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

(57) Process for the hydrocracking of a hydrocarbonaceous feedstock containing less than 500 ppmw N by contacting the feedstock at elevated temperature and pressure in the presence of hydrogen with a hydrocracking catalyst A and wherein at least a portion of the product so obtained is subsequently contacted with a hydrocracking catalyst B at elevated temperature and pressure and in the presence of hydrogen, whereby the hydrocracking catalysts A and B have a RS > 1 and a RA.RV < 5.

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The present invention relates to a process for the hydrocracking of a hydrocarbonaceous feedstock containing a relatively low amount of nitrogen.

There exists a large number of processes for hydrocracking hydrocarbonaceous feedstocks and numerous catalysts that are used in these processes. Many of these processes comprise two stages, a hydrotreating stage and a hydrocracking stage, the two stages operating with different types of catalysts.

Product from the first stage may be treated to remove ammonia, hydrogen sulphide and other light gases prior to being passed to the second stage, or product may be passed directly to the second stage. In this two stage or series-flow mode of operation the hydrocracking stage is frequently referred to as a second stage hydrocracker.

Hydrocracking is as such a well-established process in which heavy hydrocarbons are contacted in the presence of hydrogen with a hydrocracking catalyst. The temperature and pressure applied are relatively high, so that the heavy hydrocarbons are cracked to products of a lower average molecular weight and lower boiling point.

These products include gaseous material, i.e. C_1-C_4 hydrocarbons, naphtha and a middle distillate fraction, i.e. a kerosine fraction and a gas oil fraction.

Since the gaseous products are not very much wanted and since there is an increasing demand for middle distillates, it would be advantageous to have a hydrocracking process available for converting hydrocarbonaceous feedstocks that shows a considerable selectivity towards middle distillates and a low gas make.

It has now been found that a surprisingly low gas make and a high yield of middle distillates can be obtained if a hydrocarbonaceous feedstock containing a relatively low amount of nitrogen is passed over a catalyst system comprising a specific sequence of hydrocracking catalysts.

Accordingly, the present invention relates to a process for hydrocracking a hydrocarbonaceous feedstock containing less than 500 ppmw N by contacting the feedstock at elevated temperature and pressure in the presence of hydrogen with a hydrocracking catalyst A and wherein at least a portion of the product so obtained is subsequently contacted with a hydrocracking catalyst B at elevated temperature and pressure and in the presence of hydrogen, whereby the hydrocracking catalysts A and B have a RS > 1 and a RA.RV < 5.

In the context of the present invention the RS (ratio of selectivities) of two respective hydrocracking catalysts is defined as follows:

$$RS = \frac{\text{selectivity hydrocracking catalyst A}}{\text{selectivity hydrocracking catalyst B}}$$

whereby the selectivities are expressed as selectivities towards the C_1-C_4 hydrocarbons fraction (C_1-C_4), for conversion into 370 °C$^-$ products, when the hydrocracking catalysts are applied under particular (standard) process conditions. That is to say applying a particular catalyst volume, temperature, pressure, feed, space velocity, gas/feed ratio and a reactor loading-method. The selectivity towards C_1-C_4 hydrocarbons (S_{C1-C4}) is determined from the formula:

$$S_{C1-C4} = \frac{(C1\text{-}C4)_{product} - (C1\text{-}C4)_{feed}}{(370\ ^{\circ}C^{+})_{feed} - (370\ ^{\circ}C^{+})_{product}} \cdot 100\%$$

In the context of the present invention it is further observed that the RA (ratio of activities) of two respective hydrocracking catalysts is defined as follows:

$$RA = \frac{\text{k hydrocracking catalyst A}}{\text{k hydrocracking catalyst B}}$$

whereby k is defined as the reaction rate constant of the respective hydrocracking catalysts, for conversion into 370 °C$^-$ products, when applied under particular (standard) process conditions. This means a particular catalyst volume, temperature, pressure, feed, space velocity, gas/feed ratio and reactor loading-method.

In the context of the present invention it is further observed that RV (ratio of volumes) is defined as follows:

$$RV = \frac{\text{reactor volume loaded with hydrocracking catalyst A}}{\text{reactor volume loaded with hydrocracking catalyst B}}$$

whereby the same particular reactor loading-method is applied for both hydrocracking catalysts.

Both the RS and the RA are to be determined after the hydrocracking catalysts have been allowed to stabilize under the particular (standard) process conditions.

A set of particular (standard) process conditions as mentioned hereinabove may include a temperature of 390 °C, an average hydrogen partial pressure of 12.4 MPa (124 bar), a space velocity of 0.6 kg/l/hr, a hydrotreated flashed distillate containing 23 ppmw N, a gas/feed ratio of 2000 Nl/kg and a dense-bed loading method.

It is expected for a catalyst system of a hydrocracking catalyst A and a hydrocracking catalyst B that the gas make and the middle distillate yield will be the average of the individual contributions of the catalysts weighed by their respective activities and volumes. However, in accordance with the present invention surprisingly a lower gas make and a higher middle distillate yield, than expected, can be obtained by selecting a sequence of hydrocracking catalysts wherein the first hydrocracking catalyst has a higher gas make and a $RA.RV < 5$.

Suitably, the hydrocracking catalysts A and B are selected in such a way that the $RS \geqq 1.1$. Suitably, the hydrocracking catalysts A and B are selected in such a way that $1.1 \leqq RS \leqq 4$. Preferably, the hydrocracking catalysts A and B are selected in such a way that $0.1 \leqq RA.RV \leqq 3.5$, more preferably they are selected so that $0.2 \leqq RA.RV \leqq 2$.

Suitably, the hydrocracking catalysts A and B are selected so that $RS/RA > 1$. Suitably, the hydrocracking catalysts A and B are selected so that $1 < RS/RA < 3$.

At least part of the product obtained over hydrocracking catalyst A is contacted with hydrocracking catalyst B. Suitably, at least 50% by volume of the product obtained over hydrocracking catalyst A is contacted with hydrocracking catalyst B.

Suitably, at least part of the product obtained over hydrocracking catalyst A can be recycled to hydrocracking catalyst A.

Suitably, at least part of the product obtained over hydrocracking catalyst B can be recycled to hydrocracking catalyst A and/or hydrocracking catalyst B.

Suitably, the complete product obtained over hydrocracking catalyst A is contacted with hydrocracking catalyst B.

The hydrocracking catalysts A and B, respectively, can be arranged in one or more beds with hydrocracking catalyst A and one or more beds with hydrocracking catalyst B. The bed or beds with hydrocracking catalyst A and the bed or beds with hydrocracking catalyst B can be arranged in one or more reactors. Suitably, the hydrocracking catalysts A and B are applied in stacked-bed configuration.

Suitably, the $RV \leqq 5$, preferably in the range from 0.1 to 2.

Suitably, the hydrocracking catalysts A and B are selected in such a way that $RA \leqq 4$. Suitably, they are selected in such a way that $1 \leqq RA \leqq 4$.

Preferably, the process is carried out in such a way that the product obtained over hydrocracking catalyst A comprises at least 50% by weight of 370 °C$^-$ products.

Suitably, the present process is carried out in such a way that more than 30% by weight conversion of 370 °C$^+$ boiling point material is established. Preferably, more than 40% by weight conversion is established. Suitably, the amount of C_1-C_4 hydrocarbons produced is less than 20% by weight on feed.

The hydrocracking catalysts A and B may be any conventional hydrocracking catalyst provided that both the RS and RA.RV fulfil the requirements as set out hereinabove. For example, the hydrocracking catalysts A and B may be fresh and regenerated forms respectively of the same catalyst.

Suitably, the hydrocracking catalysts A and B comprise a support comprising a large pore molecular sieve and a binder.

The molecular sieves have pores larger than 6 Å, preferably between 6 and 12 Å. Suitable wide pore molecular sieves are described in the book Zeolite Molecular Sieves by Donald W. Breck, Robert E. Krieger Publishing Co., Malabar, Fla., 1984. Suitable wide pore molecular sieves comprise the crystalline aluminosilicates, the crystalline aluminophosphates, the crystalline silicaaluminophosphates and the crystalline borosilicates. Preferred are the crystalline aluminosilicates or zeolites. The zeolites are preferably selected from the group consisting of faujasite-type and mordenite-type zeolites. Suitable examples of the faujasite-type zeolites include zeolite Y and zeolite X. Other wide pore zeolites such as zeolite L, beta and omega can also be used alone or in combination with the more preferred zeolites.

The most preferred wide pore zeolite comprises a zeolite Y, preferably an ultrastable zeolite Y (zeolite USY). The ultrastable zeolites used herein are well known to those skilled in the art. They are for instance exemplified in US 3,293,192 and US 3,449,070. They are generally prepared from sodium zeolite Y using one or more ammonium ion exchanges followed by steam calcination.

Suitably, hydrocracking catalysts A and B each comprise a wide pore zeolite. Preferably, both hydrocracking catalysts A and B comprise a zeolite Y, particularly a modified zeolite Y having a unit cell size below 2.445 nm (24.45 Å). In the latter case, hydrocracking catalyst A has preferably a content of zeolite Y which is at least equal to the zeolite Y content of hydrocracking catalyst B. In other words, the ratio of the zeolite Y contents of hydrocracking catalysts A and B (Y1/Y2) is at least 1. More preferably this ratio is in the range from 2 to 12.

Hydrocracking catalysts A and B may each comprise an amount of zeolite Y in the range from 1% to 95% by weight, based on total support.

Hydrocracking catalysts A and B will each further comprise at least one hydrogenation component of a Group VI metal and/or at least one hydrogenation component of a Group VIII metal. Suitably, the catalyst composition according to the present invention comprises one or more components of nickel and/or cobalt and one or more components of molybdenum and/or tungsten or one or more components of platinum and/or palladium.

The amount(s) of hydrogenation component(s) in the hydrocracking catalysts is preferably in the range from 0.05 to 10% by weight of Group VIII metal component(s) and from 2 to 40% by weight of Group VI metal component(s), calculated as metal(s) per 100 parts by weight of total catalyst.

More preferably, the amount(s) of hydrogenation component(s) in the hydrocracking catalysts is in the range from 0.5 to 8% by weight of Group VIII metal component(s) and from 10 to 25% by weight of Group VI metal component(s), calculated as metal(s) per 100 parts by weight of total catalyst.

Preferably, the total amount of hydrogenation component(s) in hydrocracking catalyst A is equal to or less than the total amount of hydrogenation component(s) in hydrocracking catalyst B. In other words, the ratio of the amounts of hydrogenation component(s) in hydrocracking catalysts A and B (hA/hB) is at most 1. More preferably, hA/hB is in the range from 0.5 to 1. In a very attractive embodiment of the present invention hA/hB is less than 1 whereas Y1/Y2 is more than 1. In a preferred embodiment of the present invention hA/hB is in the range from 0.5 to 1 whereas Y1/Y2 is in the range from 2 to 12.

The hydrogenation components in the hydrocracking catalysts may be in the oxidic and/or sulphidic form, in particular in the sulphidic form. If a combination of at least a Group VI and a Group VIII metal component is present as (mixed) oxides, it will normally be subjected to a sulphiding treatment prior to proper use in hydrocracking.

Suitably, the supports of hydrocracking catalysts A and B may comprise a zeolite Y, a binder and/or a dispersion of silica-alumina in an alumina matrix.

Preferably, the support of hydrocracking catalyst B comprises less than 25 by weight of the zeolite Y, more than 25% by weight of binder and at least 30% by weight of the dispersion.

Preference is given to supports of hydrocracking catalyst B comprising less than 15% by weight of the zeolite Y.

Preferably, the support of hydrocracking catalyst B has a binder/zeolite Y weight ratio in the range from 2 to 40.

Suitably, the support of hydrocracking catalyst B comprises 40 to 70% by weight of the dispersion.

Suitably, the alumina matrix comprises a transitional alumina matrix, preferably a gamma-alumina matrix.

The binder(s) present in the supports of hydrocracking catalysts A and B as described hereinabove suitably comprise inorganic oxides or mixtures of inorganic oxides. Both amorphous and crystalline binders can be applied.

Examples of suitable binders comprise alumina, magnesia, titania and clays. If desired, small amounts of other inorganic oxides such as zirconia, titania, magnesia and silica may be present. Alumina is a preferred binder.

Suitably, the crystalline alumonosilicate of the zeolite Y type to be applied in hydrocracking catalysts A and B comprises a modified zeolite Y having a unit cell size below 2.435 nm (24.35 Å), a degree of crystallinity which is at least retained at increasing SiO_2/Al_2O_3 molar ratios, a water adsorption capacity (at 25 °C and p/p_0 value of 0.2) of at least 8% by weight of modified zeolite and a pore volume of at least 0.25 ml/g wherein between 10% and 60% of the total pore volume is made up of pores having a diameter of at least 8 nm. This type of modified zeolite Y has been described in detail in EP-B-247679, which is herein incorporated by reference.

Preferably, between 10% and 40% of the total pore volume of the modified zeolite Y is made up of pores having a diameter of at least 8 nm.

Suitably, the modified zeolite Y has a water adsorption capacity of 8 to 10% by weight of modified zeolite.

Preferably, the modified zeolite Y has a SiO_2/Al_2O_3 molar ratio in the range from 4 to 25, more preferably in the range from 8 to 15.

Suitable process conditions for the present hydrocracking process comprise temperatures in the range from 250 to 500 °C, hydrogen partial pressures of up to 30 MPa (300 bar) and space velocities in the range from 0.1 to 10 kg feed per litre catalyst per hour (kg/l/hr). Gas/feed ratios in the range from 100 to 5000 Nl/kg can suitably be applied. Preferably, the present hydrocracking process is carried out at a temperature in the range from 300 to 450 °C, a hydrogen partial pressure in the range from 2.5 to 20 MPa (25 to 200 bar) and a space velocity in the range from 0.2 to 5 kg feed per litre catalyst per hour. Preferably, gas/feed ratios in the range from 250 to 2500 Nl/kg are applied.

Feedstocks which can suitably be applied in the process according to the present invention comprise all sorts of hydrocarbonaceous feedstocks as long as they fulfil the requirement to contain less than 500 ppmw N. Suitably, the feedstock contains less than 200 ppmw N. Suitably, the feedstocks comprise gas oils, deasphalted oils, coker gas oils and other thermally or catalytically cracked gas oils and syncrudes, optionally originating from tar sands, shale oils, residue upgrading processes or biomass or combinations thereof, which may have been hydrotreated before being contacted with hydrocracking catalyst A. The feedstocks can for instance suitably be contacted with an alumina containing hydrotreating catalyst prior to contact with hydrotreating catalyst A. The feedstock will generally be such that a major part, say over 50% by weight, has a boiling point above 370 °C.

Suitably, the complete product obtained from such a hydrotreating step is applied as feedstock in accordance with the present invention.

In an attractive embodiment of the present invention use is made of three reaction zones arranged in series whereby the complete effluent from a first reaction zone is passed to a second reaction zone, and the complete effluent from the second reaction zone is passed to a third reaction zone. The first reaction zone comprises an amorphous hydrotreating catalyst as described hereinbefore, the second reaction zone comprises a first zeolitic hydrocracking catalyst which contains at least one metal of Group VIB and/or at least one metal of Group VIII, and the third reaction zone comprises a second zeolitic hydrocracking catalyst which contains at least one metal of Group VIB and/or at least one metal of Group VIII. The zeolitic hydrocracking catalysts fulfil the RS and RA.RV requirements in accordance with the invention.

A hydrotreatment as described hereinabove and the process according to the present invention can suitably be carried out in reactors in series or in a stacked-bed configuration.

In another embodiment of the present invention the process is carried out in a two-stage mode of hydrocracking operation. In this type of operation the effluent obtained from the first reaction zone comprising an amorphous hydrotreating catalyst is subjected to a separation treatment to remove from the effluent a gaseous phase and a liquid phase including a naphtha and a middle distillate fraction. The remaining effluent is subsequently subjected to the process according to the present invention, whereby at least a part of the residual fraction obtained is recycled to hydrocracking catalyst A.

The hydrocarbonaceous feedstock may be the effluent obtained from one or more hydrocracking stages arranged upstream in respect of hydrocracking catalyst A. The product obtained from hydrocracking catalyst B may subsequently be contacted with a further catalyst, for instance, an amorphous silica-alumina containing catalyst.

The present invention will be further understood from the following illustrative example.

Example I

A heavy vacuum gas oil feed having a sulphur content of 2.0 %w (as determined according to standard test method ASTM D2622), a nitrogen content of 1000 ppmw (as determined according to standard test method ASTM D4629), an initial boiling point of 340 °C, a 50% boiling point of 470 °C and a final boiling point in excess of 540 °C is first hydrotreated in the presence of C-424 catalyst (ex Criterion) to reduce the nitrogen content to less than 200 ppmw.

The hydrotreated feed so obtained is then contacted, in a once-through operation, in a stacked bed reactor at a temperature of 400 °C, a hydrogen partial pressure of 10.9 x 10^5 Pa (109 bar) and a space velocity of one (1) kg of feed per litre of catalyst per hour ($kg.l^{-1}.h^{-1}$) with a first bed of hydrocracking catalyst Z-713 (ex Zeolyst International) (Catalyst A) and then with a second bed of hydrocracking catalyst Z-603 (ex Zeolyst International) (Catalyst B). The ratio of the selectivity of catalyst A to the selectivity of Catalyst B (RS) is 5.2/3.1, i.e. 1.7. The ratio of the activity of catalyst A to the activity of catalyst B (RA) is 0.95/0.19, i.e. 5.0, and the ratio of the Catalyst A reactor volume to the Catalyst B reactor volume (RV) is 125/175, i.e. 0.7. Thus RA.RV is 5.0 x 0.7 = 3.5.

The distribution of 300 $°C^-$ product (in %w based on total feed) at 96% conversion is as follows:

C_1 - C_4	6.4
C_5 - 150 °C	37.6
140 °C - 300 °C	53.8

Comparison Example

If Example I is repeated but using hydrocracking catalyst Z-603 in the first catalyst bed (catalyst A') and hydrocracking catalyst Z-713 in the second catalyst bed (catalyst B'), then RS is 3.1/5.2 = 0.6, RA is 0.19/0.95 = 0.2, RV is 175/125, i.e. 1.4, and RA.RV is 0.2 x 1.4 = 0.3.

In this case, the distribution of 300 $°C^-$ product (in %w based on total feed) at 96% conversion is as follows:

C_1 - C_4	7.0
C_5 - 150 °C	37.6
140 °C - 300 °C	53.2

Thus, the above results clearly demonstrate that by using the process of the present invention in which a particular sequence of hydrocracking catalysts is employed such that RS > 1 and RA.RV < 5, it is possible to achieve higher yields of middle distillates with lower gas make compared to processes where one or both of the RS and RA.RV values do not fulfil the above requirements.

Claims

1. Process for the hydrocracking of a hydrocarbonaceous feedstock containing less than 500 ppmw N by contacting the feedstock at elevated temperature and pressure in the presence of hydrogen with a hydrocracking catalyst A and wherein at least a portion of the product so obtained is subsequently contacted with a hydrocracking catalyst B at elevated temperature and pressure and in the presence of hydrogen, whereby the hydrocracking catalysts A and B have a RS > 1 and a RA.RV < 5.

2. Process according to claim 1, wherein the hydrocracking catalysts A and B are selected in such a way that RS $\geqq$ 1.1.

3. Process according to claim 1 or 2, wherein the hydrocracking catalysts are selected in such a way that 0.1 $\leqq$ RA.RV $\leqq$ 3.5.

4. Process according to any one of claims 1 to 3, wherein at least 50% by volume of the product obtained over hydrocracking catalyst A is contacted with hydrocracking catalyst B.

5. Process according to any one of claims 1 to 4, wherein the product obtained over hydrocracking catalyst A comprises at least 50% by weight of 370 °C$^-$ products.

6. Process according to any one of claims 1 to 5, wherein hydrocracking catalysts A and B each comprise a wide pore zeolite.

7. Process according to claim 6, wherein the wide pore zeolite is a zeolite Y.

8. Process according to claim 7, wherein the ratio of the zeolite Y contents of hydrocracking catalysts A and B (Y1/Y2) is at least 1.

9. Process according to claim 8, wherein Y1/Y2 is in the range from 2 to 12.

10. Process according to any one of claims 6 to 9, wherein the hydrocracking catalysts A and B each further comprise a binder and at least one hydrogenation component of a Group VI and/or Group VIII metal.

11. Process according to claim 10, wherein hydrocracking catalyst B comprises less than 25% by weight of zeolite Y, more than 25% by weight of binder and at least 30% by weight of a dispersion of silica-alumina in an alumina matrix, calculated per 100 parts by weight of total support.

12. Process according to any one of claims 7 to 11, wherein the zeolite Y comprises a modified zeolite Y having a unit cell size below 2.445 nm (24.45 Å).

13. Process according to claim 12, wherein zeolite Y comprises a modified zeolite Y having a unit cell size below 2.435 nm (24.35 Å), a degree of crystallinity which is at least retained at increasing SiO_2/Al_2O_3 molar ratios, a water adsorption capacity (at 25 °C and p/p_0 value of 0.2) of at least 8% by weight of modified zeolite and a pore volume of at least 0.25 ml/g wherein between 10% and 60% of the total pore volume is made up of pores having a diameter of at least 8 nm.

14. Process according to claim 13, wherein between 10% and 40% of the total pore volume of the modified zeolite Y is made up of pores having a diameter of at least 8 nm.

15. Process according to claim 13 or 14, wherein the modified zeolite Y has a water adsorption capacity of 8 to 10% by weight of modified zeolite.

16. Process according to any one of claims 12 to 15, wherein the modified zeolite Y has a SiO_2/Al_2O_3 molar ratio in the range from 4 to 25.

17. Process according to any one of claims 10 to 16, wherein the hydrogenation component comprises at least one component of nickel and/or cobalt and at least one component of molybdenum and/or tungsten or at least one component of platinum and/or palladium.

18. Process according to claim 17, wherein the hydrogenation component comprises from 0.5 to 10% by weight of nickel and from 2 to 40% by weight of tungsten, calculated as metals per 100 parts by weight of total catalyst.

19. Process according to any one of claims 1 to 18, which is carried out at a temperature in the range from 250 to 500 °C, a hydrogen partial pressure up to 30 MPa (300 bar) and a space velocity in the range from 0.1 to 10 kg feed per litre of catalyst per hour.