

Description

The invention relates to a process for two-stage catalytic conversion of an olefins-containing feed and to liquid hydrocarbons thus obtained.

It is known to convert olefins having 3 or 4 carbon atoms per molecule (C_3 and C_4 olefins) in two stages in the presence of catalysts containing nickel as catalytically active metal and ZSM-5 as crystalline molecular sieve material, in order to produce dimers from olefinic feed molecules in the first stage and subsequently converting said dimers in the second stage to higher boiling hydrocarbons such as tetramers of C_3 - or C_4 -olefins.

It is furthermore known to apply crystalline aluminium silicates (e.g. mordenite) into which one or more catalytically active metals have been incorporated, in a wide variety of hydrocarbon conversion processes, including oligomerization.

A problem associated with the use of olefins-containing feeds in catalytic processes in general, and in particular in dimerization- and oligomerization processes as described hereinbefore is the catalyst stability which is often negatively influenced by undesirable compounds such as dienes which are in many cases present in olefinic feeds available in e.g. refineries.

From US-A-3,644,565 a method is known for oligomerization of hydrocarbon olefins and/or the alkylation of paraffins with hydrocarbon olefins, using a Group VIII noble metal supported on a metal alumino silicate molecular sieve, wherein this catalyst is pretreated with hydrogen at specified temperatures which imparts selective activity to the catalyst for the desired reaction.

In US-A-3,221,073 a process is described for removing diolefin and/or acetylenic hydrocarbon impurities from olefin streams by the selective polymerisation of the diolefin and/or acetylenic hydrocarbon impurities, which process comprises contacting the olefin streams with a crystalline zeolite having pore diameters of 6 to 15 angstroms, at least a portion of the ions of which have been exchanged with a polymerization promoting metal selected from the group consisting of zinc, cadmium, mercury, silver, copper, nickel and cobalt at temperatures of 200 to 350 °C and at a substantially atmospheric pressure.

From EP-A-0112736 a two-stage oligomerizing process is known comprising contacting an olefinic feed with a gaseous boron trifluoride in the absence of a catalyst carrier under such conditions and for such period of time that the isobutene and/or butadiene present polymerize; subsequently separating off the boron trifluoride and the isobutene and/or butadiene polymers obtained, and oligomerizing the olefins from the thus purified feed in the presence of a catalyst based on boron trifluoride containing a catalyst carrier.

Surprisingly, it has now been found that by using a metal-containing catalyst in a first stage under substantially non-oligomerizing conditions and a mordenite-type of catalyst carrier in combination with a catalytically active metal in a second stage under controlled conditions, liquid hydrocarbons can be prepared from an olefins-containing feed in a very stable operation.

The invention therefore relates to a process for two-stage catalytic conversion of an olefins-containing feed wherein the feed is contacted in a first stage under substantially non-oligomerizing conditions with a catalyst comprising at least one metal (X) selected from the group consisting of metals from Groups 1a, 1b, 2a, 2b, 4b, 5b, 6b and 8 of the Periodic Table of the Elements and effluent from the first stage is contacted in the second stage under olefin oligomerization conditions at a temperature which is at least 50 °C above the operating temperature of the first stage with a catalyst comprising at least one metal (Z) selected from the group consisting of metals from Groups 1b, 2a, 2b, 4b, 5b, 6b and 8 on a mordenite-type of 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 edition (1975), CRC Press, Ohio, USA.

Preferably, a catalyst is used in the second stage in which the molar ratio Z:Q is greater than n^{-1} , n being the valency of the metal Z.

The metals X and Z may be present in the catalysts in the form of metal compounds such as oxides or salts, or in the metallic- or ionic state.

In a preferred embodiment of the process according to the invention the metals X and Z are the same, both possessing catalytic activity for the conversion of olefinic hydrocarbons. However, since the first stage of the process is preferably carried out at a temperature from 30 °C to 100 °C, the extent to which oligomerization of olefins will occur is very limited in the first stage, and in some cases substantially zero. In particular at relatively low temperatures in the first stage adsorption and/or conversion of highly reactive dienes into compounds which do not quickly deactivate the second stage catalyst are thought to be the main features.

The first stage is preferably carried out at a pressure from 1-100 bar, in particular from 10-50 bar, and a space velocity from 0.1-10 kg olefins feed/kg catalyst.hour, in particular from 0.5-8 kg olefins feed/kg

catalyst.hour.

In a preferred embodiment the catalysts employed in the two stages of the process according to the invention can be the same. In a particularly preferred embodiment both stages of the present process are carried out in series flow, thus avoiding the separation of product from the first stage which is required in many known two-stage processes. Moreover, a series-flow set up has the advantage that the present two-stage process can even be carried out in a single pressure vessel, provided that a temperature profile is maintained therein in accordance with the invention e.g. by means of heat exchange internals.

The second stage of the present process is most preferably operated at a temperature which is at least 100 °C above the operating temperature of the first stage, in particular when the latter temperature is from 30-100 °C as discussed hereinbefore.

The second stage 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, the second stage of the process 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 olefins feed/kg catalyst.hour.

Preferably, at least part of the amount, and most preferably the total amount, of metal(s) X and Z has-(have) been incorporated into the catalyst by means of ion exchange. Preferably, the catalyst applied in both stages of the process according to the invention is prepared by treating a mordenite-type of carrier material, which comprises exchangeable cations such as alkali metal-, hydrogen- and/or preferably ammonium ions, 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.

The valency n of the metals Z can vary from +1 to +6. Preferably, however, at least one of the metals Z in the second stage catalyst is bivalent, 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 X and Z is nickel.

The trivalent metal Q which is present in the crystal structure of the mordenite-type of metal silicate catalyst carrier used at least in the second stage 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.

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 and/or the ready catalyst for either one of the stages can be combined with a binder material such as (a combination of) 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 0.6 - 1.5 and most preferably from 0.8 - 1.2. A molar ratio Z : Q of 0.5 or less for bivalent metals Z results in a catalyst which is in some cases less stable than a catalyst for which said ratio is greater than 0.5. A very high molar ratio Z : Q of e.g. more than 2 could lead to difficulties in the catalyst preparation and result in a relatively inactive catalyst with a relatively low surface area and pore volume due to the very high degree of loading with metal(s) Z.

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 the process according to the present invention. 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; 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.

A wide variety of olefinic hydrocarbons-containing feeds can be employed in the process according to the present invention, provided that the dimensions of the olefinic hydrocarbon molecules are such that they can be catalytically converted with a mordenite type of catalyst.

Mono olefins are preferably used as feed (components). Preferably, the feed contains more than 30% by weight of olefins having at most six carbon atoms per molecule (C_6^- olefins) such as ethene, propene, n-butenes, isobutene, n-pentenes, isopentenes, n-hexenes and isohexenes; in addition to said olefins, aliphatic hydrocarbons such as (cyclic) paraffins, di-olefins and mono-olefins having more than six carbon

atoms per molecule and/or aromatic components and/or aromatic components can be present in the feed.

Special preference is given to butene(s)-containing feeds which are suitably obtained as by-product from (fluid) catalytic cracking processes, thermal cracking processes (e.g. for the preparation of ethene), coking- and/or pyrolysis processes.

Suitable feeds for the present process can also be prepared starting from synthesis gas which is first converted into methanol and subsequently into a product substantially consisting of C_6^- olefins. Alternatively, the synthesis gas can be converted in the presence of a Fischer-Tropsch type of catalyst into a product which in addition to paraffinic hydrocarbons contains a considerable amount of C_6^- olefins.

The process according to the invention 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 two fixed bed of catalyst particles such as extrudates, pellets or spheres passing sieve openings having a width from 0.05-5 mm, and preferably from 0.1-1 mm.

The invention furthermore relates to liquid hydrocarbons prepared by a process as described hereinbefore. Such liquid hydrocarbons include products boiling in the gasoline range (40-150 °C), the middle distillate range (kerosene- and gasoil fractions boiling from 150-370 °C) and in the lubricating base oil range (above 370 °C). Products boiling below the gasoline boiling range and unconverted feed, if any, are preferably separated off from the normally liquid products and can be recycled, if desired, to the first-, and more preferably the second stage.

The invention is illustrated by the following Example.

EXAMPLE

1) preparation of catalyst A.

Mordenite in the ammonium form with a molar ratio Silicon : aluminium (=Q) of 9 is ion exchanged at a temperature of 100 °C with an aqueous solution containing one mol nickel(II) acetate/litre. The resulting catalyst has a molar ratio of nickel (=Z) : aluminium (=Q) of one, is dried at a temperature of 120 °C for 16 hours and calcined in air at a temperature of 500 °C for one hour to obtain catalyst A.

2) preparation of liquid hydrocarbons.

Experiment 1

A gas feed mixture obtained from a catalytic cracking process and containing 54.5% by volume (v) butane, 44.6 %v butene, 0.14 %v butadiene, 3.9 parts per million (v) sulphur and 0.29 mg/l water is led with a space velocity of 2 kg butene/kg catalyst.hour through a first microflow reactor containing 2 g of first stage catalyst A with a particle size of 0.2-0.6 mm at a temperature of 42 °C and a pressure of 16 bar; subsequently the total product obtained from the first stage reactor is led with a space velocity of 2 kg butene/kg catalyst.hour through a second microflow reactor containing 6 g of catalyst with a particle size of 0.2-0.6 mm at a temperature of 215 °C and a pressure of 16 bar.

Experiment 2

A similar feed mixture as used in Experiment 1 is led under the same conditions through the second stage reactor only.

The test results are given in the following Table, in which "Activity" is defined as the number of mol.butene converted/g catalyst.hour in the second or the only reactor. For Tests Nos. 1 and 2 the activity is listed after 0.5 mol butene/g catalyst has been converted, whereas 0.8 and 1.8 mol.butene/g catalyst has been converted in Tests Nos. 3 and 4, and 5, respectively. With Experiment 2 it is not possible to convert 1.8 mol.butene/g catalyst due to catalyst deactivation.

TABLE

Experiment	Test No.	Activity x 100
1	1	1.30
2	2	1.00
1	3	1.26
2	4	0.28
1	5	1.00

From the results given in the Table it is clear that in Experiment 1 according to the invention the catalyst is very stable whereas its stability decreases substantially in comparative Experiment 2.

20 Claims

1. Process for two-stage catalytic conversion of an olefins-containing feed wherein the feed is contacted in a first stage under substantially non-oligomerizing conditions comprising a temperature from 20 to 150 °C, with a catalyst comprising at least one metal (X) selected from the group consisting of metals from Groups 1a, 1b, 2a, 2b, 4b, 5b, 6b and 8 of the Periodic Table of the Elements and effluent from the first stage is contacted in the second stage under olefin oligomerization conditions at a temperature which is at least 50 °C above the operating temperature of the first stage with a catalyst comprising at least one metal (Z) selected from the group consisting of metals from Groups 1b, 2a, 2b, 4b, 5b, 6b and 8 on a mordenite-type of crystalline trivalent metal (Q) silicate.
2. Process according to claim 1 wherein the metals X and Z are the same.
3. Process according to claim 1 or 2 wherein the metal Z represents nickel.
4. Process according to any one of the preceding claims wherein mordenite is used as catalyst carrier in both stages.
5. Process according to any one of the preceding claims wherein a catalyst is used in the second stage in which the molar ratio Z:Q is greater than n^{-1} , n being the valency of the metal Z.
6. Process according to any one of the preceding claims wherein both stages are carried out in series flow.
7. Process according to any one of the preceding claims wherein the first stage is operated at a temperature from 30 °C to 100 °C.
8. Process according to any one of the preceding claims wherein the second stage is operated at a temperature which is at least 100 °C above the operating temperature of the first stage.
9. Process according to any one of the preceding claims wherein the second stage is operated at a temperature from 150 °C to 330 °C, in particular from 180 °C to 300 °C.

Revendications

1. Procédé de conversion catalytique en deux étapes d'une charge d'alimentation contenant des oléfines, selon lequel on met en contact la charge d'alimentation, dans une première étape, dans des conditions pratiquement non oligomérisantes comprenant une température de 20 à 150 °C, avec un catalyseur comprenant au moins un métal (X) choisi parmi les métaux des groupes 1a, 1b, 2a, 2b, 4b, 5b, 6b et 8

TABLE

Experiment	Test No.	Activity x 100
1	1	1.30
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10 1	3	1.26
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1	5	1.00

From the results given in the Table it is clear that in Experiment 1 according to the invention the catalyst is very stable whereas its stability decreases substantially in comparative Experiment 2.

Claims

1. Process for two-stage catalytic conversion of an olefins-containing feed wherein the feed is contacted in a first stage under substantially non-oligomerizing conditions comprising a temperature from 20 to 150 °C, with a catalyst comprising at least one metal (X) selected from the group consisting of metals from Groups 1a, 1b, 2a, 2b, 4b, 5b, 6b and 8 of the Periodic Table of the Elements and effluent from the first stage is contacted in the second stage under olefin oligomerization conditions at a temperature which is at least 50 °C above the operating temperature of the first stage with a catalyst comprising at least one metal (Z) selected from the group consisting of metals from Groups 1b, 2a, 2b, 4b, 5b, 6b and 8 on a mordenite-type of crystalline trivalent metal (Q) silicate.
2. Process according to claim 1 wherein the metals X and Z are the same.
3. Process according to claim 1 or 2 wherein the metal Z represents nickel.
4. Process according to any one of the preceding claims wherein mordenite is used as catalyst carrier in both stages.
5. Process according to any one of the preceding claims wherein a catalyst is used in the second stage in which the molar ratio Z:Q is greater than n^{-1} , n being the valency of the metal Z.
6. Process according to any one of the preceding claims wherein both stages are carried out in series flow.
7. Process according to any one of the preceding claims wherein the first stage is operated at a temperature from 30 °C to 100 °C.
8. Process according to any one of the preceding claims wherein the second stage is operated at a temperature which is at least 100 °C above the operating temperature of the first stage.
9. Process according to any one of the preceding claims wherein the second stage is operated at a temperature from 150 °C to 330 °C, in particular from 180 °C to 300 °C.

Revendications

1. Procédé de conversion catalytique en deux étapes d'une charge d'alimentation contenant des oléfines, selon lequel on met en contact la charge d'alimentation, dans une première étape, dans des conditions pratiquement non oligomérisantes comprenant une température de 20 à 150 °C, avec un catalyseur comprenant au moins un métal (X) choisi parmi les métaux des groupes 1a, 1b, 2a, 2b, 4b, 5b, 6b et 8



du Tableau Périodique des Éléments, et on met en contact dans la deuxième étape, l'effluent issu de la première étape, dans des conditions d'oligomérisation d'oléfine, à une température qui est d'au moins 50 °C supérieure à la température de traitement dans la première étape, avec un catalyseur comprenant au moins un métal (Z) choisi parmi les métaux des groupes 1b, 2a, 2b, 4b, 5b, 6b et 8, sur un silicate cristallin de métal trivalent (Q) du type mordenite.

2. Procédé selon la revendication 1, dans lequel les métaux X et Z sont les mêmes.
3. Procédé selon la revendication 1 ou 2, dans lequel le métal Z représente le nickel.
4. Procédé selon l'une quelconque des revendications précédentes, dans lequel on emploie de la mordenite comme support de catalyseur dans les deux étapes.
5. Procédé selon l'une quelconque des revendications précédentes, dans lequel on emploie un catalyseur dans la deuxième étape, dans lequel le rapport Z:Q est supérieur à n^{-1} , n étant la valence du métal Z.
6. Procédé selon l'une quelconque des revendications précédentes, dans lequel les deux étapes sont effectuées en série.
7. Procédé selon l'une quelconque des revendications précédentes, dans lequel la première étape est effectuée à une température de 30 °C à 100 °C.
8. Procédé selon l'une quelconque des revendications précédentes, dans lequel la deuxième étape est effectuée à une température qui est d'au moins 100 °C supérieure à la température de traitement dans la première étape.
9. Procédé selon l'une quelconque des revendications précédentes, dans lequel la deuxième étape est effectuée à une température de 150 °C à 330 °C, en particulier de 180 °C à 300 °C.

Patentansprüche

1. Verfahren zur zweistufigen katalytischen Umwandlung eines Olefine enthaltenden Einsatzmaterials, wobei das Einsatzmaterial in einer ersten Stufe unter im wesentlichen nicht-oligomerisierenden Bedingungen, umfassend eine Temperatur von 20 bis 150 °C, mit einem Katalysator in Kontakt gebracht wird, der wenigstens ein Metall (X), ausgewählt aus der aus Metallen der Gruppen 1a, 1b, 2a, 2b, 4b, 5b, 6b und 8 des Periodensystems der Elemente bestehenden Gruppe, umfaßt und der Abstrom aus der ersten Stufe in der zweiten Stufe unter Olefin-Oligomerisationsbedingungen bei einer Temperatur, die um wenigstens 50 °C über der Betriebstemperatur der ersten Stufe liegt, mit einem Katalysator in Berührung gebracht wird, der wenigstens ein Metall (Z), ausgewählt aus der aus Metallen der Gruppen 1b, 2a, 2b, 4b, 5b, 6b und 8 bestehenden Gruppe, auf einem kristallinen Silikat eines dreiwertigen Metalles (Q) vom Mordenit-Typus umfaßt.
2. Verfahren nach Anspruch 1, worin die Metalle X und Z gleich sind.
3. Verfahren nach Anspruch 1 oder 2, worin das Metall Z Nickel bedeutet.
4. Verfahren nach einem der vorstehenden Ansprüche, worin in beiden Stufen Mordenit als Katalysatorträger verwendet wird.
5. Verfahren nach einem der vorstehenden Ansprüche, worin in der zweiten Stufe ein Katalysator verwendet wird, worin das Molverhältnis Z:Q größer als n^{-1} ist, wobei n die Wertigkeit des Metalles Z darstellt.
6. Verfahren nach einem der vorstehenden Ansprüche, worin beide Stufen in Reihenströmung ausgeführt werden.
7. Verfahren nach einem der vorstehenden Ansprüche, worin die erste Stufe bei einer Temperatur von 30 °C bis 100 °C betrieben wird.



8. Verfahren nach einem der vorstehenden Ansprüche, worin die zweite Stufe bei einer Temperatur betrieben wird, die um wenigstens 100 °C über der Betriebstemperatur der ersten Stufe liegt.
9. Verfahren nach einem der vorstehenden Ansprüche, worin die zweite Stufe bei einer Temperatur von 150 °C bis 330 °C, insbesondere von 180 °C bis 300 °C ausgeführt wird.

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