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(54) **Catalysts for production of olefins by oxidative dehydrogenation**

Katalysatoren für die Herstellung von Olefinen durch oxidative Dehydrierung

Catalyseurs pour la production des oléfines par deshydrogènation oxydante

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to new catalysts for the production of olefinic hydrocarbons by oxidative dehydrogenation. More particularly, this invention relates to tungsten-based catalysts for the oxidative dehydrogenation of hydrocarbons to yield olefins, and preferably, to the production of light olefins from light hydrocarbons.

Description of the Related Art

[0002] Several publications are referenced in this application. These references describe the state of the art to which this invention pertains, and are incorporated herein by reference.

[0003] Olefinic hydrocarbons, such as ethylene, propene, butene, and isobutene, are critical intermediates in the petrochemical industry. In order to satisfy market demand, substantial efforts have been invested in the production of such compounds by conventional catalytic dehydrogenation methods. For example, U.S. Patent No. 5,468,710 to Resasco et al. describes the use of a composition containing sulfided nickel and non-acidic alumina as a catalyst for conventional dehydrogenation of organic compounds, such as isobutane, to yield the corresponding olefin.

[0004] However, conventional dehydrogenation has several disadvantages, including the need for high reaction temperatures (e.g., 550-650°C), the deactivation of the catalyst by coke formation, and the consequent need for periodic catalyst regeneration at 20-30 minute intervals throughout the process. In addition, there are thermodynamic limitations on the activity of catalysts for conventional dehydrogenation. For example, such catalysts are only 85% selective at 45-50% isobutane conversion.

[0005] As a result of these substantial drawbacks, the petroleum industry has sought a solution to the demand for olefinic hydrocarbons in the use of oxidative dehydrogenation methods. Oxidative dehydrogenation is not subject to the problems associated with conventional dehydrogenation because of the presence of oxygen in the reaction mixture. However, to date, no commercial catalyst systems are available for oxidative dehydrogenation methods.

[0006] Various methods have been used to develop such a catalyst system. For example, U.S. Patent Nos. 3,821,324; 3,933,933; and 4,164,519 describe oxidative dehydrogenation catalysts comprising titanium, at least one component selected from tungsten and molybdenum, and at least one additional component selected from phosphorus, bismuth, lead, antimony, and arsenic.

[0007] Japanese Patent Publication No. JP 07010782 describes the uses of an oxidative dehydrogenation catalyst to prepare isobutene and methacrolein. The catalyst contained molybdenum, iron, cobalt, cesium, silicon, bismuth, phosphorus, and nitrogen. A mixture of isobutane, oxygen, and nitrogen gas was passed through a reactor containing the mixed oxide catalyst at 440°C to yield the corresponding olefins, isobutene, propene, and methacrolein, at a 3.8% conversion, with 13.9, 3.3, and 18.9% selectively, respectively. Similarly, Japanese Patent Publication No. JP 93150371 describes the use of alkali metal- and alkaline earth metal-containing catalysts for the preparation of isobutene and methacrolein from isobutane. The oxidative dehydrogenation catalysts and mixed oxide catalysts contained bismuth and molybdenum.

[0008] Japanese patent 3-218327 describes the oxidative dehydrogenation of propane or isobutane using a catalyst comprising either tin oxide and phosphorous oxide as the main components, or indium oxide and phosphorous oxide as the main components. However, the selectivity was only 32% at 1.4% conversion. Similarly, U.S. Patent 5,759,946 describes a catalyst based on chromium oxide for oxidative dehydrogenation of hydrocarbons, and European Patent Publication No. EP 0557790 discloses the use of a catalyst containing phosphorous oxide for producing isobutene by oxidative dehydrogenation of isobutane. However, like the catalysts described above, these catalysts suffer from low selectivity and/or yield.

[0009] D. Stem and R. K. Grasselli (J. Catal., Volume 167, pages 570-572 (1997)) disclose the use of several metal tungstate catalysts containing cobalt, nickel, iron, zinc, and cerium for the oxidative dehydrogenation of propane. A maximum yield of 9.1 % was obtained using cobalt tungstate catalyst at a selectivity of 65.1 % and at a reaction temperature of 560°C.

[0010] Sodium tungstate in combination with hydrogen peroxide was used as a catalyst for the epoxidation of unsaturated aldehydes and carboxylic acids (see EP 434546 and Ballisteri et al., Stud. Org. Chem., Volume 33, pages 341-46 (1988)). This catalyst was also used for the epoxidation of a cyclohexene ring in various organic compounds (see also Japanese Patent Publication JP 62230778). However, to date, tungsten-based catalysts have not been used for olefin production by oxidative dehydrogenation of hydrocarbons at reasonably high selectivity.

[0011] In view of the foregoing, it is evident that the art has not succeeded in achieving high conversion at high selectivity, such that the yield of the desired olefin is maximized, as extraneous oxidative side reactions are minimized.

None of the prior art references disclose or suggest tungsten-based catalysts which provide selective production of olefins from hydrocarbons by oxidative dehydrogenation. Accordingly, it would be desirable to produce a new catalyst for use in the selective production of olefins from hydrocarbons by oxidative dehydrogenation.

SUMMARY OF THE INVENTION

[0012] The present invention provides a new highly selective catalyst system for the production of olefins by oxidative dehydrogenation of hydrocarbons. The catalyst compositions of the present invention are particularly well suited for the catalytic preparation of light olefins from light hydrocarbons, e.g., the production of isobutene and propene from isobutane. Using the improved catalyst, isobutane is oxidatively dehydrogenated in the presence of molecular oxygen at relatively high levels of conversion, selectivity, and productivity, with minimal side products, at temperatures between 350°C to 550°C. Further, the improved catalysts of the present invention can be used to produce isobutene and propene in combination at controllable ratios. Oxidative dehydrogenation using the improved catalysts can accommodate propane and isobutane as the feed stock, and product separation is less intensive because no partial oxidation product is formed. In addition, unreacted starting materials may be recycled after each separation step.

[0013] The catalyst compositions of the present invention include compositions of the formula:

$$X_xY_yWO_z$$

wherein:

X is at least one element selected from Li, Na, Rb, and Fr;
Y is Si;
x is 0.5-2.5;
y is 0.05-5; and
z is the number of oxygen atoms required to satisfy the valancy of X, Y and W in the formula. The catalysts are preferably produced using the methods disclosed herein.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0014] One aspect of the invention relates to a catalyst for the production of olefins from hydrocarbons via oxidative dehydrogenation. The catalyst composition comprises a composition of the formula as given above.

[0015] The catalyst of the present invention is durable and recyclable and it can be used with or without a support or binder. Suitable supports for the catalyst include alumina, silica, titania, zirconia, zeolites, silicon carbide, molecular sieves and other microporous or nonporous materials, and mixtures thereof. The amount of support used can be adjusted based on the application requirements of the desired application.

[0016] The catalyst composition of the invention may be used to produce olefins from hydrocarbons. In a preferred embodiment, the catalyst of the present invention may be used to produce light olefins, such as isobutene and propene at high selectivity, from light hydrocarbons, such as isobutane, in the presence of molecular oxygen at temperatures between 350°C to 550°C.

[0017] The catalyst may be used in an improved process for the combined catalytic preparation of isobutene and propene by the dehydrogenation of isobutane and propane in the presence of molecular oxygen at temperatures between 350°C to 550°C. In this regard, the method facilitates product separation because no partial oxidation products are formed using the catalyst of the present invention. Additionally, the method allows unreacted starting materials to be recycled.

[0018] Preferably, the process achieves an isobutane conversion of at least 10% per cycle, more preferably at least 12%, even more preferably at least 15%, and most preferably at least 25%. The selectivity in mol % for the production of olefins is greater than 80%, and more preferably greater than 90%. The yield of olefins in mol % per cycle is preferably greater than 10%, and more preferably greater than 20%. The total yield of olefins in mol % is preferably greater than 75%, more preferably greater than 80%, and most preferably greater than 85%.

[0019] The following examples are intended to be illustrative of this invention. They are, of course, not to be taken to in any way limit the scope of this invention. Numerous changes and modifications can be made with respect to the invention without departing from the scope of the present invention.

EXAMPLES

[0020] As used in the following examples, the terms below are defined as follows:

"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.
"Isobutane ($I\text{-}C_4H_{10}$) conversion" is defined as:

$$[(\text{Mols } I\text{-}C_4H_{10} \text{ in feed}) - (\text{Mols } I\text{-}C_4H_{10} \text{ in effluent})] \div (\text{Mols } I\text{-}C_4H_{10} \text{ in feed})] \times 100.$$

"Isobutene ($I\text{-}C_4H_8$) selectivity" is defined as:

$$[(\text{Mols } I\text{-}C_4H_8 \text{ in effluent}) \div (\text{Mols } I\text{-}C_4H_{10} \text{ converted})] \times 100.$$

"Isobutene ($I\text{-}C_4H_8$) yield" is defined as:

$$[(\text{Mols } I\text{-}C_4H_8 \text{ formed}) \div (\text{Mols } I\text{-}C_4H_{10} \text{ in feed})] \times 100.$$

Comparative Example 1

[0021] The catalyst used in this example had the empirical formula $Na_2Al_{3.8}WO_x$. It was prepared by dissolving the required amounts of sodium tungstate dihydrate (MERCK) in distilled water. Then alumina (γ-alumina, STREM CHEMICALS) was added slowly to the solution. This step led to a paste formation. The paste was then dried at 120°C, and calcined in air at 750-°C.

Comparative Example 2

[0022] The catalyst used in this example had the empirical formula $Na_2Al_2WO_x$. The protocol used to make this catalyst was essentially the same as that described in Example 1 with the exception that the catalyst preparation contained a 1:1 molar ratio of sodium tungstate to alumina.

Example 3

[0023] The catalyst used in this example had the empirical formula Na_2SiWO_x. The protocol used to make this catalyst was the same as that described in Example 2, with the exception that fumed silica (having high surface area, 390 m^2/gm, from SIGMA CHEMICAL CO.) was added instead of alumina to the tungstate solution.

Example 4

[0024] The catalyst formula and experimental procedure used to make the catalyst were essentially the same as that described in Example 3, with the exception that silicon dioxide (from SIGMA CHEMICAL CO.) was used instead of fumed silica.

Example 5

[0025] Calcined catalysts prepared in the Examples 1-4 were pressed into pellets and crushed to 20-40 mesh. The catalysts were tested in a fixed bed quartz reactor. In each test the catalyst was pretreated in a stream of oxygen and helium for one hour at 400 °C. Then, the feed gas was passed through the reactor at the desired temperature.
[0026] The following conditions were employed:

reaction temperature: 500 °C
catalyst: 1 gm
pressure: atmospheric
W/F: 0.8 sec.
Feed composition: isobutane/oxygen/helium : 26.5/6.6/66.9 (mol%)

[0027] After reaching a steady state, the reactor effluent was analyzed using a modem gas chromatograph (HP 6890), equipped with both FID (flame ionization detector) and TCD (thermal conductivity detector) detectors. Activity results were calculated according to the equations given above. Results are summarized below in Table 1.

Table 1: Activity results

Example No.	x (%)	$(C_3H_6/ i\text{-}C_4H_8+C_3H_6)$ x 100	$i\text{-}C_4H_8$		C_3H_6		$i\text{-}C_4H_8+C_3H_6$		CH_4xCO_x	
			Y	S	Y	S	Y	S	Y	S
1	18.0	25.3	12.6	69.8	4.2	23.6	16.8	93.4	1.2	6.6
2	25.8	34.3	16.0	62.1	8.3	32.4	24.4	94.5	1.4	5.5
3	12.1	28.6	8.2	70.0	3.4	28.0	11.9	98.0	0.2	2.0
4	14.8	31.7	11.2	66.9	4.5	31.0	14.5	97.9	0.3	2.1

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

[0028] From the results summarized above, it will be evident that each of the catalysts in Examples 1-4 exhibited high selectivity for isobutene. A considerable amount of propene was also formed in the reaction, which is desirable as well, due to the large demand for this intermediate. Total selectivity for isobutene and propene exceeds 93% at conversions higher than 12%. This finding is significant because the reaction was carried out at relatively high temperature and there was no ethylene or partial oxidation products formed. Propene formation is believed to occur by a consecutive disproportion reaction of isobutene, wherein 3 isobutene molecules give 4 propene molecules. This reaction was also demonstrated using isobutene as a feed stock. Propylene was found to be the exclusive useful product under the same conditions.

[0029] By decreasing the relative aluminum content from 3.8 to 2 in the catalyst (Examples 1 and 2), isobutane conversion increased from 18.0 to 25.8%, and isobutene yield increased consequently from 12.6 to 16.0%. Total olefin selectivity, towards isobutene and propene, and selectivity towards other products, i.e., CO, CO_2 and methane, remained nearly constant. In parallel, propene formation was enhanced. Based on these results, it can be concluded that by optimizing the aluminum content in the catalyst the reaction can be directed towards the desired propene to propene plus isobutene ratio.

[0030] When silica was used instead of alumina in the preparation of catalysts (Examples 3 and 4), total selectivity towards useful products, i.e. isobutene and propene, was enhanced to 98%. Thus, using different types of silica, i.e., different element sources or ingredients, as demonstrated in Examples 3 and 4, can desirably modify the catalyst behavior and the resultant propene to propene plus isobutene ratio. Preferably, the total selectivity for one or more olefins is increased to at least 95%.

[0031] The above description of the invention is intended to be illustrative and not limiting. Various changes or modifications in the embodiments described may occur to those skilled in the art. These can be made without departing from the scope of the invention.

Claims

1. A catalyst composition for oxidative dehydrogenation of hydrocarbons to produce olefins, said composition having the formula:

$$X_xY_yWO_z$$

wherein:

X is at least one element selected from the group consisting of Li, Na, Rb, and Fr;
Y is Si;
x is 0.5-2.5;
y is 0.05-5; and

z is an integer representing the number of oxygen atoms required to satisfy the valancy of X, Y, and W in said compound.

2. The catalyst composition of claim 1, further comprising a support.

3. The catalyst composition of claim 2, wherein said support is selected from the group consisting of alumina, silica, titania, zirconia, zeolites, silicon carbide, molecular sieves, microporous or nonporous materials, and mixtures thereof.

4. Use of the catalyst composition of claim 1 for oxidative dehydrogenation of hydrocarbons to produce olefins, wherein the hydrocarbon is selected from the group consisting of propane, n-butane, isobutane, and a mixture thereof, and the olefin is selected from the group consisting of propylene, n-butene, isobutene, and a mixture thereof.

5. Use of the catalyst composition of claim 1 for oxidative dehydrogenation of hydrocarbons to produce olefins, wherein the hydrocarbon is isobutane and the olefin is a mixture of propene and isobutene.

Patentansprüche

1. Katalysatorzusammensetzung zur oxidativen Dehydrierung von Kohlenwasserstoffen zu Olefinen mit der Formel:

$$X_xY_yWO_z$$

worin:

X für mindestens ein Element aus der Gruppe bestehend aus Li, Na, Rb und Fr steht;
Y für Si Steht;
x für 0,5 bis 2,5 steht;
y für 0,05-5 steht und
z für eine ganze Zahl steht, die die Zahl der zur Absättigung der Valenz von X, Y und W in der Verbindung benötigten Sauerstoffatome repräsentiert.

2. Katalysatorzusammensetzung nach Anspruch 1, ferner enthaltend einen Träger.

3. Katalysatorzusammensetzung nach Anpruch 2, in der der Träger aus der Gruppe bestehend aus Aluminiumoxid, Siliciumoxid, Titanoxid, Zirconiumoxid, Zeolithen, Siliciumcarbid, Molsieben, mikroporösen oder nichtporösen Materialien und Gemischen davon ausgewählt ist.

4. Verwendung der Katalysatorzusammensetzung nach Anspruch 1 zur oxidativen Dehydrierung von Kohlenwasserstoffen zu Olefinen, bei der der Kohlenwasserstoff aus der Gruppe bestehend aus Propan, n-Butan, Isobutan und einem Gemisch davon ausgewählt ist und das Olefin aus der Gruppe bestehend aus Propylen, n-Buten, Isobuten und einem Gemisch davon ausgewählt ist.

5. Verwendung der Katalysatorzusammensetzung nach Anspruch 1 zur oxidativen Dehydrierung von Kohlenwasserstoffen zu Olefinen, bei der es sich bei dem Kohlenwasserstoff um Isobutan und bei dem Olefin um ein Gemisch von Propen und Isobuten handelt.

Revendications

1. Composition de catalyseurs pour la déshydrogénation oxydante d'hydrocarbures pour la production d'oléfines, ladite composition ayant la formule :

$$X_xY_yWO_z$$

dans laquelle :

X représente au moins un élément choisi parmi le groupe constitué des atomes de Li, de Na, de Rb et de Fr ;

Y représente un atome de Si ;
x vaut de 0,5 à 2,5 ;
y vaut de 0,05 à 5 ; et
z est un nombre entier qui représente le nombre d'atomes d'oxygène requis pour satisfaire la valence de X, de Y et de W dans ledit composé.

2. Composition de catalyseurs selon la revendication 1, qui comprend en outre un support.

3. Composition de catalyseurs selon la revendication 2, dans laquelle ledit support est choisi parmi le groupe constitué de l'alumine, de la silice, du dioxyde de titane, de zircone, des zeolites de carbure de silicium, de tamis moléculaires, de matériaux microporeux ou non poreux et de mélanges de ceux-ci.

4. Utilisation de la composition de catalyseurs selon la revendication 1 pour la déshydrogénation oxydante d'hydrocarbures pour la production d'oléfines, dans laquelle l'hydrocarbure est choisi parmi le groupe constitué du propane, du n-butane, de l'isobutane et d'un mélange de ceux-ci, et l'oléfine est choisie parmi le groupe constitué du propylène, du n-butène, de l'isobutène et d'un mélange de ceux-ci.

5. Utilisation de la composition de catalyseurs selon la revendication 1 pour la déshydrogénation oxydante d'hydrocarbures pour la production d'oléfines, dans laquelle l'hydrocarbure est de l'isobutane et l'oléfine est un mélange de propène et d'isobutène.