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(54) **Process for preparing normally liquid hydrocarbons.**

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Description

The present invention relates to a process for preparing normally liquid hydrocarbons from a hydrocarbonaceous feedstock comprising olefins containing 2-6 carbon atoms and to hydrocarbons obtained in such process.

From US patent specification 4,827,069 a process is known for the conversion of light olefinic gas and catalytic reformate, comprising contacting the feedstock at a temperature of from 316 to 399 °C with a fluidized bed of zeolite catalyst. The fluidized bed is maintained by passing feed vapour upwardly through the fluidized catalyst bed under turbulent flow conditions. Coked catalyst is continuously withdrawn from the reaction zone, oxidatively regenerated and the regenerated catalyst is returned to the reaction zone. In South African patent specification No. 892236 an olefin oligomerization process is described, which process is carried out with the help of a slurry containing catalysts comprising an amorphous solid catalyst support.

In US patent specification 3,515,769, a process is described for polymerizing olefinic hydrocarbons at a temperature from 0 to 450 °C and at a pressure in the range of from about 1 to about 200 atmospheres, using a catalyst comprising crystalline aluminosilicate chemically combined with aluminium subfluoride or silicon subfluoride.

It has now surprisingly been found that a better catalyst stability can be attained by passing feedstock at a temperature of from 150 to 295 °C upwardly through a reactor containing catalyst particles comprising a crystalline support, which catalyst particles stay in the reactor for at least 1 hour at reaction conditions. A better catalyst stability results in that the desired conversion level can be attained during a longer time. Further, it has been found that in such process exothermal heat which is produced in the process, can more easily be withdrawn.

The invention therefore relates to a process for preparing normally liquid hydrocarbons from a hydrocarbonaceous feedstock comprising olefins containing 2-6 carbon atoms, which process comprises passing the feedstock upwardly at elevated pressure and at a temperature of from 150 to 295 °C through a reactor containing catalyst particles comprising a crystalline support, which catalyst particles stay in the reactor for at least 1 hour at reaction conditions.

The process is preferably carried out at a temperature from 180 °C to 295 °C, and more preferably at a temperature from 180 to 280 °C. Further, the process is preferably carried out at a pressure of from 2 to 100 bar, more preferably of from 10 to 50 bar and at a space velocity of from 0.1 to 10 kg feed/kg catalyst.hour, more preferably of from 0.2 to 5 kg feed/kg catalyst.hour.

In the process according to the present invention the feedstock is passed upwardly through a reactor. By "upwardly" is understood that the feedstock is inserted in the reactor at a place situated below the one where the product is withdrawn from the reactor. Different kinds of catalyst beds can be used in such process, e.g. a fixed bed or a fluidized bed. By a fixed bed is understood a catalyst bed having a catalyst volume density in the catalyst bed of from 0.45 to 0.70, catalyst volume density being the fraction of the volume of the catalyst bed which is taken up by catalyst particles, the internal pore volume of the catalyst particles not being taken into account; more preferably the fixed bed has a catalyst volume density of from 0.50 to 0.65. By fluidized bed is understood a catalyst bed having a catalyst volume density of from 0.35 to 0.50. Preferably, for reasons of process economy, the process is carried out in a fixed bed of catalyst particles.

The process according to the invention is preferably carried out at such process conditions that the formation of substantial gas bubbles, e.g. as in pulse flow, is prevented. A description of pulse flow is given in the article by Fukushima and Kusaka, J. Chem. Eng. Japan, vol.12, 296, 1979.

The catalyst suitably used comprises a crystalline refractory oxide, optionally containing a metal selected from the Group 1b, 2a, 2b, 4b, 5b, 6b, 7b and 8 metals of the Periodic Table of the Elements, preferably a Group 8 metal such as nickel. Crystalline supports are understood to have their atoms or molecules arranged in a regularly ordered structure as observed by diffraction techniques. Preferably, the catalyst contains a crystalline aluminosilicate. Suitable refractory oxides are faujasite, zeolite-L, ferrierite, mordenite, zeolite-beta, ZSM-5, ZSM-8, ZSM-11, ZSM-12, ZSM-20, ZSM-21 and ZSM-35; most suitably ZSM-5 and/or mordenite are applied. The following compounds can suitably be used as catalysts: mordenite in the hydrogen form, optionally comprising nickel, and/or ZSM-5 in the hydrogen form, optionally comprising nickel. The amount of metal present on the catalyst can be up to 20% by weight (%wt), based on the amount of refractory oxide, suitably from 0.1 to 20 %wt, preferably from 0.1 to 10 %wt. The catalyst may further contain binder, such as alumina, in an amount ranging from 10 to 80% by weight, based on total amount of catalyst including binder.

Due to the fact that in the process according to the present invention an improved catalyst stability is obtained, the catalyst will not need continuous regeneration. Therefore the catalyst particles can stay in the reactor at reaction conditions for at least 1 hour, suitably more than 10 hours, preferably more than 100 hours.

A wide variety of olefinic hydrocarbons containing from 2-6 carbon atoms can be employed in the process according to the present invention. Preferably, the feedstock consists for more than 50% by weight of olefins containing 2-6 carbon atoms, such as ethene, propene, n-butenes, isobutene, n-pentenes, isopentenes, n-hexenes and isohexenes; in addition to said olefins, hydrocarbons such as (cyclic) paraffins and mono-olefins having more than six carbon atoms per molecule can be present in the feedstock.

Special preference is given to propene- and/or butene-containing feedstocks which are suitably obtained in (fluid) catalytic cracking processes, thermal cracking processes, coking- and/or pyrolysis processes.

Suitable feedstocks 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 olefins containing from 2-6 carbon atoms. 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 olefins containing 2-6 carbon atoms.

With the expression "normally liquid hydrocarbons", which are prepared in the process according to the present invention, are meant hydrocarbons which are in the liquid phase at a temperature of 15 °C and atmospheric pressure. Such liquid hydrocarbons include products boiling in the gasoline range (40-150 °C), in the middle distillate range (kerosene- and gasoil fractions boiling from 150-370 °C) and in the lubricating base oil range (above 370 °C). Part of the product obtained in the process, e.g. products boiling below the gasoline boiling range and unconverted feedstock, if any, can be separated from the normally liquid products, combined with the feedstock and again passed through the reactor.

Furthermore, it is preferred to process the feedstock according to the present invention, separate the effluent obtained into at least two fractions of which at least one has a boiling range above that of the olefins present in the feedstock and recycle at least part of such fraction to the process, as described in European patent publication 0334428. The part of the fraction being recycled to the first stage can be a relatively light part or a relatively heavy part.

The process according to the invention is illustrated by the following Examples.

EXAMPLE I

A hydrocarbonaceous feedstock comprising 50% by weight (%wt) of butene and 50 %wt of butane, was passed upwardly through a reactor comprising a catalyst containing nickel on mordenite in the hydrogen form, the amount of nickel present being 11.5 %wt of nickel based on amount of mordenite, which catalyst further contained 20 %wt of alumina, based on amount of total catalyst. The catalyst volume density was 0.54. The process was carried out at a temperature of 215 °C, a pressure of 32 bar and a WHSV of 1 (kg/kg.hr) (weight feedstock/weight catalyst). After 170 hours on stream, 71 %wt of the butene present in the feedstock was observed to be converted into normally liquid hydrocarbons.

Comparative Experiment I

A comparative experiment was carried out in which a process substantially as described in Example I was carried out at a temperature of 300 °C and a pressure of 35 bar. After 170 hours on stream, 30 %wt of the butene present in the feedstock was observed to be converted into normally liquid hydrocarbons.

EXAMPLE II

A hydrocarbonaceous feedstock comprising 50 %wt of butene and 50 %wt of butane, was passed upwardly through a reactor comprising a catalyst containing mordenite in the hydrogen form. The catalyst volume density was 0.54. The process was carried out at a temperature of 215 °C, a pressure of 31 bar and a WHSV of 2.5 (kg/kg.hr) (weight feedstock/weight catalyst). After 260 hours on stream 45 %wt of the butene present in the feedstock was observed to be converted into normally liquid hydrocarbons.

EXAMPLE III

A hydrocarbonaceous feedstock comprising 50 %wt of butene and 50 %wt of butane, was passed upwardly through a reactor comprising a catalyst containing nickel on mordenite in the hydrogen form, the amount of nickel present being 10.3 %wt of nickel based on amount of mordenite, which catalyst further contained 20 %wt of alumina based on amount of total catalyst. The catalyst was present as a fixed bed during operation. The process was carried out at a temperature of 215 °C, a pressure of 30 bar and a WHSV of 1 (kg/kg.hr) (weight feedstock/weight catalyst). After 210 hours on stream, 76 %wt of the butene present in the feedstock was observed to be converted into normally liquid hydrocarbons.

Comparative Experiment III

A comparative experiment was carried out in which a process substantially as described in Example III was carried out, differing in that the feedstock was passed downwardly through the reactor. After 210 hours on stream, 30 %wt of the butene present in the feedstock was observed to be converted into normally liquid hydrocarbons.

EXAMPLE IV

A hydrocarbonaceous feedstock comprising 50 %wt of butene and 50 %wt of butane, was passed upwardly though a reactor comprising a catalyst containing nickel on mordenite in the hydrogen form, the amount of nickel present being 10 %wt of nickel based on amount of mordenite. The catalyst was present as a fixed bed during operation. The process was carried out at a temperature of 215 °C, a pressure of 30 bar and a WHSV of 1 (kg/kg.hr) (weight feedstock/weight catalyst). After 160 hours on stream, 75 %wt of the butene present in the feedstock was observed to be converted into normally liquid hydrocarbons.

Claims

1. Process for preparing normally liquid hydrocarbons from a hydrocarbonaceous feedstock comprising olefins containing 2-6 carbon atoms, which process comprises passing the feedstock upwardly at elevated pressure and at a temperature of from 150 to 295 °C through a reactor containing catalyst particles comprising a crystalline support, which catalyst particles stay in the reactor for at least 1 hour at reaction conditions.

2. Process according to claim 1, wherein the process is carried at a temperature of from 180 to 280 °C.

3. Process according to claim 1 and/or 2, wherein the catalyst contains a crystalline aluminosilicate.

4. Process according to claim 3, wherein the crystalline aluminosilicate is ZSM-5.

5. Process according to claim 3, wherein the crystalline aluminosilicate is mordenite.

6. Process according to any one of claims 1-5, wherein the catalyst contains nickel.

7. Process according to any one of claims 1-6, wherein the crystalline aluminosilicate is in the hydrogen form.

8. Process according to any one of claims 1-7, wherein the catalyst volume density is from 0.50 to 0.65.

9. Process according to any one of claims 1-8, wherein the effluent obtained is separated into at least two fractions of which at least one has a boiling range above that of the olefins present in the feedstock and at least part of such fraction is recycled to the process.

Patentansprüche

1. Verfahren zur Herstellung normalerweise flüssiger Kohlenwasserstoffe aus einem kohlenwasserstoffhaltigen Ausgangsmaterial, umfassend Olefine mit 2 bis 6 Kohlenstoffatomen, welches Verfahren das Leiten des Ausgangsmaterials bei erhöhtem Druck und einer Temperatur von 150 bis 295 °C in Aufwärtsrichtung durch einen Reaktor, der Katalysatorteilchen, umfassend einen kristallinen Träger enthält, welche Katalysatorteilchen mindestens 1 Stunde lang bei Reaktionsbedingungen im Reaktor verbleiben, umfaßt.

2. Verfahren nach Anspruch 1, in welchem das Verfahren bei einer Temperatur von 180 bis 280 °C durchgeführt wird.

3. Verfahren nach Anspruch 1 und/oder 2, in welchem der Katalysator ein kristallines Aluminosilikat enthält.

4. Verfahren nach Anspruch 3, in welchem das kristalline Aluminosilikat ZSM-5 ist.

5. Verfahren nach Anspruch 3, in welchem das kristalline Aluminosilikat Mordenit ist.

6. Verfahren nach einem der Ansprüche 1 bis 5, in welchem der Katalysator Nickel enthält.

7. Verfahren nach einem der Ansprüche 1 bis 6, in welchem das kristalline Aluminosilikat in der Wasserstofform vorliegt.

8. Verfahren nach einem der Ansprüche 1 bis 7, in welchem die Katalysatorvolumendichte 0,50 bis 0,65 beträgt.

9. Verfahren nach einem der Ansprüche 1 bis 8, in welchem der erhaltene Abstrom in mindestens 2 Fraktionen aufgetrennt wird, von welchen mindestens eine einen Siedebereich oberhalb der im Ausgangsmaterial vorliegen-

den Olefine aufweist, und mindestens ein Teil einer solchen Fraktion zum Verfahren im Kreislauf rückgeführt wird.

Revendications

1. Procédé pour la préparation d'hydrocarbures normalement liquides à partir d'une charge brute hydrocarbonée comportant des oléfines renfermant de 2 à 6 atomes de carbone, procédé selon lequel on transfère la charge brute vers le haut sous une pression élevée et à une température de 150 à 295 °C à travers un réacteur renfermant des particules de catalyseur comportant un support cristallin, ces particules de catalyseur séjournant dans le réacteur pendant au moins une heure sous des conditions de réaction.

2. Procédé selon la revendication 1, dans lequel le procédé est mis en oeuvre à une température de 180 à 280 °C.

3. Procédé selon la revendication 1 et/ou 2, dans lequel le catalyseur renferme un aluminosilicate cristallin.

4. Procédé selon la revendication 3, dans lequel l'aluminosilicate cristallin est la ZSM-5.

5. Procédé selon la revendication 3, dans lequel l'aluminosilicate cristallin est la mordénite.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel le catalyseur renferme du nickel.

7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel l'aluminosilicate cristallin est sous forme hydrogène.

8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel la densité volumique du catalyseur est de 0,50 à 0,65.

9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel l'effluent obtenu est séparé en au moins deux fractions dont au moins une présente une gamme d'ébullition au-dessus de celles des oléfines présentes dans la charge brute et au moins une partie de cette fraction est recyclée dans le procédé.