Description

The present invention relates to a process for the conversion of a feedstock comprising linear olefins into a product enriched in branched olefins.

It is foreseen that environmental legislation will bring about changes in gasoline manufacturing. It is expected that the concentration of lead anti-knock additives is to be reduced, which makes the required octane quality more difficult to attain. Components which are suitable for improving the octane quality of gasoline are certain branched ethers, e.g. methyl tertiary butyl ether (MTBE). It is known that such ethers can be formed by contacting branched olefins with methanol in the presence of a suitable acidic catalyst, such as sulphonic resins, phosphoric acid modified kieselguhr, silica/alumina and acid zeolites.

The object of the present invention is to obtain a product comprising branched olefins useful in the production of branched ethers, from a feedstock comprising linear olefins. Conversion of linear olefins generally involves a combination of operations including polymerization, dimerization and cracking. This means that in general not only the desired branched olefins are produced, but also a certain amount of, less desirable, heavier hydrocarbons.

In European patent specification 026 041 a process is described in which a mixed olefin feed is converted into an olefinic product enriched with C_4 and C_5 olefins comprising olefin isomers, which process comprises contacting the feed with an acid crystalline zeolite catalyst characterized by a pore opening of at least 5×10^{-10} m, a silica to alumina ratio of at least 12 and a constraint index within the range of 1 to 12 at an olefin pressure below 0.5 bar and a temperature between 204 °C and 316 °C. It is shown that in case the olefin pressure is above 0.5 bar, a large amount of relatively heavy hydrocarbons is produced.

It has now surprisingly been found that a feedstock comprising linear olefins can be converted into a product enriched in branched olefins at an olefin partial pressure of more than 0.5 bar without formation of large amounts of undesirable side-products, by contacting the feedstock with a tectometallosilicate having a certain specific crystal structure, i.e. a ferrierite crystal structure. Such process, which can be carried out at e.g. atmospheric olefin partial pressure, is economically attractive as no sub-atmospheric pressure needs to be attained, or, in case a diluent is used, no separation of the diluent is needed.

Further, it has been found that the tectometallosilicate according to the present invention is relatively stable in the present process, i.e. its catalytic activity does not substantially change during a relatively long time.

The present invention relates to a process for the conversion of a feedstock comprising linear olefins into a product enriched in branched olefins, which process comprises contacting the feedstock with a tectometallosilicate having a ferrierite crystal structure, at a temperature between 150 and 450 °C, an olefin partial pressure of more than 0.5 bar and a total pressure of between 0.5 and 25 bar.

The tectometallosilicate having a ferrierite structure to be employed in the process of the present invention, has in its substantially template free, hydrogen form an X-ray diffraction pattern which contains at least the d-spacings (in Angstrom) as set forth below in table 1.

The d-spacing in Angstrom is the value of the interplanar spacing of the crystal and is calculated from the measured theta (Bragg angle) by using the Bragg equation. The relative intensity of the diffraction peak corresponding to each d-spacing is given as a value: w (weak), m (medium), s (strong) or vs (very strong), determined relative to the intensity of the main diffraction peak.

Table 1

X-ray diffraction pattern of ferrierite	
d	Relative intensity
11.3 ± 0.3	w-m
9.5 ± 0.1	s-vs
7.08 ± 0.04	m
6.96 ± 0.04	m
3.98 ± 0.02	m-s
3.76 ± 0.02	m
3.54 ± 0.02	m-s
3.47 ± 0.02	m-s
3.13 ± 0.02	w-m
3.05 ± 0.02	w-m

Examples of tectometallosilicates having a ferrierite structure are ferrierite, FU-9, ISI-6, Nu-23, ZSM-21, ZSM-35 and ZSM-38. The tectometallosilicates which can be employed, contain silicon and one or more from the group consisting of iron, gallium and aluminium. In general, the tectometallosilicate will mainly contain silicon and aluminium. Preferably, the tectometallosilicate is in the hydrogen form. Tectometallosilicates which have shown an especially high stability, are tectometallosilicates having a relatively high silicon to aluminium atomic ratio, e.g. a silicon to aluminium atomic ratio of more than 10, preferably more than 15. A process for preparing tectometallosilicate which can be suitably applied in the process of the present invention is described in European patent specification No. 012 473. The tectometallosilicate can be used as such. However, often it is economically more attractive to use it in combination with a binder. Binders which can suitably be applied are amorphous refractory oxides such as alumina, silica or silica/alumina.

The tectometallosilicate may be surface moderated, by deactivation or removal of some or all acid sites at the external surface by techniques known in the art. Suitable techniques include those disclosed in S. Bhatia, "Zeolite Catalysis: Principles and Applications", CRC Press, Boca Raton (Florida), 1990. For example the catalyst may be treated with ethylenediamine tetraacetic acid (EDTA) as disclosed in D.W. Breck, "Zeolite Molecular Sieves - Structure, Chemistry and Use" John Wiley & Sons, New York 1974. The catalyst may optionally be used in the form of crystals having a low ratio of crystal surface area to pore surface area.

The feedstock which is to be used in the present invention comprises linear olefins, suitably linear olefins containing between 4 and 10 carbon atoms. Higher olefins, e.g. olefins comprising up to 20 carbon atoms, and/or lower olefins, e.g. ethene and/or propene, can be present in the feedstock. Higher olefins could for example be present if part of the product obtained is recycled to the conversion step. Suitable feedstocks for the process of the present invention are hydrocarbon streams as obtained in catalytic cracking or steam cracking. Suitably, the feedstock can comprise linear olefins containing between 4 and 8 carbon atoms. Preferred feedstocks comprise linear olefins containing 4 or 5 carbon atoms. The feedstock can further contain a certain amount of paraffins. Paraffins commonly present include butane and pentane.

Feedstocks containing excess paraffins may conveniently be passed over an olefins/paraffins separating unit prior to conversion.

Suprisingly it has also been found that in the process of the present invention it is possible to recycle to the conversion step substantially all the unconverted linear olefin fraction of the product due to the low level of paraffin produced in the conversion step. Processes using for example ZSM-5 as catalyst should include a bleed stream in a recycle to the conversion step for control of paraffin level and the fraction of the recycle which should be bled is sufficient that it is impractical to isolate olefins therefrom for recycle to the conversion unit.

In the process of the present invention a bleed stream in the recycle to conversion step may be passed for example to a paraffin/olefin extractive distillation unit and the olefin fraction returned to the conversion unit. Alternatively the bleed streams may be discarded, nevertheless incurring low wastage of linear olefins since the fraction of the recycle which must be bled is less than with known processes.

The product obtained in the process of the present invention is enriched in branched olefins. From a commercial point of view, it is advantageous to produce as much branched olefins as possible. Suitably, the product obtained comprises at least 20 % by weight of branched olefins, based on the amount of olefins

present in the feedstock; preferably, the product comprises at least 30 % by weight of branched olefins. Further, it is preferred in a process according to the present invention, to produce only a small amount of heavier hydrocarbons such as aromatics. Preferably, a product is obtained comprising less than 10 % by weight of aromatics based on the total amount of liquid product, i.e. product which is in the liquid state under normal conditions; most preferably, the product comprises less than 5 % by weight of aromatics.

The product obtained can be suitably used for the production of highly branched ethers. Before the product is used in such ether producing process, it is preferred to separate off a heavy fraction from the product obtained, and to recycle at least part of this heavy fraction to the conversion step. The heavy fraction suitably comprises hydrocarbons containing at least 5 carbon atoms. The product remaining after the heavy fraction is separated off, is contacted with a lower alcohol in the presence of a suitable acidic catalyst. In this process step mainly branched olefins react. The branched ethers produced are removed, and the remaining hydrocarbon mixture rich in linear olefins can be recycled to the conversion step.

Process conditions which can be suitably applied, comprise a temperature between 150 and 450 °C, an olefin partial pressure of more than 0.5 bar and a total pressure of between 0.5 and 25 bar. Preferred process conditions comprise a temperature between 250 and 400 °C, most preferably between 320 and 400 °C and an olefin partial pressure of at least 0.7 bar.

The invention will now be further elucidated with the aid of the following examples.

Example 1

Commercially available ferrierite ex Toyo Soda, which ferrierite was in the ammonium form and had a silicon to aluminium atomic ratio of 9, was pressed, crushed and sieved to obtain a 30-80 mesh size fraction. The particles thus obtained were calcined for 2 hours at 540 °C.

Example 2

544 g silica gel was combined with a solution of 54 g sodium hydroxide in 1000 g water and the resulting mixture was homogenized. A second solution comprising 61.4 g aluminium sulphate ($Al_2(SO_4)_3.18 H_2O$), 256 g sodium sulphate and 1000 g water was added under stirring. Finally, 218 g pyridine dissolved in 1152 g water were admixed giving a reaction gel of the composition (on a molar basis) 93.5 SiO_2 . 1 Al_2O_3 . 7.4 Na_2O . 19.6 Na_2SO_4 . ~ 30 pyridine . 1938 H_2O. This reaction gel was kept at 150 °C for a period of 75 hours until a crystalline compound was obtained. After synthesis the crystalline compound produced was separated from the reaction mixture by filtration, water washed and dried at 120 °C.

The dried compound was calcined at 500 °C, cooled down and ion exchanged such that the compound is brought in the ammonium form. The solid product was separated from the liquid by filtration, water washed, dried at 120 °C and subsequently calcined at 500 °C.

The product of the synthesis was determined by X-ray diffraction to be essentially ferrierite. The silicon to aluminium atomic ratio was found to be 36.

Before employment in the process of the present invention the ferrierite powder was pressed, crushed and sieved in order to obtain a 30-80 mesh fraction.

Example 3

For reasons of comparison a commercially available ZSM-5, CBV 3020 ex Conteka, was pressed, crushed and sieved in order to obtain particles having a 30-80 mesh size fraction. The particles thus obtained were calcined for 2 hours at 540 °C.

Example 4

A feedstock as described in Table 2, is contacted with ferrierite and ZSM-5, prepared as described in Examples 1 and 3, respectively. The process is carried out at a temperature of 350 °C, an olefin partial pressure of 1.4 bar, a weight hourly space velocity of 2 kg/kg/hour and a total pressure of 1.4 bar. The products obtained after 48 hours on-stream are described in Table 3, in % by weight of product obtained.

Table 2

Feedstock properties	
n-butene (% by weight)	99.42
iso-butene (% by weight)	0.44
butane (% by weight)	0.14

Table 3

Product obtained		
	Catalyst	
	Ferrierite	ZSM-5
hydrogen	-	0.04
C_1-C_2 paraffins	0.03	0.17
ethene	0.06	0.23
propane	0.26	9.99
propene	2.18	0.62
butane	3.54	20.87
n-butene	33.94	0.26
iso-butene	31.72	0.00
C_5^+	28.27	67.82
% by weight of aromatics in liquid product	1.4	75

Example 5

Ferrierite prepared as described in Example 2, is contacted at a temperature of 350 °C, an olefin partial pressure of 1.4 bar, a weight hourly space velocity of 2 kg/kg/hour and a total pressure of 1.4 bar with the feedstock as described in Table 2. The product obtained after 48 and 336 hours on-stream is described in Table 4.

Table 4

Product obtained		
	on-stream time	
	48 hours	336 hours
C_1-C_2 paraffins	0.00	0.00
ethene	0.04	0.01
propane	0.07	0.02
propene	1.71	0.84
butane	1.28	0.76
n-butene	40.06	49.09
iso-butene	36.95	41.18
C_5^+	19.89	8.01
% by weight of aromatics in liquid product	2.4	9.1

Example 6

A feedstock as described in Table 5, is contacted with ferrierite, prepared as described in Example 1. The process is carried out at a temperature of 350 °C, an olefin partial pressure of 1.1 bar, a weight hourly

space velocity of 2 kg/kg/hour and a total pressure of 1.1 bar. The product obtained after 61.5 hours on-stream is described in Table 6, in % by weight of product obtained.

Table 5

Feedstock properties	
n-pentene (% by weight)	97.75
iso-pentene (% by weight)	1.08
pentane (% by weight)	1.17

Table 6

Product obtained	
	Catalyst
	Ferrierite
hydrogen	-
C_1-C_2 paraffins	-
ethene	-
propane	0.09
propene	0.01
butane	0.01
n-butene	0.13
iso-butene	0.15
n-pentane	0.48
iso-pentane	0.75
n-pentene	21.00
iso-pentene	67.39
C_6^+	<10.0

Claims

1. Process for the conversion of a feedstock comprising linear olefins into a product enriched in branched olefins, which process comprises contacting the feedstock with a tectometallosilicate having a ferrierite crystal structure, at a temperature between 150 and 450 °C, an olefin partial pressure of more than 0.5 bar and a total pressure of between 0.5 and 25 bar.

2. Process according to claim 1, wherein the feedstock comprises linear olefins containing between 4 and 10 carbon atoms.

3. Process according to claim 1 and/or 2, wherein the process is carried out at a temperature between 250 and 400 °C and an olefin partial pressure of at least 0.7 bar.

4. Process according to any one of the preceding claims, wherein the tectometallosilicate has a silicon to aluminium atomic ratio of more than 15.

5. Process according to any one of the preceding claims, wherein the tectometallosilicate is in the hydrogen form.

6. Process according to any one of the preceding claims, wherein the tectometallosilicate is surface-moderated.

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space velocity of 2 kg/kg/hour and a total pressure of 1.1 bar. The product obtained after 61.5 hours on-stream is described in Table 6, in % by weight of product obtained.

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iso-pentane	0.75
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iso-pentene	67.39
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6. Process according to any one of the preceding claims, wherein the tectometallosilicate is surface-moderated.

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7. Process according to any one of the preceding claims, wherein a heavy fraction is separated off from the product obtained, at least part of which heavy fraction is optionally recycled to the conversion step.

8. Process according to claim 7, wherein the heavy fraction comprises hydrocarbons containing at least 5 carbon atoms.

9. Process according to any one of the preceding claims, wherein a part of the product obtained is separated off and recycled to the conversion step.

10. Process according to claim 9 wherein a bleed stream is included in the recycle, optionally wherein unconverted olefins in the bleed stream are separated off and returned to the conversion step.

Patentansprüche

1. Verfahren zur Umwandlung eines Einsatzmaterials, das lineare Olefine enthält, in ein an verzweigten Olefinen angereichertes Produkt, bei welchem Verfahren das Einsatzmaterial mit einem Tectometallsilikat mit einer Ferrierit-Kristallstruktur bei einer Temperatur zwischen 150 und 450 °C, einem Olefinpartialdruck von über 0,5 bar und einem Gesamtdruck zwischen 0,5 und 25 bar in Berührung gebracht wird.

2. Verfahren nach Anspruch 1, wobei das Einsatzmaterial lineare Olefine mit zwischen 4 und 10 Kohlenstoffatomen enthält.

3. Verfahren nach Anspruch 1 und/oder 2, wobei das Verfahren bei einer Temperatur zwischen 250 und 400 °C und einem Olefinpartialdruck von mindestens 0,7 bar durchgeführt wird.

4. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Tectometallsilikat ein Atomverhältnis von Silicium zu Aluminium von über 15 aufweist.

5. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Tectometallsilikat in der Wasserstoffform vorliegt.

6. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Tectometallsilikat oberflächenmoderiert ist.

7. Verfahren nach einem der vorhergehenden Ansprüche, wobei eine schwere Fraktion von dem erhaltenen Produkt abgetrennt wird, von der wenigstens ein Teil gegebenenfalls wieder in den Umwandlungsschritt eingespeist wird.

8. Verfahren nach Anspruch 7, wobei die schwere Fraktion Kohlenwasserstoffe mit wenigstens 5 Kohlenstoffatomen enthält.

9. Verfahren nach einem der vorhergehenden Ansprüche, wobei ein Teil des erhaltenen Produkts abgetrennt und wieder in den Umwandlungsschritt eingespeist wird.

10. Verfahren nach Anspruch 9, wobei die Wiedereinspeisung einen Teilstrom miteinbezieht, wobei gegebenenfalls nicht umgewandelte Olefine im Teilstrom abgetrennt und wieder in den Umwandlungsschritt eingespeist werden.

Revendications

1. Procédé pour la conversion d'une charge de départ comprenant des oléfines linéaires en un produit enrichi en oléfines ramifiées, qui comprend la mise en contact de la charge de départ avec un tectométallosilicate ayant une structure cristalline de ferriérite, à une température comprise entre 150 et 450 °C, une pression partielle d'oléfines de plus de 0,5 bar et une pression totale comprise entre 0,5 et 25 bars.

2. Procédé selon la revendication 1, dans lequel la charge de départ comprend des oléfines linéaires contenant entre 4 et 10 atomes de carbone.

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3. Procédé selon les revendications 1 et/ou 2, qui est mis en oeuvre à une température comprise entre 250 et 400 °C et à une pression partielle d'oléfines d'au moins 0,7 bar.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel le tectométallosilicate a un rapport atomique du silicium à l'aluminium de plus de 15.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le tectométallosilicate est dans la forme hydrogène.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le tectométallosilicate est modéré en surface.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel une fraction lourde est séparée du produit obtenu et au moins une partie de cette fraction lourde est éventuellement recyclée à l'étape de conversion.

8. Procédé selon la revendication 7, dans lequel la fraction lourde comprend des hydrocarbures contenant au moins 5 atomes de carbone.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel une partie du produit obtenu est séparée et recyclée à l'étape de conversion.

10. Procédé selon la revendication 9, dans lequel un courant soutiré est inclus dans le courant recyclé, et éventuellement les oléfines non transformées présentes dans le courant soutiré sont séparées et ramenées à l'étape de conversion.