plant draft tube conical spouted bed reactor. Chem. Eng. Process. Process Intensif. 2011;50:790798. doi: 10.1016/j.cep.2011.05.013. [DOI] [Google Scholar]29.Kunwar B., Moser B.R., Chandrasekaran S.R., Rajagopalan N., Sharma B.K. Catalytic and thermal depolymerization of low value post-consumer high density polyethylene plastic. Energy. 2016;111:884892. doi: 10.1016/j.energy.2016.06.024. [DOI] [Google Scholar]30.Anuar Sharuddin S.D., Abnisa F., Wan Daud W.M.A., Aroua M.K. A review on pyrolysis of plastic wastes. Energy Convers. Manag. 2016;115:308326. doi: 10.1016/j.enconman.2016.02.037. [DOI] [Google Scholar]31.Manos G., Garforth A., Dwyer J. Catalytic Degradation of High-Density Polyethylene over Different Zeolitic Structures. Ind. Eng. Chem. Res. 2000;39:11981202. doi: 10.1021/ie990512q. [DOI] [Google Scholar]32.Lin Y.H., Yen H.Y. Fluidised bed pyrolysis of polypropylene over cracking catalysts for producing hydrocarbons. Polym. Degrad. Stab. 2005;89:101108. doi: 10.1016/j.polymdegradstab.2005.01.006. [DOI] [Google Scholar]33.Smiekov A., Hudec P., Kumar N., Salmi T., Murzin D.Y., Jork V. Aromatization of methane on Mo modified zeolites: Influence of the surface and structural properties of the carriers. Appl. Catal. A Gen. 2010;377:8391. doi: 10.1016/j.apcata.2010.01.021. [DOI] [Google Scholar]34.Pierella L.B., Saux C., Caglieri S.C., Bertorello H.R., Bercoff P.G. Catalytic activity and magnetic properties of Co-ZSM-5 zeolites prepared by different methods. Appl. Catal. A Gen. 2008;347:5561. doi: 10.1016/j.apcata.2008.05.033. [DOI] [Google Scholar]35.Morais E.K.L., Jimnez-Snchez S., Hernando H., Ochoa-Hernndez C., Pizarro P., Araujo A.S., Serrano D.P. Catalytic Copyrolysis of Lignocellulose and Polyethylene Blends over HBeta Zeolite. Ind. Eng. Chem. Res. 2019;58:62436254. doi: 10.1021/acs.iecr.8b06158. [DOI] [Google Scholar]36.Khan M.A., Nisar J., Iqbal M., Shah A., Khan R.A., Sirajuddin, Bhatti I.A., Amin R. Pyrolysis of polypropylene over a LZ-Y52 molecular sieve: Kinetics and the product distribution. Iran. Polym. J. 2019;28:839847. doi: 10.1007/s13726-019-00747-x. [DOI] [Google Scholar]37.Nisar J., Khan M.A., Ali G., Shah A., Iqbal M., Bhatti I.A. Cobalt-doped molecular sieve for efficient degradation of polypropylene into fuel oil: Kinetics and fuel properties of the oil. Chem. Eng. Res. Des. 2022;177:751758. doi: 10.1016/j.cherd.2021.11.038. [DOI] [Google Scholar]38.Aguado J., Sotelo J.L., Serrano D.P., Calles J.A., Escola J.M. Catalytic Conversion of Polyolefins into Liquid Fuels over MCM-41: Comparison with ZSM-5 and Amorphous SiO2Al2O3. Energy Fuels. 1997;11:12251231. doi: 10.1021/ef970055v. [DOI] [Google Scholar]39.Nikolov A., Rostovsky I., Nugteren H. Geopolymer materials based on natural zeolite. Case Stud. Constr. Mater. 2017;6:198205. doi: 10.1016/j.cscm.2017.03.001. [DOI] [Google Scholar]40.He Y., Cui X.-M., Liu X.-D., Wang Y.-P., Zhang J., Liu K. Preparation of self-supporting NaA zeolite membranes using geopolymers. J. Membr. Sci. 2013;447:6672. doi: 10.1016/j.memsci.2013.07.027. [DOI] [Google Scholar]41.Su Q., He Y., Yang S., Wan H., Chang S., Cui X. Synthesis of NaA-zeolite microspheres by conversion of geopolymer and their performance of Pb (II) removal. Appl. Clay Sci. 2021;200:105914. doi: 10.1016/j.clay.2020.105914. [DOI] [Google Scholar]42.Zhang Z., Yu H., Xu M., Cui X. Preparation, characterization and application of geopolymer-based tubular inorganic membrane. Appl. Clay Sci. 2021;203:106001. doi: 10.1016/j.clay.2021.106001. [DOI] [Google Scholar]43.Xuemin C., Yan H., Leping L., Jinyu C. NaA zeolite synthesis from geopolymer precursor. MRS Commun. 2011;1:4951. doi: 10.1557/mrc.2011.15. [DOI] [Google Scholar]44.Sakata Y., Azhar Uddin M., Muto A., Kanada Y., Koizumi K., Murata K. Catalytic degradation of polyethylene into fuel oil over mesoporous silica (KFS-16) catalyst. J. Anal. Appl. Pyrolysis. 1997;43:1525. doi: 10.1016/S0165-2370(97)00052-1. [DOI] [Google Scholar]45.Onwudili J.A., Insura N., Williams P.T. Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: Effects of temperature and residence time. J. Anal. Appl. Pyrolysis. 2009;86:293303. doi: 10.1016/j.jaap.2009.07.008. [DOI] [Google Scholar]46.Aboulkas A., El Harfi K., El Bouadili A. Thermal degradation behaviors of polyethylene and polypropylene. Part I: Pyrolysis kinetics and mechanisms. Energy Convers. Manag. 2010;51:13631369. doi: 10.1016/j.enconman.2009.12.017. [DOI] [Google Scholar]47.Williams P.T., Williams E.A. Fluidised bed pyrolysis of low density polyethylene to produce petrochemical feedstock. J. Anal. Appl. Pyrolysis. 1999;51:107126. doi: 10.1016/S0165-2370(99)00011-X. [DOI] [Google Scholar]This section collects any data citations, data availability statements, or supplementary materials included in this article.Not applicable. Optimization of low-temperature catalytic cracking of polyolefin waste in open-batch reactors using zeolite beta with controlled intrinsic properties Environmental problems are worsening due to the complexity in managing plastic waste. Chemical recycling emerges as a pivotal technology that can suppress carbon introduction into the carbon cycle and provide petroleum alternatives for current petrochemical processes. The utilization of zeolites can reduce energy consumption by lowering the operation temperature for pyrolysis. Here, we demonstrate low-temperature catalytic cracking of polyethylene (PE) utilizing an open-batch reactor configuration and *BEA-type zeolite catalysts. With the optimized open-batch setup and zeolites, high PE conversion (~80%) and liquid selectivity (~70%) were achieved at 330C. We systematically explored the effects of aluminum (Al) site density and crystal size, revealing that zeolite crystal size is another critical factor determining the liquid production. This work not only demonstrates that an effective combination and optimization of reactor and catalysts can enhance the overall catalytic activity but also offers insights into designing catalysis systems for effective recycling of polyolefin wastes. Plastics have emerged as pivotal materials that buttress current human civilizations, assuming an irreplaceable role in maintaining human well-being. Consequently, the production of plastics has been experiencing substantial global growth, primarily driven by the versatility and extensive applicability of polymer-based products across various sectors of industry, encompassing automotive, construction, electronics, aerospace, and packaging1. As a result, in 2015, an estimated 6300 MT of plastic waste had been generated, posing a formidable environmental challenge these days2,3,4. Additionally, the utilization and subsequent disposal of single-use plastics contribute to the prospection of additional carbons for make-up inputs, primarily from oil reserves. Within this context, plastic recycling assumes considerable importance, as it serves not only to mitigate immediate environmental threats but also plays a crucial role in achieving carbon neutrality by curbing additional fossils into the carbon cycle. Chemical recycling, comprising both conventional and innovative technologies aimed at converting plastic waste into value-added chemicals, encompassing monomers, aromatics, and olefins, has attracted substantial interest from the scientific and engineering communities. This interest majorly stems from its capability to leverage existing chemical processes, keeping the carbon quantity in circulation5,6,7.Polyolefin wastes, including polyethylene (PE) and polypropylene (PP), have gained substantial attention in the field of chemical recycling of plastic waste due to their prevalence, comprising over 50% of the global plastic waste stream8. The polyolefin polymer backbone comprises of C-C bonds, necessitating controlled cleavage to yield liquid hydrocarbons suitable for use as feedstocks in downstream processes. These subsequent processes may encompass traditional processes, such as the fluidized catalytic cracking preceded by hydrotreatment, as well as innovative technologies such as the plasma gasification, which yields ethylene and acetylene under arc discharge9. In this context, it is essential to prioritize the optimization of liquid hydrocarbon yield with controlled selectivity distribution to meet the downstream process requirements, thereby enhancing overall operational efficiency. Many technologies have been developed and utilized for the conversion of polyolefin waste into a spectrum of hydrocarbons, spanning from light olefins to wax10,11,12. Pyrolysis, conducted at high temperatures ranging from 450 to 600C in an inert atmosphere, entails thermal cleavage of the main backbone of polyolefins13. Although the pyrolysis process has the highest technological maturity, it presents several challenges, including high energy consumption resulting from high temperature conditions14,15,16. To tackle these challenges, hydrogenolysis17,18,19,20 and alkane tandem metathesis21,22 at low temperature (200250C) have been suggested and widely studied as alternative processes. However, the cost viability of these approaches is hindered by the requirement for high-pressure hydrogen and/or the utilization of platinum group metal catalysts like Pt or Ru.Catalytic cracking process efficiently decomposes polyolefins at lower temperatures than pyrolysis, employing a solid acid catalyst. Extensive research has focused on reducing energy consumption and carbon deposition in the reactor23,24,25,26,27. Zeolites, common microporous solid acid catalysts, reduce the activation energy necessary for breaking C-C bond chains of polyolefins through mechanisms such as the -scission and protonolysis over their Brnsted acid sites28. The final distribution of products is primarily determined by the shape selectivity of the micropore structures of zeolites28,29,30,31. Among various commercialized zeolites, zeolite beta, with 12-membered-ring (12MR) micropores measuring 78 in pore opening and interconnected channels in three dimensions, is recognized for its high selectivity in producing liquid products (C530) in the catalytic cracking of polyolefin32,33,34. Furthermore, zeolite beta serves as an ideal platform for investigating the correlation between catalytic performance and intrinsic properties of zeolites, including crystal sizes and Si/Al ratios, as modification of these properties through hydrothermal synthesis has extensively studied35,36.While zeolite have been commonly considered as capable of reducing the operation temperature of pyrolysis under non-hydrogen conditions, the catalytic cracking of polyolefins using zeolites has primarily been investigated within a temperature range exceeding 380C8,33,37,38. Although there is a systematic study reporting the decomposition behavior of PE by ZSM-5 zeolite at temperatures below 300C39, it indicates that the liquid products, which are of primary interest in the polyolefins valorization processes, are scarcely produced. Furthermore, existing studies using zeolite have rarely reported optimization from the perspective of process variables rather than zeolite structures and properties8,37,38. In this study, we demonstrate the potential to further reduce the operating temperature of catalytic cracking of PE (namely, 330C) while maintaining polyolefin conversion above 80% and liquid selectivity exceeding 70%, through appropriate control of the intrinsic properties of zeolite beta, in conjunction with the optimization of reactor design and associated process parameters. A series of zeolite beta catalyst samples were synthesized, with independent control over parameters including Si/Al ratio and crystal size, specifically the external surface area. Under the optimized condition at 330C, the correlation between catalytic performance and intrinsic properties of zeolites were established, demonstrating that decreased particle size and increased external surface area enhances liquid selectivity, thereby providing a direction for catalyst design for polyolefin conversion processes. Figure1 presents schematic illustrations that encapsulate the central concept of this study.Fig. 1: Schematic summary of the reactor design and mechanism in this work.a *BEA-type zeolites with varying Al contents and crystal sizes in an open-batch reactor setup and b the open-batch configuration with an inert gas flow facilitating liquid product recovery and preventing over-cracking and coke formation that reduce liquid selectivity through reactive distillation.The structure and operation modes of batch reactors containing a PE/catalyst slurry during catalytic contact are crucial for improving the conversion and product distribution in low-temperature PE catalytic cracking. The reactor used for this work could operate in either closed-batch or open-batch mode by simply closing or opening the downstream valve that connects to the condenser/collector units as shown in Fig.1a and Supplementary Fig.3. The primary purpose of catalytic decomposition of PE is to obtain liquid hydrocarbon products suitable for further processing in downstream processes. Typically, an improved liquid selectivity can be achieved by minimizing excessive contact between zeolite and hydrocarbon species (Fig.1b). This approach helps to prevent irreversible coke formation and evolution of gas species from over-cracking, as demonstrated by a recent hydrogenolysis study using a supported Pt catalyst40. Indeed, employing a selected *BEA-type zeolite catalyst (S-BEA-30, see below for the sample information), an open-batch configuration at 330C resulted in higher conversion and liquid selectivity (45.1% and 62.3%, respectively) than the conventional closed-batch configuration (38.3% and 44.9%, respectively), by allowing the evaporated products to escape the reactor (Fig.2a). The formation of uncrackable solid phase that deactivates the catalysis, is considerably reduced in an open-batch configuration compared to a closed-batch configuration as shown in Supplementary Fig.4.Fig. 2: Optimization of the open-batch reactor configuration and types of zeolite catalysts for the low-temperature open-batch catalytic cracking of polyethylene (PE).a PE conversion, liquid selectivity, and b liquid product selectivity distributions with varied open-batch reactor configurations. c PE conversion, liquid selectivity, and d liquid product selectivity distributions with varied operation temperatures. e PE conversion, liquid selectivity, and f liquid product selectivity distributions from various commercial zeolites. Polyethylene to catalyst ratio denoted as PE/Cat ratio.The inert-gas flow rate is a crucial parameter influencing the conversion and liquid selectivity in the open-batch catalytic cracking of PE. Figure 2b demonstrates that increasing the inert-gas flow rate shifts the selectivity distribution towards heavier products, suggesting fewer catalytic scissions in PE chains due to reduced contact time. The PE conversion increases monotonously with the inert-gas flow rate, while liquid selectivity showed an optimum at 10mL/min in our reactor setup, which was adopted as the standard reaction condition for subsequent experiments. Increasing the flow rate up to 30mL/min decreased the liquid selectivity, presumably due to insufficient condensation in the condenser assembly, an issue that could be mitigated with improved design. These results highlight the significance of the reactor design and operation modes in the catalytic PE decomposition into liquid hydrocarbons. Obviously, temperature is a key parameter affecting the rate of catalytic scissions of the main backbone of PE chains. At the optimized inert-gas flow rate of 10mL/min with the selected zeolite catalyst (S-BEA-30), the conversion of PE is dramatically influenced by the operation temperature as depicted in Fig.2c. A high conversion of 98.3% was observed at 390C, near the typical temperature range of the conventional pyrolysis process. Conversely, at the low limit of 260C, the conversion was low, under 20%, even with the zeolite catalyst. The selectivity towards light C5 and C6 liquid hydrocarbons was noticeably low at 260C, implying sluggish scission of C-C backbones of linear hydrocarbons (Fig.2d). In this work, we

evaluated various zeolite catalysts at 330C, achieving acceptably high conversion and high liquid selectivity, highlighting disparities among samples.The use of zeolites greatly enhances the conversion of PE at low temperatures by accelerating C-C bond scission, catalyzed by Brnsted acid sites that promote the carbenium or carbonium mechanisms28. In absence of zeolites, just a 0.2 % PE conversion was observed at 330C. To evaluate the effect of zeolite topologies, several commercially available zeolites, including ZSM-5 (MFI), zeolite beta (*BEA), and zeolite Y (FAU) were examined (Supplementary Fig.5). These zeolites achieved PE conversions ranging from 20% to 80% at the same temperature. Details on the tested commercial zeolites are provided in the Supplementary Figs.1, 2 and Supplementary Table1. All zeolites demonstrated notable isomerization, as indicated by the complexity of the resulting gas chromatograph (GC) profiles (see Supplementary Figs.6, 7). Among the tested commercial zeolites, ZSM-5 having micropores limited by 10MR pore openings, exhibited the highest conversion, but its liquid selectivity was lower than that of zeolite beta due to its high gas selectivity as depicted in Fig.2e, which originated from its narrow pore system. ZSM-5 also tended to produce lighter liquid products than the other two frameworks (Fig.2f). The 1H and 13C NMR spectra for the same liquid product mixtures are also presented in Supplementary Fig.8. The 1H NMR spectra indicate that the products contain the most olefinic sp2 C-H in the order of ZSM-5>zeolite beta>zeolite Y. This matches the order of PE conversion (Fig.2e), presumably due to the high frequency of chain scission via the -scission occurred over ZSM-5. Conversely, the lowest PE conversion and olefinic proton content observed in the zeolite Y samples are likely due to their relatively weak acid sites41. The zeolite beta sample of 12MR pore openings achieved a PE conversion comparable to ZSM-5 with the highest liquid selectivity. In this work, the effects of the intrinsic properties of zeolite on the *BEA framework were investigated. The synthesis of *BEA-type zeolites, which has been extensively studied for decades35,42,43, offers great synthetic flexibility in terms of Si/Al ratios and crystal sizes.Intrinsic properties-controlled beta zeolite catalytic cracking of LDPE*BEA-type zeolites can be crystallized with a wide synthetic window of hydrothermal synthesis using tetraethylammonium hydroxide (TEAOH) as the organic structure-directing agent (OSDA)35. It has been observed that the crystal size of the resulting *BEA-type zeolite crystals is strongly correlated with the Al content in the hydrothermal *BEA-crystallizing systems35. As the Si/Al ratio of the system increases, the crystal size also increases, thereby reducing the relative contribution of acid sites in on external surfaces compared to those within micropores. To decouple the Si/Al ratio from the crystal size, we employed three different hydrothermal methods from the literature and modified them to prepare three series of *BEA-type zeolites, denoted as L-, M-, and S-series. For the preparation of large crystals (L-series, 0.651.7m), fluoride was used as the mineralizer, known to stabilize small composite building unites of the *BEA framework42,44. The medium- and small-sized *BEA-type zeolites (M- and S-series, 130170nm and 30140nm, respectively) were obtained using conventional hydroxide media36,43. The S-series were synthesized at a low crystallization temperature of 100C, much below the conventional temperature (140C) for *BEA synthesis. As noted above, trends observed here indicate that reducing the Al content generally led to larger crystal sizes (Fig.3a). The scanning electron micrographs (SEMs) of three representative samples from the three series are shown in Fig.3bd. In this work, samples are denoted as X-BEA-y, where X represents the series code (L, M, or S) and y indicates the approximate Si/Al ratio of the zeolites, as characterized by the energy dispersive spectroscopy (EDS). The sample information is summarized in Table1. Their synthetic details and additional characterization results are provided in the Supplementary Table2 and Supplementary Figs.912.Fig. 3: Relation between the Al content and crystal size of the resulting *BEA-type zeolite.a Schematic summary of intrinsic properties-controlled beta zeolite, scanning electron microscope images of synthesized beta zeolite with Si/Al 10: b L-BEA-10, c M-BEA-10, and d S-BEA-10. Each data was provided with an error bar which was calculated via standard deviation of 10 parallel data. Large, Medium, Small crystal sized zeolite beta with y (Si/Al) denoted as L-, M-, S-BEA-y.Table 1 Physical properties of the intrinsic properties-controlled beta zeolitesThe catalytic cracking of PE using the prepared *BEA-type zeolites was tested in an open-batch configuration under optimal conditions (10mL N2/min, 330C, 2h) as previously discussed. Figure4ac show the conversion and liquid selectivity, achieved with the *BEA-type zeolites listed in Table1. The justification for comparing the cracking behavior of zeolite beta sample series synthesized through different methods is supported by the independent 1,3,5-triisopropylbenzene (TIPB) cracking results provided in Supplementary Fig.14. The framework Al sites primarily act as Brnsted acid sites in zeolites, serving as active sites for the catalytic cracking of long-chain hydrocarbons28. Thus, the decrease in Si/Al ratios led to an increase in the PE conversion across all sample series, indicating enhanced apparent catalytic activity. Crystal size also played a crucial role in the PE conversion. The S-series samples, with higher specific external surface area values (Table1), showed higher PE conversions than the L-series samples. A similar trend was observed in liquid selectivity (Fig.4b). Al sites can be located within either the micropores or external surfaces of the zeolite samples. The catalytic conversion of PE over *BEA-type zeolites may occur in two steps: bulky molecule scission at the external surface acid sites, followed by additional scission of smaller molecules within the micropores. We think that the molecular weight distribution of liquid products primarily depends on the spatial distributions of these acid sites as shown in Fig.4e. The S-BEA-10 sample having the most Al sites and the highest external surface area showed a high PE conversion (~80%) and liquid selectivity (~70%) at a low temperature of 330C. This result offers experimental evidence that reducing crystal size also meaningfully enhances the PE conversion and liquid selectivity by facilitating the external scission process of polymer chains. Moreover, the increase in mesopore volume associated with decreasing crystal size suggests an improvement in mass transfer efficiency, which may contribute to the observed enhancement in catalytic performance. Further analysis on the conversion and liquid selectivity is provided in the Supplementary Figs.1321.Fig. 4: Intrinsic properties-controlled beta zeolite catalytic cracking of low-density polyethylene (LDPE) at 330C, 2h, 10ml N2/min.a Conversion, b liquid selectivity, c liquid selectivity by conversion, d hydrocarbon distribution in liquid products, and e schematic description for the relation between acid site distribution and liquid product molecular weight. Large, Medium, Small crystal sized zeolite beta with y (Si/Al) denoted as L-, M-, S-BEA-y.The simulated distillation (SIMDIS) results confirmed that over 99% of the liquid portion comprises hydrocarbons in the range from C5 to C30 (Supplementary Figs.22, 23 and Table3). Figure4d illustrates the hydrocarbon distribution in liquid products from the catalytic cracking of PE over L-BEA-10, M-BEA-10, and S-BEA-10, which have similar Si/Al ratios but vary in crystal sizes. L-BEA-10 and M-BEA-10 predominantly yielded hydrocarbons in the gasoline (C510) range, whereas S-BEA-10 yielded heavier products under the same reaction conditions. Considering the total number of Al sites is similar across the three samples, it suggests that L-BEA-10 and M-BEA-10 have more micropore Al sites than S-BEA-10, providing a greater extent of secondary scission to lighter products. This serves as an example of the reactant shape selectivity.The spent catalysts were recovered as entangled chunks mixed with residues, including deposited coke species. The SIMDIS analysis of the Soxhlet extract, using toluene as the solvent, revealed a minimal composition of remaining product-range (C5C30) hydrocarbons in the solid phase (Supplementary Fig.15 and Table3). The spent catalysts should be recoverable and reusable from the remaining solid phase. However, mechanical separation of inorganic catalyst components from the mixture was unsuccessful due to the polymeric organic components remaining in the solid phase, showing a sturdy texture at room temperature. To assess catalyst reusability, a new PE feed of the same amount was directly added to the spent mixture for a second run. The conversion and liquid selectivity in the second run decreased compared to the first, from 78% to 67% and from 68% to 54%, respectively (Fig.5a). However, the product distribution of the liquid product within the range from C5 to C15 remained almost unchanged, as shown in Fig.5b, indicating that coke-induced deactivation primarily influenced the external surfaces of zeolite rather than the micropores. The zeolite catalysts could be separated by removing the residue through air calcination at 580C for 6h. The regenerated catalyst was found to have physical properties very similar to those of the virgin catalyst, as confirmed by PXRD, SEM, EDS, and BET analyses (Supplementary Fig.24). Consequently, in the catalytic cracking of PE using the regenerated catalyst, both the conversion and liquid selectivity were almost identical (Fig.5c, d). Finally, the optimized 330C open-batch reaction conditions were applied to an actual post-consumer PE waste sample collected from a local recycling center, and it was compared to two model virgin PEs with different molecular weights (4kDa and 204kDa), confirming that the resulting PE conversion and liquid selectivity were similar to those observed with the virgin PE model feed with heavier molecular weight, as illustrated in Supplementary Fig.25.Fig. 5: Catalytic cracking to evaluate reusability and regenerability of deactivated zeolite beta (S-BEA-10) at 330C, 2h, 10ml N2/min. Continuous secondary reaction compared to the first reaction.a Conversion and liquid selectivity, b hydrocarbon distribution in liquid products; show the regenerated zeolite beta catalytic cracking compared to the virgin zeolite beta, namely c conversion, d hydrocarbon distribution in liquid products. Small crystal sized zeolite beta with y (Si/Al) denoted as S-BEA-y.Conventionally, the catalytic cracking of polyolefins using zeolite catalysts have adopted operation temperatures higher than 380C (Supplementary Fig.26)33,45,46. This work demonstrates the temperature can be greatly reduced to 330C while maintaining high PE conversion and liquid selectivity, provided the reactor configuration and catalysts are adequately optimized. The open-batch configuration effectively prevents over-cracking or excess coke formation by properly regulating the contact between the feed molecules and the zeolites, removing the distillates to the gas phase. Proper selection of inert-gas flow rate, which further regulates the contact time, can further enhance the PE conversion and liquid selectivity. Among the tested commercial zeolites, zeolite beta having the *BEA topology exhibited excellent acid site strength, ensuring high conversion of PE even at low temperature and an adequate shape selectivity towards aliphatic liquid products. Along with the Al content of zeolites, the crystal size was confirmed as a crucial factor determining the PE conversion and liquid phase selectivity. Reducing the crystal size ensures high liquid selectivity regardless of the Al content by enhancing the chain scission on the external surfaces of zeolites. This work not only highlights the potential for the low-temperature catalytic cracking of PE using zeolite catalysts but also provides insights into other plastic waste chemical recycling technologies in terms of selection of catalysts47.All *BEA-type zeolites presented in this work were synthesized using conventional hydrothermal methods, recipes that are modifications of the previously reported methods in the literature36,42,43. Initially, Al sources, OSDA(TEAOH), mineralizers, and water were mixed to achieve a desired gel composition in 40mL PTFE liners. Subsequently, Si sources were added, ensuring complete dispersion and homogenization by subsequent stirring. The general gel composition can described as 1.0 SiO2: x Al: y TEAOH: z (NH4F or NaOH): w H2O. x determines the Al content, while y, z, and w depend on the different sample series yielding different crystal sizes. Additional aging steps can be added depending on the sample series. The PTFE liners charged with gels were clad in steel autoclaves and transferred to a convection oven preheated to the desired temperature, which could be rotating or static. The progress of crystallization was tracked by analyzing PXRD patterns of aliquots collected every 37 days. Following crystallization, the products were thoroughly rinsed with distilled water and acetone and calcined at 580C for 6h. The resultant *BEA-type zeolites were then converted into their H-forms through ion exchange with ammonium nitrate (NH4NO3) and subsequent calcination at 580C for 6h. The details of the preparations of the three series of samples (L-, M-, and S-series), including specified gel compositions, are provided in the Supplementary Information, together with the characterizations of the resulting zeolites.Open-batch catalytic cracking process of PEPolyolefin catalytic cracking was conducted using open-batch reactive distillation setup in a stirring batch reactor (CheMReSys, R-201) with custom modifications to allow an inert gas flow. Initially, 1g of zeolite catalyst and 10g of model feed PE (LDPE, melt index 25g/10min at 190C/2.16kg, average Mw ~204kDa by GPC, Sigma-Aldrich) were placed in a 75mL stainless steel liner and sealed within the stirring reactor. The stainless tubing and fitting connected to the reactor were heated to 330C during the operation with heating tapes to minimize condensation and residue within the tubing and fitting. The reaction was performed for 2h at a bulk temperature of 330C with stirring at 200rpm using an impeller-type stirrer. Simultaneously, inert gas (N2) flowed at a desired rate. The liquid product was collected via a condensation device connected to a cold constant-temperature circulation column set at 15C, comprising two stages to minimize the process loss. The gaseous product was collected in a gas sampling bag connected to the end of the reactive distillation setup and analyzed using a GC-FID. The details of quantification methods and reactor structure/operation modes are provided in the Supplementary Information.CharacterizationsPowder X-ray diffraction (XRD) patterns were obtained with a SMARTLAB instrument (Rigaku, Japan). Scanning electron microscopy (SEM) images and elemental compositions of the zeolites were analyzed using a JSM-7800F Prime microscope equipped with an energy-dispersive spectroscopy (EDS) unit, specifically SDD type with active area of 80mm2. EDS was standardized using Certified Reference Materials (CRMs) to ensure accuracy by JEOL Ltd. N2 physisorption (77K) isotherms were measured using a BELSORP MINI X sorption analyzer. Prior to measurements, samples underwent a 3-h degassing step at 300C using a BELPREP VAC II instrument (MicrotracBEL, Japan). Raman spectra of solid samples were recorded with a DXR2xi instrument (Thermo Fisher Scientific, USA). The selectivity distributions of liquid products were determined using a ChroZen gas chromatography-flame ionization detector (GC-FID, Youngin, Korea), and product identification was carried out with a TSQ 3000 Evo gas chromatography-mass spectrometry (GC-MS) system (Thermo Fisher Scientific, USA) based on the NIST library. The data used in this study are available from the corresponding author upon reasonable request. Chang, C.-F. & Rangarajan, S. Machine learning and informatics based elucidation of reaction pathways for upcycling model polyolefin to aromatics. J. Phys. Chem. A 127, 29582966 (2023).Article MATH Google Scholar Cressey, D. Bottles, bags, ropes and toothbrushes: the struggle to track ocean plastics. Nature 536, 263265 (2016).Article Google Scholar Geyer, R., Jambeck, J. R. & Law, K. L. Production, use, and fate of all plastics ever made. Sci. Adv. 3, e1700782 (2017).Article Google Scholar Joshi, C., Browning, S. & Seay, J. Combating plastic waste via Trash to Tank. Nat. Rev. Earth Environ. 1, 142142 (2020).Article Google Scholar Alonso, J. A., Aguado, J. & Serrano, D. P. Feedstock recycling of plastic wastes (Royal society of chemistry, 1999).Jiang, J. et al. From plastic waste to wealth using chemical recycling: a review. J. Environ. Chem. Eng. 10, 106867 (2022).Article MATH Google Scholar Kleme, J. J., Fan, Y. V. & Jiang, P. Plastics: friends or foes? The circularity and plastic waste footprint. Energy Sources A Recov. Util. Environ. Eff. 43, 15491565 (2021).MATH Google Scholar Wang, Y. et al. Elucidating the structure-performance relationship of typical commercial zeolites in catalytic cracking of low-density polyethylene. Catal. Today 405-406, 135143 (2022).Article MATH Google Scholar Ma, W. et al. Characterization of tar evolution during DC thermal plasma steam gasification from biomass and plastic mixtures: parametric optimization via response surface methodology. Energy Convers. Manage. 225, 113407 (2020).Article MATH Google Scholar Wang, N. M. et al. Chemical recycling of polyethylene by tandem catalytic conversion to propylene. JACS 144, 1852618531 (2022).Article MATH Google Scholar Conk, R. J. et al. Catalytic deconstruction of waste polyethylene with ethylene to form propylene. Science 377, 15611566 (2022).Article MATH Google Scholar Aguado, R., Olazar, M., San Jos, M. J., Gaisn, B. & Bilbao, J. Wax formation in the pyrolysis of polyolefins in a conical spouted bed reactor. Energy Fuels 16, 14291437 (2002).Article Google Scholar Anuar Sharuddin, S. D., Abnisa, F., Wan Daud, W. M. A. & Aroua, M. K. A review on pyrolysis of plastic wastes. Energy Convers. Manage. 115, 308326 (2016).Article Google Scholar Pandey, D. S., Katsaros, G., Lindfors, C., Leahy, J. J. & Tassou, S. A. Fast pyrolysis of poultry litter in a bubbling fluidised bed reactor: energy and nutrient recovery. Sustainability 11, 2533 (2019).Article Google Scholar Songip, A. R., Masuda, T., Kuwahara, H. & Hashimoto, K. Test to screen catalysts for reforming heavy oil from waste plastics. Appl. Catal. B 2, 153164 (1993).Article Google Scholar Ng, S. H., Seoud, H., Stanciulescu, M. & Sugimoto, Y. Conversion of polyethylene to transportation fuels through pyrolysis and catalytic cracking. Energy Fuels 9, 735742 (1995).Article Google Scholar Rorrer, J. E., Troyano-Valls, C., Beckham, G. T. & Romn-Leshkov, Y. Hydrogenolysis of polypropylene and mixed polyolefin plastic waste over Ru/C to produce liquid alkanes. ACS Sustain. Chem. Eng. 9, 1166111666 (2021).Article Google Scholar Bin Jumah, A., Anbumuthu, V., Tedstone, A. A. & Garforth, A. A. Catalyzing the hydrocracking of low density polyethylene. Ind. Eng. Chem. Res. 58, 2060120609 (2019).Article Google Scholar Liu, S., Kots, P. A., Vance, B. C., Danielson, A. & Vlachos, D. G. Plastic waste to fuels by hydrocracking at mild conditions. Sci. Adv. 7, eabf8283 (2021).Article Google Scholar Rorrer, J. E., Beckham, G. T. & Romn-Leshkov, Y. Conversion of polyolefin waste to liquid alkanes with Ru-based catalysts under mild conditions. JACS Au 1, 812 (2020).Article Google Scholar Kim, D. et al. Metathesis, molecular redistribution of alkanes, and the chemical upgrading of low-density polyethylene. Appl. Catal. B 318, 121873 (2022).Article Google Scholar Ellis, L. D. et al. Tandem heterogeneous catalysis for polyethylene depolymerization via an olefin-intermediate process. ACS Sustain. Chem. Eng. 9, 623628 (2021).Article Google Scholar Okonsky, S. T., Krishna, J. J. & Toraman, H. E. Catalytic co-pyrolysis of LDPE and PET with HZSM-5, H-beta, and HY: experiments and kinetic modelling. React. Chem. Eng. 7, 21752191 (2022).Article Google Scholar Figueiredo, A. L. et al. Catalytic cracking of LDPE over nanocrystalline HZSM-5 zeolite prepared by seed-assisted synthesis from an organic-template-free system. J. Anal. Appl. Pyrolysis 117, 132140 (2016).Article MATH Google Scholar Uemichi, Y., Kashiwaya, Y., Tsukidate, M., Ayame, A. & Kanoh, H. Product distribution in degradation of polypropylene over silica-alumina and CaX zeolite catalysts. Bull. Chem. Soc. Jpn. 56, 27682773 (1983).Article Google Scholar Audisio, G., Bertini, F., Beltrame, P. L. & Carniti, P. Catalytic degradation of polyolefins. Makromol. Chem. Marcromol. Symp. 57, 191209 (1992).You, Y. S., Shim, J.-S., Kim, J.-H. & Seo, G. Liquid-phase degradation of polyethylene wax over mordenite catalysts with different Si/Al molar ratios. Catal. Lett. 59, 221227 (1999).Article MATH Google Scholar Corma, A., Planelles, J., Sanchez-Marin, J. & Tomas, F. The role of different types of acid site in the cracking of alkanes on zeolite catalysts. J. Catal. 93, 3037 (1985).Article Google Scholar Kissin, Y. V. Chemical mechanisms of catalytic cracking over solid acidic catalysts: alkanes and alkenes. Catal. Rev. 43, 85146 (2001).Article MATH Google Scholar Amin, A. M., Croiset, E. & Epling, W. Review of methane catalytic cracking for hydrogen production. Int. J. Hydrogen Energy 36, 29042935 (2011).Article MATH Google Scholar Lin, Q.-F. et al. A stable aluminosilicate zeolite with intersecting three-dimensional extra-large pores. Science 374, 16051608 (2021).Article MATH Google Scholar Gaca, P., Drzewiecka, M., Kaleta, W., Kozubek, H. & Nowiska, K. Catalytic degradation of polyethylene over mesoporous molecular Sieve MCM-41 modified with heteropoly compounds. Pol. J. Environ. Stud. 17, 2531 (2008).Serrano, D. P., Aguado, J. & Escola, J. M. Catalytic cracking of a polyolefin mixture over different acid solid catalysts. Ind. Eng. Chem. Res. 39, 11771184 (2000).Article MATH Google Scholar Park, J. W., Kim, J.-H. & Seo, G. The effect of pore shape on the catalytic performance of zeolites in the liquid-phase degradation of HDPE. Polym. Degrad. Stab. 76, 495501 (2002).Article MATH Google Scholar Camblor, M., Mifsud, A. & Prez-Pariente, J. Influence of the synthesis conditions on the crystallization of zeolite Beta. Zeolites 11, 792797 (1991).Article Google Scholar Mintova, S. et al. Variation of the Si/Al ratio in nanosized zeolite Beta crystals. Microporous Mesoporous Mater. 90, 237245 (2006).Article Google Scholar Caldeira, V. P. et al. Properties of hierarchical Beta zeolites prepared from protozeolitic nanounits for the catalytic cracking of high density polyethylene. Appl. Catal. A Gen. 531, 187196 (2017).Article MATH Google Scholar Peral, A. et al. Bidimensional ZSM-5 zeolites probed as catalysts for polyethylene cracking. Catal. Sci. Technol. 6, 27542765 (2016).Article MATH Google Scholar Hittinger, J. P. & Shantz, D. F. Systematic study of low temperature cracking of low-density polyethylene with ZSM-5. Microporous Mesoporous Mater. 343, 112170 (2022).Article MATH Google Scholar Wang, Y.-Y. et al. Catalytic hydrogenolysis of polyethylene under reactive separation. ACS Catal. 14, 20842094 (2024).Article MATH Google Scholar Sandoval-Daz, L.-E., Gonzlez-Amaya, J.-A. & Trujillo, C.-A. General aspects of zeolite acidity characterization. Microporous Mesoporous Mater. 215, 229243 (2015).Article MATH Google Scholar Jon, H., Lu, B., Oumi, Y., Itabashi, K. & Sano, T. Synthesis and thermal stability of beta zeolite using ammonium fluoride. Microporous Mesoporous Mater. 89, 8895 (2006).Article Google Scholar Xie, B. et al. Organotemplate-free and fast route for synthesizing beta zeolite. Chem. Mater. 20, 45334535 (2008).Article MATH Google Scholar Xia, Q.-H., Shen, S.-C., Song, J., Kawi, S. & Hidajat, K. Structure, morphology, and catalytic activity of zeolite synthesized in a fluoride medium for asymmetric hydrogenation. J. Catal. 219, 7484 (2003).Article Google Scholar Lpez, A., de Marco, I., Caballero, B. M., Adrados, A. & Laresgoiti, M. F. Deactivation and regeneration of ZSM-5 zeolite in catalytic pyrolysis of plastic wastes. Waste Manage. 31, 18521858 (2011).Article Google Scholar Williams, P. T. & Brindle, A. J. Catalytic pyrolysis of tyres: influence of catalyst temperature. Fuel 81, 24252434 (2002).Article MATH Google Scholar Rorrer, J. E. et al. Role of Bifunctional Ru/Acid catalysts in the selective hydrocracking of polyethylene and polypropylene waste to liquid hydrocarbons. ACS Catal. 12, 1396913979 (2022).Article Google Scholar Download referencesThis research was supported by Korea Institute of Industrial Technology (KITECH) through the Korea Environmental Industry & Technology Institute (KEITI) funded by the Ministry of Environment (ARQ202209004001). The authors declare no competing financial interest. Communications Engineering thanks Makenna Pennel and the other, anonymous, reviewers for their contribution to the peer review of this work. Peer review reports are available.

Cracking plastic. Polyethylene cracking.