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(54) **Process for the conversion of a hydrocarbonaceous feedstock.**

(57) A process for the conversion of a hydrocarbonaceous feedstock comprises contacting the feedstock with a solid cracking catalyst at a temperature of at least 400 °C for less than 10 seconds and subsequently contacting at least part of a lower olefin rich fraction of the effluent therefrom to oligomerization in the presence of a suitable catalyst and recycling at least a portion of the oligomerized product.

**EP 0 392 590 A1**

## PROCESS FOR THE CONVERSION OF A HYDROCARBONACEOUS FEEDSTOCK

The present invention relates to a process for the conversion of a hydrocarbonaceous feedstock, and is particularly concerned with the production of olefins from hydrocarbonaceous feedstocks.

There is considerable interest in the production of olefins, especially lower olefins such as ethylene and propylene, from hydrocarbonaceous materials, in view of the importance of such olefins as starting materials for the preparation of further more complex chemical products.

It is known to convert hydrocarbonaceous feedstocks, such as light distillates, to products rich in lower olefins, especially ethylene and propylene, by high temperature steam cracking. The typical product slate obtained in such steam cracking processes is not entirely suited to the needs of the chemical industry in that it represents a comparatively low overall conversion to lower olefins, with a relatively high methane production level and a high ratio of ethylene to propylene.

There have recently been developed alternative processes for the production of lower olefins, for example as described in copending UK Patent Applications Nos. 8828206, 8904408.5 and 8904409.3, from a wide range of hydrocarbonaceous feedstocks. Those processes have been found to give surprisingly high yields of lower olefins, low amounts of methane and a low ratio of ethylene to propylene and C<sub>4</sub> olefins when compared with conventional steam cracking.

Ethylene and propylene are valuable starting materials for many chemical processes, while C<sub>4</sub> olefins can find use as a starting material for alkylation and/or oligomerization procedures in order to produce high octane gasoline and/or middle distillates. Isobutene can be usefully converted to methyl t-butyl ether. However, in order to meet fluctuating demand for production of C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> olefins, there is a need to provide a process with a flexible product slate of lower olefins.

Accordingly, the present invention provides a process for the conversion of a hydrocarbonaceous feedstock comprising the following steps:

- (i) contacting the feedstock with a solid cracking catalyst at a temperature of at least 400 °C during less than 10 seconds,
- (ii) separating a fraction comprising one or more lower olefins from the effluent from step (i),
- (iii) contacting at least a portion of said lower olefin-comprising fraction with an oligomerization catalyst under oligomerization conditions, and
- (iv) recycling at least a portion of the effluent from step (iii) to step (i).

The term "lower olefins" is intended primarily to include ethylene, propylene, butene and i-butene, but may extend to other olefins having up to 6 carbon atoms.

The feedstock is contacted with the solid cracking catalyst in step (i) for less than 10 seconds. Suitably, the minimum contact time is 0.1 second. Very good results are obtainable with a process in which the feedstock is contacted with the solid cracking catalyst during 0.2 to 6 seconds.

The temperature during the reaction is relatively high. However, the combination of high temperature and short contact time allows a high conversion of olefins in step (i). A preferred temperature range is 480 to 900 °C, more preferably 500 to 750 °C.

The solid cracking catalyst preferably comprises at least one zeolite with a pore diameter of from 0.3 to 0.7 nm, preferably 0.5 to 0.7 nm. The catalyst suitably further comprises a refractory oxide that serves as binder material. Suitable refractory oxides include alumina, silica, silica-alumina, magnesia, titania, zirconia and mixtures thereof. Alumina is especially preferred. The weight ratio of refractory oxide and zeolite suitably ranges from 10:90 to 90:10, preferably from 50:50 to 85:15. The catalyst may also comprise further zeolites with a pore diameter above 0.7 nm. Suitable examples of such zeolites include the faujasite-type zeolites, zeolite beta, zeolite omega and in particular zeolite X and Y. The zeolitic catalyst preferably comprises as zeolite substantially only zeolites with a pore diameter of from 0.3 to 0.7 nm.

The term zeolite in this specification is not to be regarded as comprising only crystalline aluminium silicates. The term also includes crystalline silica (silicalite), silicoaluminophosphates (SAPO), chromosilicates, gallium silicates, iron silicates, aluminium phosphates (ALPO), titanium aluminosilicates (TASO), boron silicates, titanium aluminophosphates (TAPO) and iron aluminosilicates.

Examples of zeolites that may be used in the process of the invention and that have a pore diameter of 0.3 to 0.7 nm, include SAPO-4 and SAPO-11, which are described in US-A-4,440,871, ALPO-11, described in US-A-4,310,440, TAPO-11, described in US-A-4,500,651, TASO-45, described in EP-A-229,295, boron silicates, described in e.g. US-A-4,254,297, aluminium silicates like erionite, ferrierite, theta and the ZSM-type zeolites such as ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-23, and ZSM-38. Preferably the zeolite is selected from the group consisting of crystalline metal silicates having a ZSM-5 structure, ferrierite, erionite and mixtures thereof. Suitable examples of crystalline metal silicates with ZSM-5 structure are aluminium,

gallium, iron, scandium, rhodium and/or scandium silicates as described in e.g. GB-B-2,110,559.

During the preparation of the zeolites usually a significant amount of alkali metal oxide is present in the prepared zeolite. Preferably the amount of alkali metal is removed by methods known in the art, such as ion exchange, optionally followed by calcination, to yield the zeolite in its hydrogen form. Preferably the zeolite  
5 used in the present process is substantially in its hydrogen form.

The pressure in step (i) of the present process can be varied within wide ranges. It is, however, preferred that the pressure is such that at the prevailing temperature the feedstock is substantially in its gaseous phase or brought thereinto by contact with the catalyst. Then it is easier to achieve the short contact times envisaged. Hence, the pressure is preferably relatively low. This can be advantageous since  
10 no expensive compressors and high-pressure vessels and other equipment are necessary. A suitable pressure range is from 1 to 10 bar. Subatmospheric pressures are possible, but not preferred. It can be economically advantageous to operate at atmospheric pressure. Other gaseous materials may be present during the conversion such as steam and/or nitrogen.

Step (i) is carried out preferably in a moving bed. The bed of catalyst, preferably fluidized may also  
15 move upwards or downwards. When the bed moves upwards a process somewhat similar to fluidized catalytic cracking process is obtained.

During the process some coke forms on the catalyst. Therefore, it is advantageous to regenerate the catalyst. Preferably the catalyst is regenerated by subjecting it, after having been contacted with the feedstock, to a treatment with an oxidizing gas, such as air. A continuous regeneration, similar to the  
20 regeneration carried out in a fluidized catalytic cracking process, is especially preferred.

If the coke formation does not occur at too high a rate, it would be possible to arrange for a process in which the residence time of the catalyst particles in a reaction zone, is longer than the residence time of the feedstock in the reaction zone. Of course the contact time between feedstock and catalyst should be less than 10 seconds. The contact time generally corresponds with the residence time of the feedstock. Suitably  
25 the residence time of the catalyst is from 1 to 20 times the residence time of the feedstock.

The catalyst/feedstock weight ratio in step (i) may vary widely, for example up to 200 kg of catalyst per kg of feedstock including recycled material. Preferably, the catalyst/feedstock weight ratio is from 20 to 100:1.

The feedstock which is to be converted in the process of the present invention can vary within a wide  
30 boiling range. Examples of suitable feedstocks are relatively light petroleum fractions such as feedstocks comprising  $C_{3-4}$  hydrocarbons (e.g. LPG), naphtha, gasoline fractions and kerosine fractions. Heavier feedstocks may comprise, for example, vacuum distillates, long residues, deasphalted residual oils and atmospheric distillates, for example gas oils and vacuum gas oils.

One example of a suitable feedstock has been found to comprise hydrotreated and/or hydrocracked  
35 hydrocarbons, preferably, though not necessarily, heavy feedstocks. Suitable feedstocks of this type may be obtained by hydrotreating and/or hydrocracking heavy flashed distillate fractions from long residue or deasphalted oils obtained from short residue.

The effluent from step (i) may be subjected to any suitable separation means dependent on the composition of the effluent which will vary somewhat dependent on the feedstock employed. However, in  
40 accordance with the invention, a fraction comprising one or more lower olefins is separated from the effluent. The lower olefin-comprising fraction suitably comprises one or more of ethylene, propylene, butene and isobutene and may include other light olefinic and/or paraffinic products but is preferably free of heavier products. The olefin-comprising fraction which is separated depends on the product slate desired. Thus, for example, a fraction rich in  $C_4$  olefins is separated, if it is desired to produce a final product slate rich in  $C_2$   
45 and/or  $C_3$  olefins. A preferred lower olefin rich fraction will be rich in one or two of  $C_2$ ,  $C_3$  and  $C_4$  olefins.

At least a portion of the olefin-comprising fraction is contacted with an oligomerization catalyst under oligomerization conditions. It will be appreciated that any suitable oligomerization process can be employed. Examples of such processes include those employing solid catalysts such as ZSM-5 (e.g. US Patents 4,456,779 and 4,433,185) and fluorided silica/alumina (Ind. Pet. Gaz. - Chim 1978, (501), p 13-20),  
50 hydrocarbon-soluble catalysts such as a mixture of an organo-nickel compound and a hydrocarbyl aluminium halide (e.g. US Patents 4,366,087 and 4,398,049) and heterogeneous catalyst systems such as phosphoric acid on silica (C.L. Thomas, "Catal. Proc. and Proven Catalysts", McGraw Hill, 1970, p 67-69).

A preferred catalyst employed in step (iii) of the process according to the invention comprises at least one metal (Z) selected from the group consisting of metals from Groups 1b, 2a, 2b, 3a, 4b, 5b, 6b and 8 of  
55 the Periodic Table of the Elements and a crystalline trivalent metal (Q) silicate.

Reference is made to the Periodic Table of the Elements as published in the "Handbook of Chemistry and Physics", 55th addition (1975), CRC Press, Ohio, USA.

Preferably, at least part of the amount, and most preferably the total amount, of metal(s) Z has(have)

been incorporated into the catalyst by means of ion exchange. Preferably, the catalyst applied in step (iii) of the process according to the invention is prepared by using a zeolite carrier material, including such zeolites as mordenite, faujasite, omega, L, ZSM-5, -11, -12, -35, -23 and -38, ferrierite, erionite, theta, beta and mixtures thereof. A preferred zeolite is mordenite (see for example EP-A-233382). The carrier

5 comprises exchangeable cations such as alkali metal-, hydrogen- and/or preferably ammonium ions. The carrier material is suitably treated one or more times with a solution of at least one metal salt such as an aqueous solution of a metal nitrate or -acetate. The ion exchange treatment is suitably carried out at a temperature from 0 °C up to the boiling temperature of the solution, and preferably at a temperature from 20-100 °C.

10 The valency n of the metals Z can vary from +1 to +6. Preferably, however, at least one of the metals Z in the catalyst is bivalent or trivalent, in which case the molar ratio Z:Q is preferably greater than 0.5. Z is preferably selected from the group consisting of the bivalent metals copper, zinc, cadmium, magnesium, calcium, strontium, barium, titanium, vanadium, chromium, manganese, iron, cobalt and nickel. A particularly preferred metal Z is nickel.

15 The trivalent metal Q which is present in the crystal structure of the preferred metal silicate catalyst carrier used in step (iii) preferably comprises at least one metal selected from the group consisting of aluminium, iron, gallium, rhodium, chromium and scandium. Most preferably Q consists substantially of aluminium; the resulting crystalline aluminium silicate preferably comprises a major part of mordenite and most preferably consists substantially completely of mordenite.

20 The molar ratio silicon:Q in the catalyst is suitably in the range from 5:1 to 100:1 and preferably in the range from 7:1 to 30:1. This ratio is in most cases substantially identical to the molar ratio Si:Q in the crystalline metal silicate employed as carrier material, except when some of the metal Q has been removed from the crystal structure during the catalyst preparation e.g. by means of acid leaching.

If desired (e.g. in order to increase the crushing strength of the catalyst particles), the carrier material

25 and/or the ready catalyst for either one of the steps of the present process can be combined with a binder material such as refractory oxide(s), clay and/or carbon. Suitable refractory oxides comprise alumina, silica, magnesia, zirconia, titania and combinations thereof.

The molar ratio Z:Q in the ready catalyst is preferably from 0.1-1.5 and most preferably from 0.2-1.2.

In an alternative preferred embodiment of the process according to the invention the metal Z is identical

30 with the metal Q and is incorporated in the crystal structure of the silicate; most preferably gallium is the metal Q in the case where no additional metal Z is present in the catalyst.

After loading of the carrier material with the metal(s) Z, the catalytically active composition thus obtained is preferably dried and calcined before being employed as catalyst in step (iii). Drying is suitably carried out at a temperature from 100-400 °C, and preferably from 110-300 °C, for a period of 1-24 hours;

35 the calcination temperature is suitably from 400-800 °C and preferably from 450-650 °C. The calcination treatment is suitably carried out at (sub-)atmospheric or elevated pressure for a period of 0.1-24 hours, and preferably of 0.5-5 hours in air or in an inert (e.g. nitrogen) atmosphere.

Step (iii) can be carried out in one or more fixed-, moving- and/or fluidized beds or in a slurry-type of reactor; preferably, the process is carried out in a fixed bed of catalyst particles such as extrudates, pellets

40 or spheres passing sieve openings having a width from 0.05-5 mm, and preferably from 0.1-2.5 mm.

Step (iii) is preferably carried out at a temperature from 150-330 °C, a pressure from 1-100 bar and a space velocity from 0.1-10 kg olefins feed/kg catalyst.hour. Most preferably, step (iii) is carried out at a temperature from 180-300 °C, a pressure from 10-50 bar and a space velocity from 0.2-5 kg olefin feed/kg catalyst.hour.

45 At least a portion of the effluent from step (iii) as described above is recycled to step (i), suitably by combining it with the feed to step (i). It is not necessary that the entire effluent from step (iii) be recycled to step (i). However in a preferred mode of operation, substantially the entire C<sub>2</sub> and/or C<sub>3</sub> and/or C<sub>4</sub> olefin content of the effluent from step (i) is subjected to oligomerization in step (iii) and substantially the entire effluent from step (iii) is recycled to step (i), thus achieving ultimately high conversion of the less desired

50 lower olefin fraction to desired lower olefins.

The following example illustrates the invention, together with the accompanying Figure which is a flow diagram of the process of the example.

## 55 EXAMPLE

The process according to the invention was carried out as shown diagrammatically in the Figure using as initial feedstock a hydrocracked heavy flashed distillate supplied on line 1 and having the properties

described in Table 1 below.

The feedstock was treated in a downflow reactor 2 by passing it downwards co-currently with a flow of catalyst particles. The catalyst comprised ZSM-5 in an alumina matrix (weight ratio ZSM-5/alumina 1:3). The reaction was carried out at atmospheric pressure. Further process conditions are given in Table 1.

TABLE 1

Feedstock:	
IBP, °C	330
50 %wt	432
FBP, °C	620
fraction boiling below 370 °C, %wt	7.7
density 70/4	0.8157 kg/l
sulphur	20 ppmw
nitrogen	2 ppmw
Process conditions:	
Reactor temperature, °C	580
Catalyst/oil ratio, g/g	155
Contact time, s	2.8

The product from reactor 2 was separated by distillation in unit 3. The C<sub>4</sub><sup>+</sup> olefin fraction was withdrawn on line 4 while products including C<sub>2</sub> and C<sub>3</sub> olefins were withdrawn on one or more lines 5. The C<sub>4</sub><sup>+</sup> olefin stream was passed to oligomerization unit 6 comprising a bed of nickel/mordenite catalyst prepared by ion exchange of mordenite in the ammonium form at a temperature of 100 °C with an aqueous solution containing one mol nickel(II) acetate/litre. The resulting catalyst had a molar ratio of nickel:aluminium of 1.5:1 after drying at a temperature of 120 °C.

The nickel mordenite catalyst was mixed with 20 %wt pseudo-boehmite as a binder, 1 %wt acetic acid as peptising agent and water such that the loss on ignition amounts to 45%. After kneading the mixture was extruded into 1.5 mm extrudates and the catalyst dried at 120 °C for two hours and successively calcined in air at 500 °C for two hours.

The reaction conditions were as follows:

Reaction temperature, °C	483
Total pressure, bar	30
WHSV, hr <sup>-1</sup>	0.5

The oligomerized product was recycled on line 7 to the feedstock 1 to the reactor 2.

Table 2 below gives (A) the results obtained for the product stream 5 from unit 2 when recycling C<sub>4</sub> olefins from unit 2 via unit 6 as described above to give a ratio of recycled product/fresh feed entering unit 2 of 0.23 and (B) comparative results obtained for the product stream from unit 2 without recycle via unit 6.

TABLE 2

Product, %w on feed	(A)	(B)
C <sub>1</sub>	1.9	1.6
C <sub>2</sub>	1.3	1.0
C <sub>2</sub> =	18.0	14.7
C <sub>3</sub>	4.8	3.9
C <sub>3</sub> =	45.9	37.3
C <sub>4</sub>	5.7	4.6
C <sub>4</sub> =	-	11.0
C <sub>5</sub> -221 °C	10.6	8.6
221-370 °C	2.3	2.3
370 °C +	0.3	0.3
Coke	7.7	6.3

It will be seen from the above results that, when operating in accordance with the invention (Run A), enhanced C<sub>2</sub> and C<sub>3</sub> olefin yields are obtained when compared with the comparative results (Run B), while still maintaining a high conversion to lower olefin product.

## Claims

1. A process for the conversion of a hydrocarbonaceous feedstock comprising the following steps:
  - (i) contacting the feedstock with a solid cracking catalyst at a temperature of at least 400 °C during less than 10 seconds,
  - (ii) separating a fraction comprising one or more lower olefins from the effluent from step (i),
  - (iii) contacting at least a portion of said lower olefin-comprising fraction with an oligomerization catalyst under oligomerization conditions, and
  - (iv) recycling at least a portion of the effluent from step (iii) to step (i).
2. A process according to claim 1 wherein the solid cracking catalyst used in step (i) comprises at least one zeolite having a pore diameter of 0.3 to 0.7 nm.
3. A process according to claim 2 wherein the at least one zeolite is selected from crystalline metal silicates having a ZSM-5 structure, ferrierite, erionite and mixtures thereof.
4. A process according to any one of the preceding claims wherein the feedstock is contacted in step (i) with a moving bed of solid cracking catalyst.
5. A process according to any one of the preceding claims wherein the feedstock is contacted with the solid cracking catalyst in step (i) during 0.2 to 6 seconds.
6. A process according to any one of the preceding claims wherein the contacting temperature in step (i) is from 500 to 750 °C.
7. A process according to any one of the preceding claims in which the catalyst/feedstock weight ratio in step (i) is from 20 to 100:1.
8. A process according to any one of the preceding claims wherein the oligomerization catalyst employed in step (iii) is a solid oligomerization catalyst comprising at least one metal selected from metals from Groups 1b, 2a, 2b, 3a, 4b, 5b, 6b and 8 and a crystalline trivalent metal silicate.
9. A process according to claim 8 wherein the metal comprises nickel and the crystalline silicate comprises mordenite.
10. A process according to any one of the preceding claims wherein the oligomerization conditions in step (iii) comprise a temperature of from 150 to 330 °C, a pressure of from 1 to 100 bar and a space velocity of from 0.1 to 10 kg olefins feed/kg catalyst.hour.
11. A hydrocarbonaceous product, or a fraction thereof, when obtained by the process of any one of the preceding claims.

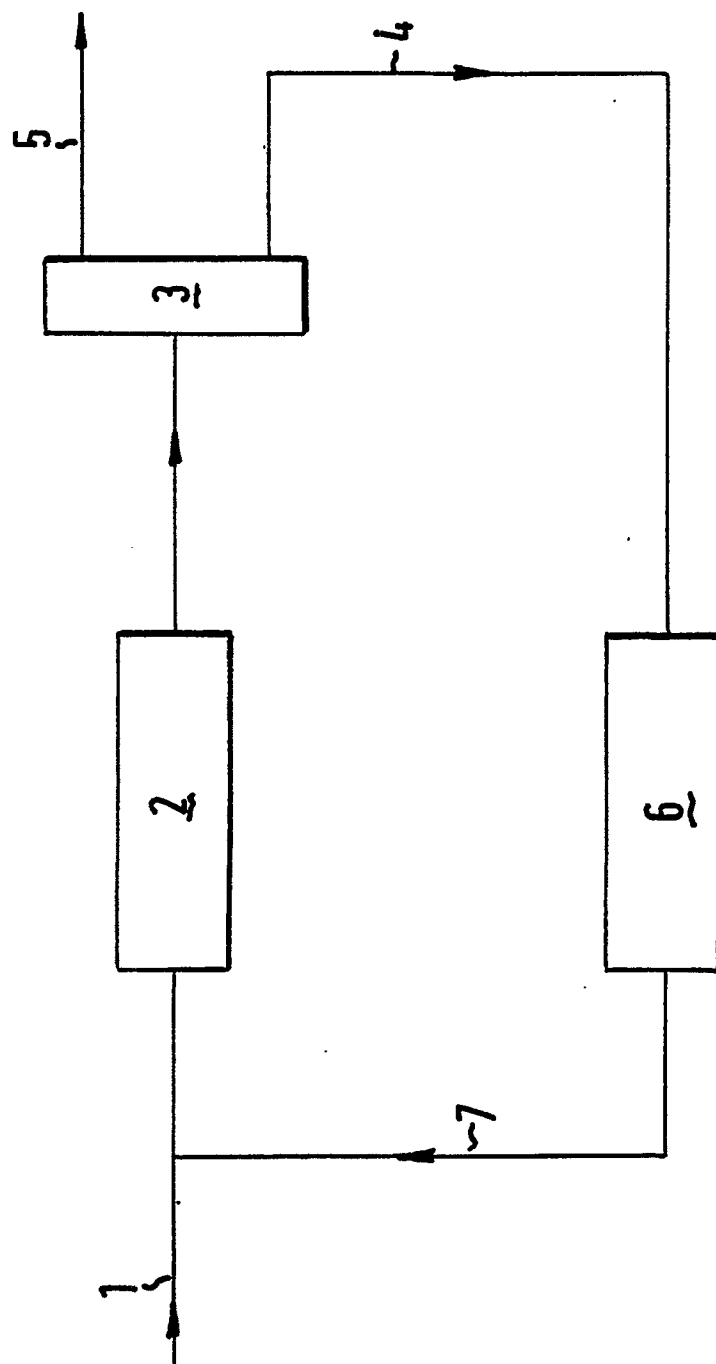


FIG.1



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	GB-A- 513 545 (STANDARD OIL) * Claims 1,2,6; page 1, lines 61-69; page 2, lines 106-114 *	1,6	C 10 G 57/02
P,Y	EP-A-0 347 003 (SHELL) * Claims 1-7,9,11 *	1,6	
P,A		2,3,4,5 ,7	
P,A	EP-A-0 349 036 (SHELL)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18-07-1990	Examiner DE HERDT O.C.E.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	