(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 103 302 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
11.04.2007 Bulletin 2007/15

(51) Int Cl.:
B01J 23/18 *(2006.01)* ***C07C 5/48*** *(2006.01)*
B01J 23/843 *(2006.01)*

(21) Application number: **00118101.5**

(22) Date of filing: **25.08.2000**

(54) **Oxidative dehydrogenation of paraffins**

Oxidative Dehydrierung von Paraffinen

Deshydrogènation par oxydation des paraffines

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

(30) Priority: **24.11.1999 EP 99123447**

(43) Date of publication of application:
30.05.2001 Bulletin 2001/22

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EP-A- 0 470 626	**DE-A- 2 030 699**
DE-A- 2 440 329	**DE-B- 1 238 009**

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Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

[0001] The present invention relates to a process for oxidative dehydrogenation of paraffins. It is directed to processes exhibiting very high olefin selectivity.
A number of oxidative dehydrogenation catalysts are known in this field like US Pat Nos. 5,759,946, 5,468,710, Japanese. Pat Nos. 93150371, 07010782 A2, 3-218327, German Pat No. 2,124,438, and EP Pat. No. 0557790 A2.

BACKGROUND OF THE INVENTION

[0002] Olefinic hydrocarbons are very important intermediates in the petrochemical industry. Examples of commercial production interests include ethylene, propylene, butenes, isobutene, and styrene. Substantial efforts were directed towards the production of such compounds by conventional catalytic dehydrogenation. Conventional dehydrogenation has several disadvantages, such as the need of high reaction temperature (600-800 °C), the catalyst deactivation by coke formation, the consequent need of periodic catalyst regeneration, and the thermodynamic limitation of the catalyst activity. These drawbacks can be avoided in the case of oxidative dehydrogenation (ODH), due to the presence of oxygen in the reaction mixture. However, up to date there is no commercial catalyst system available for this purpose.

DESCRIPTION OF RELATED ART

[0003] In the US patent 5,468,710, a composition containing sulfided nickel and non-acidic alumina was used as a normal dehydrogenation catalyst of organic compounds, e.g., isobutane to give isobutene.
Isobutene and methacrolein were prepared according to the JP 07010782 A2 by treatment of isobutane with molecular oxygen in the gas phase in the presence of oxidative dehydrogenation catalyst mainly containing Mo and Bi. Isobutane, oxygen and nitrogen gas mixture was passed through a reactor containing mixed oxide catalyst of molybdenum, bismuth, iron, cobalt, cesium and silicon and oxidative dehydrogenation catalyst containing nickel and phosphorous at 440 °C to show 3,8% conversion and 13.9, 3.3 and 18.9% selectivity for isobutene, propene, and methacrolein, respectively.
In the Japanese patent 93150371 (Publication number JP 07-010782), alkali metals and alkaline earth metals containing catalysts were used for preparation of isobutene and methacrolein from isobutane with oxidative dehydrogenation catalysts and mixed oxide catalysts containing bismuth and molybdenum.

[0004] German patent 2,124,438 describes the oxidative dehydrogenation of isobutane in the presence of hydrogen iodide. The conversion of isobutane was 28% and the selectivity to isobutene was 85%. The method, however, has the disadvantage of requiring the addition of hydrogen iodide.

[0005] Japanese patent discloses oxidative dehydrogenation of propane or isobutane using a catalyst comprising tin oxide and phosphorous oxide as the main components. It also discloses a catalyst comprising indium oxide and phosphorous oxide as the main components. However, the selectivity is low; 32% at 1.4 conversion.
The US patent 5,759,946 uses a catalyst based on chromium oxide for oxidative dehydrogenation of hydrocarbons.
EP patent 0557790A2 claims a catalyst containing phosphorous oxide for producing isobutene by oxidative dehydrogenation of isobutane.
As seen from above, it is a major challenge to achieve high conversion to olefin at high selectivity, i.e. to achieve maximum yield of the desired product, while minimizing the further oxidation activity. None of the prior art references discloses or suggests catalysts, which provide high performance of the selective production of olefins from their corresponding paraffins. Accordingly, it would be desirable to produce an improved catalyst for use in the selective production of olefins from their corresponding paraffins.

[0006] EP 0 470 626 A1 (D1) discloses a catalyst for steam reforming of hydrocarbons comprising nickel as its main catalytic component supported on a refractory carrier material, the catalyst including also at least one metal selected from group IVa and Va of the periodic table. The catalyst may comprise bismuth in an amount of between 0.1 and 30% by weight.

[0007] DE 20 30 699 (D2) discloses a process for the synthesis of diolefins and aromatic hydrocarbons with a catalyst based on bismuth, nickel and oxygen.

[0008] DE 24 40 329 (D4) discloses a catalyst composition which can be used in a broad area of oxidation, ammoxidation and oxidative dehydrogenation processes. The catalyst composition therein comprises a number of metals, such as nickel, cobalt, chrome, bismuth and molybdenum.

OBJECTS OF THE INVENTION

[0009] It is an object of this invention to overcome the difficulties presented in the prior art processes for producing olefins as outlined above.

The another object of the invention is to provide a useful process for producing olefins from their corresponding paraffins selectively by performing the oxidative dehydrogenation in the presence of a catalyst comprising bismuth, nickel and alumina.

The foregoing and other objects and advantages of the invention will be set forth in or apparent from the following description.

SUMMARY OF THE INVENTION

[0010] The present invention relates to a new process for the production of olefins by the oxidative dehydrogenation of their corresponding paraffins. The reaction can be carried out at low reaction temperature with no partial oxidation product formation.

[0011] The catalyst used in the inventive process has a catalytic composition having the atomic ratios described by the empirical formula set forth below:

$$Bi_aNi\ O_b\ /Al_2O_3$$

Where:

a = 0.001 to 0,28

b = the number of oxygen required to satisfy the valency requirements of the elements present.

[0012] The numerical values of a and b represent the relative gram-atom ratios of the elements, respectively, in the catalyst composition, where b is a number required to satisfy the valence requirements of the other elements. The elements are present in combination with oxygen, preferably in the form of various oxides. Other objects as well as aspects, features and advantages of the present invention will be apparent form a study of the present specification, including the claims and specific examples.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0013] The object of the present invention is achieved by a process for the oxidative dehydrogenation of their corresponding paraffins using a supported catalyst composition, the catalyst composition having the empirical formula:

$$Bi_aNiO_b$$

where:

a = 0.001 to 0,28 and

B = the number of oxygen required to satisfy the valency requirements of the elements present.

[0014] Preferably, the support for the catalyst composition is selected from the group consisting of alumina, silica, titania, zirconia, zeolites, silicon carbides, or mixtures thereof.

[0015] More preferably, the support is alumina and, even preferably, the alumina comprises 70-98% by weight of the catalyst composition.

[0016] Finally, the hydrocarbon preferably used is iso-butane.

CATALYTIC OXIDATIVE DEHYDROGENATION

[0017] The following examples are illustrative of some of the products and methods of making and using the same falling within the scope of the present invention. They are, of course, not to be considered in any way limitative of the invention. Numerous changes and modifications can be made with respect to the invention. Illustrative examples were made for production of isobutene from isobutane.

[0018] The basic catalyst of present invention is a mixed metal oxide catalyst, which could be prepared according to any procedure well known by a skilled person in the art. Methods used to prepare representative catalyst are given below.

[0019] As used in the following examples, the following terms are defined in the following manner:

1. "W/F" is defined as the weight of the catalyst in grams divided by the flow rate of reactant stream in ml/sec measured at S.T.P.

2. "Isobutane (i-C_4H_{10}) conversion" is defined as:

$$\frac{\text{Mols i-}C_4H_{10}\text{ in feed} - \text{Mols i-}C_4H_{10}\text{ in effluent}}{\text{Mols i-}C_4H_{10}\text{ in feed}} \times 100\%$$

3. " Isobutene (i-C_4H_8) selectivity" is defined as:

$$\frac{\text{Mols i-}C_4H_8\text{ in effluent}}{\text{Mols i-}C_4H_{10}\text{ converted}} \times 100\%$$

4. "Isobutene (i-C_4H_8) yield" is defined as:

$$\frac{\text{Mols i-}C_4H_8\text{ formed}}{\text{Mols i-}C_4H_{10}\text{ in feed}} \times 100\%$$

[0020] The following conditions were employed:

- reaction temperature: 250-450 °C
- catalyst: 1 gm (2.1 cc)
- pressure: atmospheric
- W/F: 0.8 sec.
- Feed composition: isobutane/oxygen/helium: 26.5/6.6/66.9 (mol%)

CATALYST TEST

[0021] Calcined catalysts were pressed into pellets then crushed to 20-40 mesh fraction. The catalysts were tested in fixed bed quartz reactor. In each test the catalyst was pretreated in a stream of a mixture of oxygen and helium for one hour at 400 °C. Then, the feed gas was passed through the reactor at desired temperature.

[0022] After reaching the steady state, the reactor effluent was analyzed by using a modern gas chromatograph (HP 6890), equipped with both FID and TCD detectors. Activity results were calculated according to the equations given above.

Example 1 (COMPARATIVE)

[0023] The catalyst used in this example has the empirical formula of $Bi_{0.42}Ni/Al_2O_3$. It was prepared by dissolving the required amounts of nickel nitrate hexahydrate, and bismuth nitrate pentahydrate in 150 ml distilled water. Then alumina (Catapal A, from CONDEA) was added to the mixture. The formed paste was then dried at 120 °C, and calcined in air at 700 °C. After calcination and pretreatment the catalyst was tested at 250 °C. Results are summarized in table1.

Examples 2 and 3 (COMPARATIVE)

[0024] The experimental procedures of Examples 2 and 3 were essentially the same as described for Example 1 with the exception that the reaction temperature was changed to 350 °C and 450 °C, respectively Results are given in table 1.

Example 4

[0025] The catalyst used in this example has the empirical formula of $Bi_{0.28}Ni/Al_2O_3$. It was prepared by same method described in Example 1. After calcination and pretreatment the catalyst was tested at 250 °C. Results are summarized in table1.

Examples 5 and 6

[0026] The experimental procedures of Examples 5 and 6 were essentially the same as described for Example 4 with the exception that the reaction temperature was changed to 350 °C and 450 °C, respectively. Results are given in table 1.

Example 7

[0027] The catalyst used in this example has the empirical formula of $Bi_{0.07}Ni/Al_2O_3$. It was prepared by same method described in Example 1 After calcination and pretreatment the catalyst was tested at 250 °C. Results are summarized in table1.

Examples 8 and 9

[0028] The experimental procedures of Examples 8 and 9 were essentially the same as described for Example 7 with the exception that the reaction temperature was changed to 350 °C and 450 °C, respectively. Results are given in table 1.

Example 10 (COMPARATIVE)

[0029] The catalyst used in this example has the empirical formula of Ni/Al_2O_3. It was prepared by same method described in Example 1 using nickel nitrate only. After calcination and pretreatment the catalyst was tested at 330 °C. Results are summarized in table1.

Examples 11 to 13 (COMPARATIVE)

[0030] The experimental procedures of Examples 11 to 13 were essentially the same as described for Example 10 with the exception that the reaction temperature was changed to 380 °C, 420 °C and 450 °C, respectively. Results are given in table 1.

Table 1: Activity results

Example No.	T (°C)	X (%)	$i-C_4H_8$		C_3H_6		CO_x	
			Y	S	Y	S	Y	S
1	250	0.9	0.7	77.2	0.0	0.0	0.2	22.8
2	350	7.4	3.6	48.0	0.2	3.2	3.6	48.5
3	450	9.2	4.0	43.3	0.8	8.2	4.2	45.6
4	250	2.8	2.7	97.6	0.0	0.0	0.1	2.4
5	350	6.2	3.4	55.0	0.1	2.0	2.7	43.5
6	450	8.9	4.2	47.4	0.5	5.2	4,1	45.5
7	250	3.5	3.5	99.0	0.0	0.0	0.0	0.0
8	350	4.4	3.0	67.0	0.1	1.1	1.4	31.9
9	450	10.8	6.0	55.1	0.4	4.0	4.2	38.6
10	330	0.9	0.8	92.1	0.0	0.0	0.1	7.9
11	380	4.4	3.0	66.7	0.1	1.6	1.4	17.6
12	420	10.5	5.6	53.4	0.4	3.3	3.4	27.9
13	450	11.3	5.9	52.2	0.4	3.9	4.8	28.4

X: $i-C_4H_{10}$-Conversion
Y: Yield in mol %
S: Selectivity in mol %
CO_x: Carbon dioxide and carbon monoxide

[0031] As shown in the above table the nickel alumina appears to be a good catalyst for isobutane oxidative dehydro-

genation (examples 10-13). By incorporating small amount of bismuth into this catalyst, activity and selectivity towards the desired product, isobutene, could be dramatically enhanced (examples 4 to 9). Thus, in example 7, 3.5% isobutane conversion and 99% selectivity for isobutene were obtained at 250 °C using a bismuth-nickel-alumina catalyst, while 0.9% conversion at 330 °C and 92% selectivity on the nickel-alumina catalyst (Example 10).
As seen from these results, nickel-alumina catalyst is suitable for the oxidative dehydrogenation reaction. The addition of bismuth to this catalyst improves the hydrocarbon conversion, increases olefin selectivity, and lowers the reaction temperature.

[0032] The forgoing description of the preferred embodiments of the invention has been presented for purpose of illustration and obviously many modifications and variations are possible.

[0033] It is intended that the scope of the invention is defined by the claims appended hereto

[0034] The features disclosed in the foregoing description and in the claims may, both separately and in any combination thereof, be material for realising the invention in diverse forms thereof.

Claims

1. Process for the production of olefins by oxidative dehydrogenation of their corresponding paraffins using a supported catalyst composition, the catalyst composition having the empirical formula:

   Bi_aNiO_b

   where:

   a = 0.001 to 0.28 and
   b = the number of oxygen required to satisfy the valency requirements of the elements present.

2. The process of claim 1, wherein the support for the catalyst composition is selected from the group comprising alumina, silica, titania, zirconia, zeolites, silicon carbides, alone or as a mixture.

3. Process according to claim 1 or 2, wherein the support is alumina.

4. Process according to claim 3, wherein the alumina comprises 70-98% by weight of the catalyst composition.

5. The process according to any of the preceding claims, wherein the paraffin is isobutane.

Patentansprüche

1. Verfahren zur Herstellung von Olefinen durch oxidative Dehydrierung der entsprechenden Paraffine unter Verwendung einer geträgerten Katalysatorzusammensetzung mit der Summenformel:

   Bi_aNiO_b

   worin:

   a = 0,001 bis 0,28 und
   b = Zahl der Sauerstoffatome zur Erfüllung der Valenzerfordernisse der vorliegenden Elemente.

2. Verfahren nach Anspruch 1, bei dem der Träger für die Katalysatorzusammensetzung aus der Gruppe enthaltend Aluminiumoxid, Siliciumoxid, Titanoxid, Zirconiumoxid, Zeolithen und Siliciumcarbiden für sich alleine oder in Form einer Mischung ausgewählt wird.

3. Verfahren nach Anspruch 1 oder 2, bei dem es sich bei dem Träger um Aluminiumoxid handelt.

4. Verfahren nach Anspruch 3, bei dem das Aluminiumoxid 70-98 Gew.-% der Katalysatorzusammensetzung ausmacht.

5. Verfahren nach einem der vorhergehenden Ansprüche, bei dem es sich bei dem Paraffin um Isobutan handelt.

Revendications

1. Procédé de production d'oléfines par déshydrogénation oxydative de leurs paraffines correspondantes à l'aide d'une composition de catalyseur sur support, la composition de catalyseur présentant la formule empirique :

   Bi_aNiO_b

   dans laquelle :

   a = 0,001 à 0,28 et
   b = nombre d'atomes d'oxygène requis pour satisfaire les exigences de valence des éléments présents.

2. Procédé de la revendication 1, dans lequel le support pour la composition de catalyseur est choisi parmi le groupe contenant de l'alumine, de la silice, du dioxyde de titane, de la zircone, de zéolites, de carbures de silicium, seuls ou en mélange.

3. Procédé selon l'une des revendications 1 ou 2, dans lequel le support est l'alumine.

4. Procédé selon la revendication 3, dans lequel l'alumine constitue de 70 à 98 % en poids de la composition de catalyseur.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel la paraffine est l'isobutane.