

METHODS FOR PREPARING OLEFINS FROM POLYOLEFINS**FIELD OF INVENTION**

The present invention provides methods for preparing olefin mixtures from polyolefins via
5 thermal catalytic cracking.

BACKGROUND

The listing or discussion of a prior-published document in this specification should not
10 necessarily be taken as an acknowledgement that the document is part of the state of the art
or is common general knowledge.

Plastic waste management has been a long-standing issue globally, especially for land-
constrained Singapore. Plastic waste cannot be broken down by microorganisms easily and
15 hence, the most common practice for disposal is by incineration which emits carbon dioxide,
a greenhouse gas that contributes to global warming. Most of Singapore's plastic waste
(982,000 tons per year with ~6% recycling rate ([https://www.nea.gov.sg/our-services/waste-
management/waste-statistics-and-overall-recycling](https://www.nea.gov.sg/our-services/waste-management/waste-statistics-and-overall-recycling))) are incinerated and the ash disposed at
landfills at a cost of \$77-97 per ton, culminating in an amount of ~\$80 million per year of
20 disposal fees. Furthermore, Singapore's landfill is expected to reach maximum capacity by
~2035.

Thus, there is a need for alternative and/or improved methods suitable for converting plastic
waste into valuable products.

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SUMMARY

Aspects and embodiments of the current invention will now be described by reference to the
following numbered clauses.

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1. A method for preparing an olefin mixture, the method comprising the steps of:
(a) providing a polymeric material comprising a polyolefin; and
(b) contacting the polymeric material with a catalyst at a temperature of from 300°C to 800°C
for a period of time of from 15 min to 1 hour, thereby obtaining the olefin mixture,
35 wherein the catalyst comprises a metal oxide formed on a porous solid support.

2. The method according to clause 1, wherein the metal in the metal oxide is selected from one or more of the group consisting of Zn, Mg, Ca, Ba, Cu and Mn.
3. The method according to clause 2, wherein the metal oxide is magnesium oxide.
- 5 4. The method according to any one of the preceding clauses, wherein the porous solid support is selected from one or more of a group consisting of a Y-type zeolite, an ultrastable Y zeolite (USY zeolite), a X-type zeolite, a ZSM-5 zeolite, a nanocrystalline zeolite, a faujasite and silica.
- 10 5. The method according to clause 4, wherein the porous solid support is a ZSM-5 zeolite, optionally wherein the porous solid support is a dealuminated ZSM-5 zeolite or a desilicated ZSM-5 zeolite.
- 15 6. The method according to clause 5, wherein the ZSM-5 zeolite has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 5 to 300, such as 30 to 280, optionally wherein the ZSM-5 zeolite has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of about 30, about 80 or about 280, optionally wherein the ZSM-5 zeolite has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of about 280.
- 20 7. The method according to any one of the preceding clauses, wherein the metal oxide loading is from 1 wt% to 40 wt% based on the combined mass of the metal oxide and the porous solid support, such as 2.5 wt% to 30 wt%, such as 5 wt% to 20 wt%, optionally wherein the metal oxide loading is about 20 wt% based on the combined mass of the metal oxide and the porous solid support.
- 25 8. The method according to any one of the preceding clauses, wherein the catalyst is provided at from 40 to 60 wt% based on the mass of the polymeric material, such as from 45 to 55 wt%, optionally wherein the catalyst is provided at about 50 wt% based on the mass of the polymeric material.
- 30 9. The method according to any one of the preceding clauses, wherein the temperature is from 400°C to 700°C, such as from 500°C to 600°C, optionally wherein the temperature is about 550°C.
- 35 10. The method according to any one of the preceding clauses, wherein the method is conducted at a pressure of from 0.5 atm to 5 atm, such as about 1 atm.

11. The method according to any one of the preceding clauses, wherein the period of time is from 20 min to 50 min, such as 20 min to 40 min, optionally wherein the period of time is about 20 min.
- 5 12. The method according to any one of the preceding clauses, wherein the olefin mixture comprises a mixture of C₂ to C₄ olefins.
13. The method according to clause 12, wherein the method further comprises (c) bringing the temperature down to about room temperature, thereby isolating the mixture of C₂ to C₄ olefins from other non-gaseous products.
- 10 14. The method according to clause 12 or clause 13, wherein the mixture of C₂ to C₄ olefins is obtained at a yield of at least 50 wt%, optionally wherein the olefin mixture is obtained at a yield of at least 60 wt%, such as at least 70 wt%.
- 15 15. The method according to any one of the preceding clauses, wherein the polyolefin is selected from polyethylene, polypropylene and combinations thereof.
16. The method according to clause 15, wherein the polyethylene is selected from low-density polyethylene (LDPE), high-density polyethylene (HDPE) or combinations thereof, optionally wherein the polyethylene is high-density polyethylene.
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DESCRIPTION

- 25 The present inventors have found a cheap, fast and convenient method for breaking down polyolefins into light olefins (e.g., C₂ to C₄ olefins). The method may be conducted under milder reaction conditions (for example, at about 550°C and about 1 atm) and completed under a shorter reaction time (e.g., 20 min) when compared to the current state of the art methods for the catalytic cracking of plastics. The method disclosed herein utilises a metal oxide and/or a solid porous support as catalyst and the present inventors have found a synergistic effect when the metal oxide and solid porous support are used in combination to catalyse the reaction, resulting in a high polyolefin conversion, and product yield (e.g., at least 70 wt% C₂ to C₄ olefin yield). Without wishing to be bound by theory, the metal oxide and solid porous support work synergistically together to provide a porous structure with an optimal amount of acid sites to catalyse the catalytic cracking reaction.
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Thus, in a first aspect of the invention, there is provided a method for preparing an olefin mixture, the method comprising the steps of:

- (a) providing a polymeric material comprising a polyolefin; and
 - (b) contacting the polymeric material with a catalyst at a temperature of from 300°C to 800°C
- 5 for a period of time of from 15 min to 1 hour, thereby obtaining the olefin mixture,
wherein the catalyst comprises a metal oxide formed on a porous solid support.

In embodiments herein, the word “comprising” may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word “comprising”
10 may also relate to the situation where only the components/features listed are intended to be present (e.g. the word “comprising” may be replaced by the phrases “consists of” or “consists essentially of”). It is explicitly contemplated that both the broader and narrower interpretations can be applied to all aspects and embodiments of the present invention. In other words, the word “comprising” and synonyms thereof may be replaced by the phrase “consisting of” or the
15 phrase “consists essentially of” or synonyms thereof and *vice versa*.

The phrase, “consists essentially of” and its pseudonyms may be interpreted herein to refer to a material where minor impurities may be present. For example, the material may be greater than or equal to 90% pure, such as greater than 95% pure, such as greater than 97% pure,
20 such as greater than 99% pure, such as greater than 99.9% pure, such as greater than 99.99% pure, such as greater than 99.999% pure, such as 100% pure.

As disclosed herein, the term “polyolefin” refers to a type of polymer with the general formula $(CH_2CHR)_n$ where R is H or an alkyl group.
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The term “alkyl” as used herein may refer to an unbranched or branched, cyclic or acyclic saturated hydrocarbyl radical, which may be substituted or unsubstituted (with, for example, one or more halo atoms). Where the term “alkyl” refers to an acyclic group, it is preferably C_{1-10} alkyl and, more preferably, C_{1-6} alkyl (such as ethyl, propyl, (e.g. *n*-propyl or isopropyl),
30 butyl (e.g. branched or unbranched butyl), pentyl or, more preferably, methyl). Where the term “alkyl” is a cyclic group (which may be where the group “cycloalkyl” is specified), it is preferably C_{3-12} cycloalkyl and, more preferably, C_{5-10} (e.g. C_{5-7}) cycloalkyl.

As disclosed herein, the term “olefin” refers to an unsaturated hydrocarbon compound which
35 contains at least one carbon-to-carbon double bond, such as ethene, propene, *n*-butene, isobutene and *n*-pentene. As used herein, the term “light olefins” refers to C_2 to C_4 olefins, such as ethene, propene, *n*-butene, isobutene.

As disclosed herein, the term "catalyst" refers to any suitable catalyst that is capable of preparing an olefin mixture, including a light olefin mixture, from a polyolefin. In certain embodiments, the catalyst may comprise a metal oxide, a porous solid support or a metal oxide formed on a porous solid support. As demonstrated herein, the metal oxide and the porous solid support (whether separately or in combination) display varying degrees of catalytic activity in the catalytic cracking of plastics. In certain exemplary embodiments, the catalyst may comprise a metal oxide formed on a porous solid support, for example, by wet impregnation – a solid porous support is impregnated by a metal precursor solution (e.g., a metal nitrate) of a suitable concentration and then dried and calcined to convert the metal precursor into metal oxide.

In certain embodiments, the metal in the metal oxide is selected from one or more of the group consisting of Zn, Mg, Ca, Ba, Cu and Mn. In certain exemplary embodiments, the metal oxide may be magnesium oxide. For the avoidance of doubt, the catalyst may also comprise multiple different metal oxides formed on the solid porous support.

As disclosed herein, the term "porous solid support" refers to any suitable porous solid material to which a catalyst is affixed. In certain embodiments, the porous solid support may be selected from one or more of a group consisting of a Y-type zeolite, an ultrastable Y zeolite (USY zeolite), a X-type zeolite, a ZSM-5 zeolite, a nanocrystalline zeolite, a faujasite and silica. In certain exemplary embodiments, the porous solid support may be a ZSM-5 zeolite. For the avoidance of doubt, ZSM-5 zeolite may include dealuminated and desilicated ZSM-5 zeolites.

The ZSM-5 zeolite may be provided in a suitable $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio. In certain embodiments, the ZSM-5 zeolite may have a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 5 to 300, such as 30 to 280. In certain exemplary embodiments, the ZSM-5 zeolite has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of about 30, about 80 or about 280. In further embodiments, the ZSM-5 zeolite may have a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of about 280. As demonstrated herein, a ZSM-5 zeolite having a higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio lead to a higher olefin yield (with or without a metal oxide formed on the support). Advantageously, a higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio corresponds to fewer Brønsted acidic sites in the ZSM-5 zeolite which reduces the occurrence of unwanted hydrogen-transfer reactions responsible for the formation of alkanes and aromatics from olefins, thereby increasing the yield of olefins.

When used herein, the term "about", in the context of molar ratios, metal oxide loadings, masses, temperatures, pressures and periods of time, may mean a variation of $\pm 5\%$ of the

stated value, more typically $\pm 4\%$ of the stated value, more typically $\pm 3\%$ of the stated value, more typically, $\pm 2\%$ of the stated value, even more typically $\pm 1\%$ of the stated value, and even more typically $\pm 0.5\%$ of the stated value.

- 5 The metal oxide may be provided in a suitable loading value on the solid porous support. In certain embodiments, the metal oxide loading may be from 1 wt% to 40 wt% based on the combined mass of the metal oxide and the porous solid support, for example, 2.5 wt% to 30 wt% and 5 wt% to 20 wt%. In certain exemplary embodiments, the metal oxide loading may be about 20 wt% based on the combined mass of the metal oxide and the porous solid support.
- 10 As will be appreciated, the metal oxide loading may be controlled to maximise the yield of the olefins from the reaction.

- The catalyst may be provided in any suitable amount in the reaction mixture. In certain embodiments, the catalyst may be provided from 40 to 60 wt% based on the mass of the polymeric material, for example, from 45 to 55 wt%. In certain embodiments, the catalyst may be provided at about 50 wt% based on the mass of the polymeric material. As will be appreciated, the amount of catalyst may be controlled to maximise the yield of the olefins from the reaction.
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- 20 The method disclosed herein may be conducted at any suitable temperature. As noted, this temperature may be from 400°C to 700°C. In certain embodiments, the temperature may be from 500°C to 600°C. In certain exemplary embodiments, the temperature may be about 550°C. The method disclosed herein may be conducted at any suitable pressure. In certain embodiments, the method may be conducted at a pressure of from 0.5 atm to 5 atm. In further
- 25 embodiments, the method may be conducted at a pressure of about 1 atm. Advantageously, the reaction conditions of the method disclosed herein are significantly milder than those used in current state of the art methods for the catalytic cracking of plastics.

- As will be appreciated, the period of time for the method to be conducted may be determined by the skilled person based on their knowledge of the field and whether the reaction has been deemed to be completed or not. As demonstrated herein, the catalytic cracking reaction disclosed herein may end within about 20 min as observed by a mass spectrometer. As such, in certain embodiments, the period of time may be from 20 min to 50 min, for example, 20 min to 40 min. In certain exemplary embodiments, the period of time may be about 20 min.
- 30
- 35 Advantageously, the method disclosed herein may be completed in a shorter amount of the time (e.g., about 20 min) compared to current state of the art methods for the catalytic cracking of plastics.

As demonstrated herein, the disclosed method can break down polyolefins into useful olefins. In certain embodiments, the olefin mixture may comprise a mixture of C₂ to C₄ olefins, for example, ethene, propene, *n*-butene, isobutene and combinations thereof. In certain
5 embodiments, the mixture of C₂ to C₄ olefins may be obtained at a yield of at least 50 wt% based on the mass of the polymeric material. In certain exemplary embodiments, the olefin mixture may be obtained at a yield of at least 60 wt% based on the mass of the polymeric material, for example, at least 70 wt% based on the mass of the polymeric material. Advantageously, the method disclosed herein achieves a higher C₂ to C₄ olefin yield compared
10 to other current state of the art methods for the catalytic cracking of plastics.

As will be appreciated, the mixture of C₂ to C₄ olefins are in gaseous form at room temperature and pressure. As such, the method disclosed herein may further comprise a step (c) bringing the temperature down to about room temperature, thereby isolating the gaseous mixture of C₂
15 to C₄ olefins from other non-gaseous-products.

In certain embodiments, the polyolefin may be selected from polyethylene, polypropylene and combinations thereof. In further embodiments, the polyethylene may be selected from low-density polyethylene (LDPE), high-density polyethylene (HDPE) and combinations thereof. In
20 certain exemplary embodiments, the polyethylene may be high-density polyethylene (HDPE).

The following Examples illustrate the invention.

EXAMPLES

25 *Example 1: Preparation of Catalyst*

The commercial ZSM-5 zeolites used in the catalyst preparation were supplied from Zeolyst International with varying SiO₂/Al₂O₃ ratio of 30, 80 and 280 (abbreviated as "ZSM5-1", "ZSM5-2" and "ZSM5-3" respectively). The metal nitrate precursors were purchased from Sigma
30 Aldrich and Alfa Aesar (Ba(NO₃)₂, Ca(NO₃)₂, Cu(NO₃)₂ and Mn(NO₃)₂ from Sigma Aldrich and Mg(NO₃)₂ from Alfa Aesar). The ZSM-5 zeolites were initially in NH₄-form and hence, subjected to calcination in air at 550°C for 5h (10°C/min) to convert them to H-form prior to catalyst synthesis. The catalysts were prepared via wet impregnation – the ZSM-5 zeolite supports were impregnated with the respective metal nitrate precursor solution (based on 20
35 wt% metal oxide loading) and then air-calcined at 650°C for 5h (ramping speed: 10°C/min) to convert the loaded metal nitrate precursors into metal oxides.

To prepare dealuminated ZSM-5-3 (DeAl ZSM-5-3), calcined H-ZSM-5-3 was treated with 1M hydrochloric acid at 90°C for 24h under reflux. The DeAl ZSM5-3 was filtered, washed with deionised water and dry at 120°C for 12h in oven. The solid product was calcined in air at 550°C before the catalytic cracking reaction. To prepare desilicated ZSM-5-3 (DeSi ZSM-5-3), calcined H-ZSM-5-3 was treated with 0.1M sodium hydroxide at 65°C for 2h under reflux. The DeSi ZSM5-3 was filtered, washed with deionised water and dry at 120°C for 12h in oven. The Na-form DeSi ZSM-5-3 was converted to H-form by ion exchange in 0.1M NH_4NO_3 . The solid product was calcined in air at 550°C before the catalytic cracking reaction.

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Results and Discussion

X-ray diffraction (XRD) was measured using Cu K α on the catalysts. From the XRD results, the characteristics of the MFI zeolite structure were observed in all catalysts. The ZSM-5 major peaks were observed at 2θ ($^\circ$) angle of 7.9, 8.8, 23.1 and 23.9. For comparison, MgO/ZSM-5-2 and MgO/ZSM-5-3 presented additional major peaks at 2θ ($^\circ$) angle of 42.9 and 62.3 which correspond to MgO periclase in the XRD PDF database (PDF no. 87-0651). CuO/ZSM-5-2 showed additional peaks at 2θ ($^\circ$) angle of 35.4, 38.6, 48.8 and 61.8 which corresponds to CuO tenorite in XRD PDF database (PDF no. 00-045-0937). For other metal oxides Ba, Ca and Mn, no additional peaks were observed.

Micromeritics BET ASAP 2420 was used to measure the surface area, pore diameter and pore volume of the catalysts. The commercial zeolite, ZSM5-3, has a BET surface area of 355 m^2/g , average pore diameter of 43 Å and pore volume of 0.223 cm^3/g . For comparison, MgO/ZSM-5-3, has a BET surface area of 232 m^2/g , average pore diameter 45 Å and pore volume of 0.173 cm^3/g . The decrease in surface area indicates that the MgO has partially covered the porous support structure. Similar trend was observed for BaO/ZSM-5-2 with BET surface area of 327 m^2/g , average pore diameter 41 Å and pore volume of 0.228 cm^3/g and MnO/ZSM-5-3 with BET surface area of 297 m^2/g , average pore diameter 38 Å and pore volume of 0.179 cm^3/g - the surface area decreases when metal oxide is loaded onto the ZSM-5 support.

Isopropylamine Temperature-Programmed Desorption Mass Spectrometry (IPA-TPD-MS) was used to measure the Lewis and Brønsted acidity of the catalysts. Results show that commercial zeolites with low $\text{SiO}_2/\text{Al}_2\text{O}_3$ have more acid sites compared to those with high $\text{SiO}_2/\text{Al}_2\text{O}_3$ (lower content of Al_2O_3). ZSM5-2 exhibited 3020 $\mu\text{mol}/\text{g}_{\text{cat}}$ Lewis acid sites and 513 $\mu\text{mol}/\text{g}_{\text{cat}}$ Brønsted acid sites while ZSM5-3 exhibited 716 $\mu\text{mol}/\text{g}_{\text{cat}}$ Lewis acid sites and 134 $\mu\text{mol}/\text{g}_{\text{cat}}$ Brønsted acid sites. For comparison, for MgO/ZSM5-3 (20 wt% loading), there is a

shift in having more Lewis acid sites but fewer Brønsted acid sites compared to the commercial zeolite – MgO/ZSM5-3 (20 wt% loading) exhibited 1110 $\mu\text{mol/g}_{\text{cat}}$ Lewis active sites and 81 $\mu\text{mol/g}_{\text{cat}}$ Brønsted active sites. As will be appreciated, acid sites are needed to activate the polymer for catalytic cracking into shorter chains and olefins. However, too many Brønsted acid sites can result in unwanted secondary reactions (hydrogen-transfer reactions) that converts olefins into alkanes and aromatics, thereby decreasing the olefin yield.

Example 2: Conversion of HDPE into olefins

1g of HDPE (recycled HDPE pellets purchased from Mao Feng Recycle Trading Pte Ltd) was used as feedstock. The catalyst, 0.5g was added into the feedstock. The mixture was then packed into a quartz tube and loaded into a vertical two-stage furnace. A constant gas flow of 50mL/min (He: N₂, 4:1) was introduced into the setup. During the reaction, the reactor tube was subjected to radiant heating at a ramp speed of 30°C/min from ambient temperature to 550°C and holding at the temperature for 1 h. It is noted that the reaction ended within 20 minutes as observed from the mass spectrometer (MS).

After the reaction, the heavy gaseous components were condensed as oil products at 5°C and analysed using GC-MS. The light gaseous products were analysed and quantified using an on-line gas chromatograph (Agilent 6890N Network Gas Chromatograph). The gas chromatograph (GC) was calibrated using a standard calibration gas purchased from Air Liquide for hydrocarbons: methane, ethane, ethylene, propane, propylene, n-butane, 1,3-butadiene, 1-butene, isobutylene (C₁ – C₄) and permanent gases: H₂, CO, CO₂, N₂. For GC parameters, it was set as constant flow, split ratio of 25:1, oven temperature profile: hold 10 minutes at 40°C, ramp rate 10°C min⁻¹ to 250°C hold for 4 minutes then cooled. The hydrocarbon gases were separated in a capillary column (Agilent CP7945 CP-Sil PONA 150m x 0.25mm OD, 1 μ m ID) and analysed by flame ionization detector (FID). Permanent gases were separated in a packed column (Carbosieve SII. 80/100 mesh 4m x 1/8-inch OD, 2.1mm ID) and analysed by thermal conductivity detector (TCD).

Results and Discussion

The HDPE conversion and the product yield (including light olefin (C₂ to C₄) yield) are summarised in Table 1. The HDPE conversion was obtained from the mass of HDPE subtracting solid residue collected at the end of reaction. The solid residue are inorganic contaminants present in the recycled feedstock that cannot be removed even at elevated temperatures. The light olefin yield was calculated based on the peak area of the respective

C₂-C₄ olefin as measured by GC-FID-TCD. Other product yields such as oil, wax and solid residue were calculated based on their weight as measured by an analytical balance.

- As observed from Table 1, the method disclosed herein show a synergistic effect when the metal oxide and solid porous support are used in combination to catalyse the reaction. For example, the light olefin yields of ZSM-5-2 and MgO/ZSM-5-2 are 49 wt% and 58 wt% respectively and that of ZSM-5-3 and MgO/ZSM-5-3 are 56 wt% and 61 wt% respectively. Notably, the light olefin yield of MgO is only 2 wt%.
- For comparison, the process was performed as a one-stage (OS) and a two-stage (TS) reaction using the same catalyst (i.e., MgO/ZSM-5-3). The reaction conditions were kept the same for both processes (including the reaction temperature of 550°C). For the one-stage process, the catalyst was added directly into the feedstock (HDPE) as described above. For the two-stage process, the feedstock and catalyst were separated in the furnace - the feedstock undergoes pyrolysis without the catalyst at the first stage, after which the products in the gas phase comes into contact with the catalyst and undergoes further catalytic cracking at the second stage. The light olefin yield increased from 61 wt% to 71 wt% when the process was performed as a one-stage reaction as compared to a two-stage reaction. Without wishing to be bound by theory, the pyrolysis without catalyst at the first stage causes random thermal cracking of the HDPE which results in lower selectivity and yield of light olefins at the second stage. In comparison, the thermal cracking of HDPE in the one-stage reaction occurs at the surface of the solid catalyst, which selectively promotes the production of light olefins.

Table 1: Summary of experimental results of Example 2

Entry	Catalyst	Metal Oxide Loading (wt%)	Conversion (%)	Yield %				
				Gas	Oil	Wax	Solid residue	C ₂ -C ₄ (olefinic)
1	No catalyst	NA	97	61	15	21	3	33
2	ZSM-5-1 (SiO ₂ /Al ₂ O ₃ = 30)	NA	97	86	7	2	3	39
3	ZSM-5-2 (SiO ₂ /Al ₂ O ₃ = 80)	NA	97	85	4	8	3	49
4	ZSM-5-3 (SiO ₂ /Al ₂ O ₃ = 280)	NA	95	89	5	0	5	56

Entry	Catalyst	Metal Oxide Loading (wt%)	Conversion (%)	Yield %				
				Gas	Oil	Wax	Solid residue	C ₂ -C ₄ (olefinic)
5	Y-zeolite-1 (SiO ₂ /Al ₂ O ₃ = 5.1)	NA	97	78	12	7	3	42
6	Y-zeolite-2 (SiO ₂ /Al ₂ O ₃ = 30)	NA	95	90	4	1	5	36
7	BaO/ZSM-5-2	20	94	87	7	0	6	58
8	MgO/ZSM-5-2	20	97	84	3	10	3	58
9	CaO/ZSM-5-2	20	95	79	6	10	5	48
10	CuO/ZSM-5-2	20	97	84	6	7	3	51
11	MgO/ZSM-5-3- TS (TS: Two Stage)	20	95	89	6	0	5	61
12	MgO/ZSM5-3-OS (OS: One Stage)	20	97	96	0	0	1	71
13	MnO/ZSM-5-3	20	93	87	7	0	7	51
14	MgO/ZSM-5-3	4	97	87	10	0	3	57
15	FS S-1 (silica support formed from fumed silica (FS))	NA	96	47	50	0	4	25
16	TEOS S-1 (silica support formed from tetraethyl orthosilicate (TEOS))	NA	97	63	33	0	3	12
17	MgO/FS S-1	20	92	50	42	0	8	26
18	DeAl ZSM-5-3 Dealuminated ZSM-5-3	NA	93	88	4	0	7	56

Entry	Catalyst	Metal Oxide Loading (wt%)	Conversion (%)	Yield %				
				Gas	Oil	Wax	Solid residue	C ₂ -C ₄ (olefinic)
19	DeSi ZSM-5-3 Desilicated ZSM-5-3	NA	94	80	14	0	6	53
20	MgO	NA	95	69	26	0	5	2

CLAIMS

1. A method for preparing an olefin mixture, the method comprising the steps of:
(a) providing a polymeric material comprising a polyolefin; and
(b) contacting the polymeric material with a catalyst at a temperature of from 300°C to 800°C for a period of time of from 15 min to 1 hour, thereby obtaining the olefin mixture,
wherein the catalyst comprises a metal oxide formed on a porous solid support.
2. The method according to Claim 1, wherein the metal in the metal oxide is selected from one or more of the group consisting of Zn, Mg, Ca, Ba, Cu and Mn.
3. The method according to Claim 2, wherein the metal oxide is magnesium oxide.
4. The method according to any one of the preceding claims, wherein the porous solid support is selected from one or more of a group consisting of a Y-type zeolite, an ultrastable Y zeolite (USY zeolite), a X-type zeolite, a ZSM-5 zeolite, a nanocrystalline zeolite, a faujasite and silica.
5. The method according to Claim 4, wherein the porous solid support is a ZSM-5 zeolite, optionally wherein the porous solid support is a dealuminated ZSM-5 zeolite or a desilicated ZSM-5 zeolite.
6. The method according to Claim 5, wherein the ZSM-5 zeolite has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 5 to 300, such as 30 to 280, optionally wherein the ZSM-5 zeolite has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of about 30, about 80 or about 280, optionally wherein the ZSM-5 zeolite has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of about 280.
7. The method according to any one of the preceding claims, wherein the metal oxide loading is from 1 wt% to 40 wt% based on the combined mass of the metal oxide and the porous solid support, such as 2.5 wt% to 30 wt%, such as 5 wt% to 20 wt%, optionally wherein the metal oxide loading is about 20 wt% based on the combined mass of the metal oxide and the porous solid support.
8. The method according to any one of the preceding claims, wherein the catalyst is provided at from 40 to 60 wt% based on the mass of the polymeric material, such as from 45 to 55 wt%, optionally wherein the catalyst is provided at about 50 wt% based on the mass of the polymeric material.

9. The method according to any one of the preceding claims, wherein the temperature is from 400°C to 700°C, such as from 500°C to 600°C, optionally wherein the temperature is about 550°C.
10. The method according to any one of the preceding claims, wherein the method is conducted at a pressure of from 0.5 atm to 5 atm, such as about 1 atm.
11. The method according to any one of the preceding claims, wherein the period of time is from 20 min to 50 min, such as 20 min to 40 min, optionally wherein the period of time is about 20 min.
12. The method according to any one of the preceding claims, wherein the olefin mixture comprises a mixture of C₂ to C₄ olefins.
13. The method according to Claim 12, wherein the method further comprises (c) bringing the temperature down to about room temperature, thereby isolating the mixture of C₂ to C₄ olefins from other non-gaseous products.
14. The method according to Claim 12 or Claim 13, wherein the mixture of C₂ to C₄ olefins is obtained at a yield of at least 50 wt% based on the mass of the polymeric material, optionally wherein the olefin mixture is obtained at a yield of at least 60 wt%, such as at least 70 wt%.
15. The method according to any one of the preceding claims, wherein the polyolefin is selected from polyethylene, polypropylene and combinations thereof.
16. The method according to Claim 15, wherein the polyethylene is selected from low-density polyethylene (LDPE), high-density polyethylene (HDPE) or combinations thereof, optionally wherein the polyethylene is high-density polyethylene.