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(54) **PROCESS FOR THE OLIGOMERIZATION OF ALKENES**

VERFAHREN ZUR OLIGOMERISATION VON ALKENEN

PROCEDE D'OLIGOMERISATION D'ALCENES

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Description

[0001] The present invention relates to a process for the oligomerization of light alkenes, in particular butenes, in the presence of ZSM-5 zeolite catalysts, to diesel oil and lubricating oil fractions having improved properties, in particular an improved cetane number and an improved viscosity index.

[0002] Light alkenes can be oligomerized to heavier hydrocarbons by using acid-form zeolites. The temperature must be sufficiently high (above 170 °C), and in terms of oligomerization it is also preferable to use a high pressure. Although hydrocarbons of the gasoline grade (boiling at temperatures below 180 °C) are always also formed as an oligomerization product, it makes sense in the oligomerization of light alkenes to maximize the proportion of more valuable products, such as high-quality diesel oil, paraffinic solvents, and lubricating oils.

[0003] When alkenes are oligomerized by using a zeolite catalyst, the cold properties of the product are usually good. However, the quality of the products is strongly affected by the degree of branching of the products. If the catalyst used is a non-form-selective catalyst, branching is vigorous. Branching lowers the cetane number of diesel oil and the value of the viscosity index of lubricating oil. Thus it is preferable to use a form-selective zeolite catalyst by means of which the degree of branching of the oligomerization products can be lowered. Especially suitable catalysts include zeolite catalysts having a pore size close to the ZSM-5 pore size (5.1*5.5 Å). The use of HZSM-5 catalyst as an oligomerization catalyst is also justified by its low coke forming and its stability at high temperatures. The quality and yield of the oligomerization products can be affected by modifying either the reaction conditions or the properties of the oligomerization catalyst.

[0004] The use of HZSM-5 zeolite as an oligomerization catalyst is generally known. The properties of HZSM-5 zeolite have been affected, for example, by modifying its aluminum content and particle size (US 4 517 399), the number of metal ions in the crystal (US 4 554 396) and at ion exchange sites (US 4 542 251). Furthermore, the acidity distribution of HZSM-5 zeolite has been modified, for example, by dealuminization (US 5 043 307) or by selective destruction of acid sites on the outer surface (US 4 520 221).

[0005] It is also known to modify ZSM-5 zeolites used in oligomerization by replacing a certain number of the original cations with, for example, Zn, Ni, Pt, Pd, Re, and Cr cations. Typically such replacing is carried out by the ion exchange technique, in which the zeolite is treated with a dilute aqueous solution of a salt containing the substituting cation. Thus, for example, from US patent 3 960 978 there are known ZSM-5 catalysts which contain small amounts of chromium and zinc and which have been applied to the oligomerization of light alkenes, mainly propylene, to gasoline fractions.

[0006] The present invention relates to a process for the oligomerization of light alkenes, in particular butenes, by using chromium-containing HZSM-5 zeolites as the catalyst. According to the invention it has been observed, surprisingly, that when at least a certain amount of chromium is added to HZSM-5 zeolite and the catalyst thus obtained is used for the oligomerization of light alkenes, in particular butenes or butene-containing hydrocarbon blends, fractions suitable for diesel and lubricating oils and having a substantially improved cetane number and an improved viscosity index are obtained, with a good yield.

[0007] The process according to the invention is mainly characterized by the characteristics stated in Claim 1.

[0008] It is not possible to obtain by ion exchange the desired quantity of chromium ions from a liquid phase to ZSM-5 zeolite, since they form large-sized complexes with water molecules. Therefore, according to the invention, chromium is added to HZSM-5 zeolite by two alternative procedures. In the impregnation technique the zeolite is treated with a chromium salt solution the volume of which at maximum corresponds to the combined pore volume of the zeolite. Preferably, a solution amount is used which approximately corresponds to the said pore volume. Thereafter the zeolite is calcined by a method known per se by heating it at 300-800 °C. What is in question in this case is the so-called dry impregnation technique.

[0009] According to the other alternative, the chromium salt is mixed, while dry, with zeolite to form a homogenous mixture. Thereafter the zeolite is calcined by a method known per se, whereby a portion of the cations of the zeolite are replaced with chromium. What is in question in this case is the so-called dry ion exchange technique.

[0010] The concentration of chromium in the zeolite can be regulated by changing the amount of chromium in the impregnation solution or in the solution of chromium salt and zeolite. The concentration of chromium in the zeolite may also be modified by using different chromium salts in the feedstock. According to the invention, the amount of chromium in the HZSM-5 zeolite is within a range of 0.7-5 %, preferably 1-3 % by weight, of the weight of zeolite. The chromium source used in dry impregnation may be water-soluble chromium salts, for example, chlorides or nitrates. In the dry ion exchange technique, any chromium compounds suitable for the purpose can be used.

[0011] After the adding of chromium, silica, which will render the catalyst harder and mechanically more durable, can be added to the zeolite as a carrier. The adding of silica is preferably done by mixing silica as a colloidal solution with the zeolite before the calcination of the catalyst.

[0012] If an HZSM-5 zeolite to which chromium has been added is used as the oligomerization catalyst, the cetane number of the diesel fraction of the obtained oligomerization product is considerably higher than if the corresponding

HZSM-5 zeolite is used as the catalyst. Respectively, the viscosity index of the lubricating oil fraction of the oligomerization product is high.

[0013] By the process according to the invention it is possible to oligomerize light alkenes, such as C₂-C₆ alkenes and blends thereof. The feedstocks may be pure or they may be refinery streams containing various alkenes and alkanes. The process according to the invention is advantageous for the oligomerization of hydrocarbon blends containing butenes to diesel oil and lubricating oil fractions.

[0014] The oligomerization is usually performed at a temperature of 160-350 °C, preferably 200-310 °C, preferably at a pressure of 10-80 bar. The flow rates vary according to the oligomerization reactor. In a conventional tubular reactor the WHSV is usually 0.5-10, preferably approx. 1-5. The flow rates and the temperature may also be changed during the reaction in order to obtain a steady degree of conversion.

[0015] The process according to the invention can also be applied so that the catalyst is placed in two or more separate reactors. Zeolite catalysts modified in accordance with the invention can be used especially advantageously in an oligomerization apparatus according to Finnish patent application FI 925608, wherein two or more side reactors are linked to the distillation column. In this case the catalyst is placed in the side reactors, which may be in series or in parallel. Thereby substantial additional improvements in the cetane numbers and viscosity indices of the diesel oil and lubricating oil fractions are accomplished.

[0016] The invention is described below in greater detail, with reference to the accompanying examples.

Example 1

[0017] A zeolite of the ZSM-5 type was prepared by the following method, known per se (US 3 926 782). 5.25 kg of waterglass and 6.57 kg of water were mixed together. A second solution was prepared by mixing together 322 g of Al₂(SO₄)₃·18 H₂O, 657 g of tetrapropylammonium bromide, 1965 g of NaCl, 473 g of 95 % H₂SO₄ and 9 kg of water. The solutions were mixed. The combined solution was placed in an autoclave. The reaction temperature was 100 °C and the reaction time was 6 days. After a wash and calcination the sodium ions of the zeolite were replaced with ammonium ions by using an NH₄NO₃ solution, whereafter the NH₄-ZSM-5 zeolite was calcined at 500 °C for two hours. Thereby the ammonium ions were decomposed and an H-ZSM-5 zeolite was formed. The aluminum concentration in the H-ZSM-5 zeolite was 1.6 % by weight. The zeolite was screened to a particle size of 0.15-0.35 mm. This zeolite was used as the reference catalyst.

Example 2

[0018] HZSM-5 zeolite prepared in accordance with Example 1 was impregnated with a chromium nitrate solution. The HZSM-5 zeolite was dried at 400 °C. A chromium solution amount corresponding to the total pore volume of the zeolite was added to dry HZSM-5 zeolite. Chromium was added to the zeolite at a rate of one mole per one mole of aluminum in the HZSM-5 zeolite. After the adding of the chromium solution the zeolite was calcined at 500 °C for two hours. After the calcination the zeolite contained chromium 2.4 % by weight. The chromium zeolite was screened to a particle size of 0.15-0.35 mm.

Example 3

[0019] HZSM-5 zeolite prepared in accordance with Example 1 was impregnated by using a chromium chloride solution. The impregnation was performed in accordance with Example 2. After the calcination, the zeolite contained chromium 2.1 % by weight. The zeolite contained aluminum 1.5 % by weight. The chromium zeolite was screened to a particle size of 0.15-0.35 mm.

Example 4

[0020] Chromium in a solid phase was added to HZSM-5 zeolite prepared in accordance with Example 1. The chromium nitrate salt and HZSM-5 zeolite were mixed carefully. A mixture of chromium nitrate and HZSM-5 zeolite was prepared by adding one mole of chromium in the chromium nitrate per one mole of aluminum in the HZSM-5 zeolite. Thereafter the mixture was treated at 500 °C in a nitrogen flow for two hours. After the heat treatment the zeolite was washed three times with distilled water. 5 g of washing water per one gram was used in one wash. Thereafter the chromium zeolite was dried at 400 °C. After the drying the zeolite contained chromium 2.5 % by weight. The chromium zeolite was screened to a particle size of 0.15-0.35 mm.

Example 5

[0021] Chromium in a solid phase was added, in the form of chromium chloride salt, to HZSM-5 zeolite prepared in accordance with Example 1. Solid ion exchange was performed in accordance with Example 4. After drying, the zeolite contained chromium 1.7 % by weight. The zeolite contained aluminum 1.4 % by weight. The chromium zeolite was screened to a particle size of 0.15-0.35 mm.

Example 6

[0022] A sample was prepared from the zeolite described in Example 2 by adding a colloidal SiO₂ solution Ludox AS-40. 27 ml of the colloidal solution was added to 20 g of zeolite. The catalyst was formulated, dried, and crushed to a particle size of 0.15-0.35 mm, and was calcined at 500 °C. The carrier content in the catalyst was 35 % by weight.

Example 7

[0023] The zeolite of Example 1 was tested in a microreactor at a pressure of 50 bar and a temperature of 230 °C. The zeolite had been diluted with silicon carbide at a volume ratio of 1:3. The WHSV was 5 g of feedstock/h/g of catalyst. The feedstock was a stream from oil refining, having the following composition, in per cent by weight:

Propane 1.15 % by weight
Butanes 57.5 % by weight
Butenes 42.3 % by weight

[0024] The conversions of the butenes in the course of the run were as follows:

Catalyst age g feedstock/g catalyst	19.1	30.5	38.0	121.4	134.0	142.9	153.0
Conversion, wt. %	99	99	99	96	93	93	92

[0025] The GC cetane number was determined from the samples collected. The GC cetane number is a value calculated on the basis of a GC analysis and corresponding to the cetane number. The GC cetane numbers determined from the samples were 48-49. The amount of coke which had formed in the catalyst was 11 % by weight.

Example 8

[0026] The zeolite of Example 2 was tested in a microreactor in a manner corresponding to that in Example 7. The catalyst age being 39 g of feedstock/g of catalyst, the WHSV was changed from a value of 5 to a value of 2 g of feedstock/h/g of catalyst.

[0027] The conversions of the butenes in the course of the run were as follows:

Catalyst age g feedstock/g catalyst	19.1	29.0	38.9	91.0	97.7	102.3
Conversion, wt. %	73	67	65	74	84	92

[0028] The GC cetane numbers determined from the samples were 52-53. The amount of coke which had formed in the catalyst was 9 % by weight.

Example 9

[0029] The zeolite of Example 3 was tested in a microreactor in a manner corresponding to that in Example 7. When the catalyst age was 119 g of feedstock/g of catalyst, the WHSV was changed from a value of 5 to a value of 3 g of feedstock/h/g of catalyst.

[0030] The conversions of the butenes in the course of the run were as follows:

Catalyst age g feedstock/g catalyst	20.9	31.2	42.4	118.5	127.6	132.9	139.1
Conversion, wt. %	91	89	87	83	88	91	92

[0031] The GC cetane numbers determined from the samples were 50-51. The amount of coke which had formed in the catalyst was 12 % by weight.

Example 10

[0032] The zeolite of Example 4 was tested in a microreactor in a manner corresponding to that in Example 7.

[0033] The conversions of the butenes in the course of the run were as follows:

Catalyst age g feedstock/g catalyst	21.5	31.4	40.1	117.0	126.6	137.6	147.3
Conversion, wt. %	99	99	99	95	91	91	89

[0034] The GC cetane numbers determined from the samples were 48-49. The amount of coke which had formed in the catalyst was 10 % by weight.

Example 11

[0035] The zeolite of Example 5 was tested in a microreactor in a manner corresponding to that in Example 7. The conversions of the butenes in the course of the run were as follows:

Catalyst age g feedstock/g catalyst	21.6	31.8	39.4	120.0	136.5	146.6	
Conversion, wt. %	98	96	94	85	76	72	

[0036] The GC cetane numbers determined from the samples were 49-50. The amount coke which had formed in the catalyst was 9 % by weight.

Example 12

[0037] The catalyst of Example 6 was tested in a bench-scale oligomerization apparatus which was made up of a distillation column and side reactors linked to it. The reaction apparatus has been described in patent application FI 925608. The apparatus has a distillation column and two or more side reactors. Fresh feedstock and recycled feedstock are fed to the side reactors from different heights of the distillation column. The pressure in the column is typically below 5 bar and the pressure in the reactors typically above 50 bar. Three side reactors were used in the bench-scale test. Two of the reactors were coupled in series, and each contained 60 g of HZSM-5 catalyst. A feedstock having in the main a distillation cut point below 200 °C was fed from the distillation column to the first of these reactors. In addition, a refinery feedstock in accordance with Example 7 was fed to both of the reactors. The third reactor contained 120 g of a catalyst prepared in accordance with Example 6. A feedstock having in the main a distillation cut range of 120-150 °C was fed from the distillation column to this reactor. In addition, a refinery feedstock which contained propane 20 % by weight and propene 80 % by weight was fed to this reactor. The reactor temperatures during the runs were 210-250 °C and pressures 50 bar. The flow rate of the refinery feedstock to the first reactor coupled in series was 280 g/h. The flow rate to the second reactor coupled in series was 130 g/h. To the third reactor the refinery feedstock was fed at 150 g/h. The product obtained from the bottom of the distillation column was distilled. The results were as follows:

Distillation range, °C	TA-30	30-180	180-200	200-350	350-410	410+
Fraction, wt. %	6.0	18.5	10.6	53.9	8.6	2.5

[0038] The fraction 200-350 °C was hydrogenated. Thereafter the cetane number was determined from the product; it was 55. From the fraction 410 °C+, viscosities at 100 °C and 40 °C were determined, and the viscosity index was determined from these. The viscosity at 100 ° was 6.71 mm²/cm and at 40 °C it was 42.9 mm²/cm. The calculated viscosity index was 111. The pour point of the fraction 410 °C+ was -48 °C.

Example 13

[0039] The catalyst of Example 6 was tested in the apparatus described in Example 12. With the exception of the refinery feedstock flow rates, the conditions were the same. The flow rates of the refinery feedstock were: 280 g/h to the first reactor coupled in series, 60 g/h to the second reactor coupled in series, and 90 g/h to the third reactor. The

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product proportions obtained from the bottom of the distillation column were as follows:

Distillation range, °C	TA-30	30-180	180-200	200-350	350-410	410+
Fraction, wt. %	4.8	31.5	13.4	41.6	4.0	2.0

[0040] The fraction 200-350 °C was hydrogenated. Thereafter the cetane number was determined from the product; it was 57. From the fraction 410 °C+, viscosities at 100 °C and 40 °C were determined, and the viscosity index was then calculated from these. At 100 °C the viscosity was 7.07 mm²/cm and at 40 °C it was 47.98 mm²/cm. The calculated viscosity index was 105.

Example 14

[0041] A commercial ZSM-5 catalyst was tested in the same test apparatus, in conditions in accordance with Example 13. 90 g of catalyst had been packed into each of the two reactors coupled in series. 316 g of catalyst had been packed into the third reactor. The product proportions obtained from the bottom of the distillation column were as follows:

Distillation range, °C	TA-200	200-350	350-410	410+
Fraction, wt. %	19.7	54.7	17.5	5.0

[0042] The fraction 200-350 °C was hydrogenated. Thereafter the cetane number was determined from the product; it was 53. From the fraction 410 °C+, viscosities at 100 °C and 40 °C were determined, and the viscosity index was then calculated from these. At 100 °C the viscosity was 7.54 mm²/cm and at 40 °C it was 55.206 mm²/cm. The calculated viscosity index was 98. The pour point was -45 °C.

Example 15

[0043] The catalyst of Example 6 was tested in the apparatus described in Example 12. With the exception of the refinery feedstock flow rates, the conditions were the same. The flow rates of the refinery feedstock were: 180 g/h to the first reactor coupled in series, 130 g/h to the second reactor coupled in series, and 90 g/h to the third reactor. The product proportions obtained from the bottom of the distillation column were as follows:

Distillation range, °C	TA-30	30-180	180-200	200-350	350-410	410+
Fraction, wt. %	3.5	20.2	8.6	57.3	7.4	2.5

[0044] The fraction 200-350 °C was hydrogenated. Thereafter the cetane number was determined from the product; it was 55. From the fraction 410 °C+, viscosities at 100 °C and 40 °C were determined, and the viscosity index was then calculated from these. At 100 °C the viscosity was 5.6 mm²/cm and at 40 °C it was 32.4 mm²/cm. The calculated viscosity index was 111.

Example 16

[0045] The catalyst of Example 6 was tested in the apparatus described in Example 12. With the exception of the refinery feedstock flow rates, the conditions were the same. The flow rates of the refinery feedstock were: 180 g/h to the first reactor coupled in series, 60 g/h to the second reactor coupled in series, and 150 g/h to the third reactor. The product proportions obtained from the bottom of the distillation column were as follows:

Distillation range, °C	TA-30	30-180	180-200	200-350	350-410	410+
Fraction, wt. %	6.7	23.6	11.0	51.8	4.1	2.4

[0046] The fraction 200-350 °C was hydrogenated. Thereafter the cetane number was determined from the product; it was 55. From the fraction 410 °C+, viscosities at 100 °C and 40 °C were determined, and the viscosity index was then calculated from these. At 100 °C the viscosity was 7.03 mm²/cm and at 40 °C it was 47.5 mm²/cm. The calculated viscosity index was 105. The pour point of the fraction 410 °C+ was -48 °C.

Example 17

[0047] A commercial ZSM-5 catalyst was tested in the same test apparatus, in conditions in accordance with Example 16. 90 g of catalyst had been packed into each of the reactors coupled in series. 300 g of catalyst had been packed into the third reactor. The product proportions obtained from the bottom of the distillation column were as follows:

Distillation range, °C	TA-200	200-350	350-410	410+
Fraction, wt. %	16.2	68.1	7.8	5.6

[0048] The fraction 200-350 °C was hydrogenated. Thereafter the cetane number was determined from the product; it was 51. From the fraction 410 °C+, the viscosities at 100 °C and 40 °C were determined, and the viscosity index was then calculated from these. At 100 °C the viscosity was 7.84 mm²/cm and at 40 °C it was 62.9 mm²/cm. The calculated viscosity index was 87. The pour point was -42 °C.

Example 18

[0049] The catalysts of Example 16 were regenerated at 500 °C, until all the coke had been removed from the catalysts. The test runs with regenerated catalysts were performed in the reactor apparatus described in Example 12. The regenerated catalysts were packed as follows: 60 g of a regenerated catalyst prepared in accordance with Example 6 was packed into each of the two reactors coupled in series. 120 g of HZSM-5 catalyst was packed into the third reactor. A feedstock having in the main a distillation cut range of 30-200 °C was fed from the distillation column into the reactor into which 120 g of catalyst had been packed. In addition, refinery feedstock in accordance with Example 7 was fed to the reactor at 500 g/h. A feedstock having in the main a distillation cut range of 120-150 °C was fed at 500 g/h to the first reactor coupled in series. In addition, refinery feedstock in accordance with Example 12 was fed at 80 g/h to each of the reactors coupled in series. The temperatures in the reactors were within the range 230-280 °C. The pressure in the reactors was 50 bar. The composition of the product obtained from the bottom of the distillation column was as follows:

Distillation range, °C	TA-30	30-180	180-200	200-350	350-410	410+
Fraction, wt. %	1.7	16.7	47.6	21.0	8.1	3.7

[0050] The fraction 200-350 °C was hydrogenated. Thereafter the cetane number was determined from the product; it was 55. From the fraction 410 °C+, viscosities at 100 °C and 40 °C were determined, and the viscosity index was then calculated from these. At 100 °C the viscosity was 5.077 mm²/cm and at 40 °C it was 27.588 mm²/cm. The calculated viscosity index was 112. The pour point was -57 °C.

Claims

1. A process for the oligomerization of light alkenes, in particular butenes, for the purpose of preparing diesel oil and lubricating oil fractions having an improved cetane number and an improved viscosity index, in the presence of a ZSM-5 zeolite catalyst at temperature and pressure conditions which maintain oligomerization, **characterized in that** the catalyst used is an HZSM zeolite containing chromium in an amount of 0.7-5 % by weight of the weight of the zeolite.
2. The process according to Claim 1, **characterized in that** the HZSM-5 zeolite contains chromium 1-3 % by weight.
3. The process according to Claim 1 or Claim 2 for the oligomerization of hydrocarbons or hydrocarbon blends containing light alkenes, in particular butenes, to diesel oil and lubricant oil fractions having a high cetane number and a high viscosity index, **characterized in that** the catalyst is placed in one or several side reactors in connection with a distillation column.
4. The process according to Claim 3, **characterized in that** a portion of the catalyst is chromium-modified HZSM-5 zeolite and a portion is non-modified ZSM-5 zeolite.
5. The process according to any of claims 1 to 4, **characterized in that** the catalyst contains silica as a carrier.

Patentansprüche

1. Verfahren zur Oligomerisierung von leichten Alkenen, insbesondere Butenen, zum Zwecke der Herstellung von Dieselöl und Schmierölfractionen mit verbesserter Cetanzahl und verbessertem Viskositätsindex in der Gegenwart von ZSM-5 Zeolith-Katalysator bei Temperatur- und Druckbedingungen, welche die Oligomerisierung aufrechterhalten, **dadurch gekennzeichnet**, daß der verwendete Katalysator HZSM Zeolith, der Chrom in einer Menge von 0,7-5 Gew.-%, bezogen auf das Gewicht des Zeoliths, enthält, ist.
2. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet**, daß der HZSM-5 Zeolith 1-3 Gew.-% Chrom enthält.
3. Verfahren gemäß Anspruch 1 oder Anspruch 2 zur Oligomerisierung von Kohlenwasserstoffen oder Kohlenwasserstoffgemischen, die leichte Alkene, insbesondere Butene, enthalten, zu Dieselöl und Schmierölfractionen mit hoher Cetanzahl und hohem Viskositätsindex, **dadurch gekennzeichnet**, daß der Katalysator in einem oder mehreren Nebenreaktoren in Verbindung mit einer Destillationskolonne angeordnet ist.
4. Verfahren gemäß Anspruch 3, **dadurch gekennzeichnet**, daß ein Teil des Katalysators Chrom-modifizierter HZSM-5 Zeolith und ein Teil nicht modifizierter ZSM-5 Zeolith ist.
5. Verfahren gemäß einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet**, daß der Katalysator Silica als Träger enthält.

Revendications

1. Procédé d'oligomérisation d'alcènes légers, notamment des butènes, afin de préparer des fractions d'huile diesel et d'huile lubrifiante ayant un indice amélioré de cétane et un indice amélioré de viscosité, en présence d'un catalyseur zéolitique ZSM-5 dans les conditions de température et de pression qui assurent l'oligomérisation, caractérisé en ce que le catalyseur utilisé est une zéolite HZSM contenant du chrome, selon une teneur représentant de 0,7 à 5 % en poids du poids de la zéolite.
2. Procédé selon la revendication 1, caractérisé en ce que la zéolite HZSM-5 contient de 1 à 3 % en poids de chrome.
3. Procédé selon la revendication 1 ou 2, pour l'oligomérisation d'hydrocarbures ou de mélanges d'hydrocarbures contenant des alcènes légers, notamment des butènes, pour l'obtention de fractions d'huile diesel et d'huile lubrifiante ayant un indice élevé de cétane et un indice élevé de viscosité, caractérisé en ce que le catalyseur est placé dans un ou plusieurs réacteur(s) latéral(latéraux) en liaison avec une colonne de distillation.
4. Procédé selon la revendication 3, caractérisé en ce qu'une partie du catalyseur est de la zéolite HZSM-5 modifiée par du chrome, et une partie étant de la zéolite ZSM-5 non modifiée.
5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que le catalyseur contient de la silice, en tant que support.