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(71) Applicant (for all designated States except US): **NOVA CHEMICALS (INTERNATIONAL) S. A.** [CH/CH]; Avenue de la Gare 14, 1700 Fribourg (CH).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **KUSTOV, Leonid Modestovich** [RU/RU]; Khalturinskaya str., 11, apt.30, 107392 Moscow (RU). **KUCHEROV, Aleksey, Victorovich** [RU/RU]; Bratskaya str., 17/2, apt. 197, 111397 Moscow (RU). **KUCHEROVA, Tatyana, Nikolaevna** [RU/RU]; Soyuznyi prospekt, 9/14, apt. 200, 111398 Moscow (RU). **FINASHINA, Elena, Dmitrievna** [RU/RU]; Kievskaya str., 16, apt. 39, 121165 Moscow (RU). **ISAEVA, Vera, Ilyichna** [RU/RU]; Biriuliovskaya str., 27, apt. 111, 115404 Moscow (RU). **CAL, Haiyong** [CA/CA]; 4831 - 48 Street NW, Calgary, Alberta

T3A 0S5 (CA). **KRZYWICKI, Andrzej** [CA/CA]; 2403 Westmount Road NW, Calgary, Alberta T2N 3N9 (CA).

(74) Agents: **TROTT, Trevor** et al.; 2928 - 16 Street NE, Calgary, Alberta T2E 7K7 (CA).

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(54) Title: SUPPORTED OXIDATIVE DEHYDROGENATION CATALYST

(57) Abstract: The present invention provides a process for the manufacture of an efficient and robust catalyst for the oxidative dehydrogenation of paraffins to olefins, preferably lower C₂₋₄ paraffins. The present invention provides a process for the preparation of an oxidative dehydrogenation catalyst for C₂₋₄ paraffins to olefins comprising comminuting: from 10 to 99 weight % of a mixed oxide catalyst of the formula V₇Mo₃Nb₂Te_mMe_nO_p, wherein Me is a metal selected from the group consisting of Ta, Ti, W, Hf, Zr, Sb and mixtures thereof; with from 90 to 1 weight % of an inert matrix selected from oxides of titanium, zirconia, aluminum, magnesium, yttria, lanthana, silica and their mixed compositions or a carbon matrix to produce particles having a size from 1 to 100 microns and forming the resulting particles into pellets having a size from 0.1 to 2 mm.



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SUPPORTED OXIDATIVE DEHYDROGENATION CATALYST**TECHNICAL FIELD**

The present invention relates to a method to prepare an oxidative dehydrogenation catalyst having a high productive and a high hourly space velocity, preferably for the dehydrogenation of ethane to ethylene. In a preferred embodiment the present invention relates to a dry method for the preparation of such a catalyst including the dry comminution of the active catalyst and the support.

BACKGROUND ART

The thermal cracking of paraffins to olefins, particularly lower paraffins such as C₂₋₄ paraffins typically ethane and propane to corresponding olefins is an energy intensive process. It has been proposed to catalytically dehydrogenate lower paraffins in the presence of oxygen. Typically a support is impregnated with a liquid catalyst and dried for subsequent use. While these types of catalysts are useful they generally have a low productivity.

Dehydrogenation processes are widely used in modern refining and petrochemistry. Processes of synthesis of butadiene, isoprene, long-chain olefins are commercialized. However, the area of dehydrogenation of light alkanes remains to be underexplored and the processes are far from the commercial scale. The most advanced are the processes of oxidative dehydrogenation based on the use of transition metal oxide catalysts and a robust oxidant, such as oxygen or air. The oxidative conversion makes the process of dehydrogenation thermodynamically advantageous and decreases the reaction temperature as compared to non-oxidative processes (e.g. thermal cracking). The conversion of ethane, which is the second major component of natural gas, to ethylene requires development of new catalysts and processes.

Several catalytic systems are known in the art for the oxidative dehydrogenation of ethane. United States Patent no 4,450,313, issued May 22, 1984 to Eastman et al., assigned to Phillips Petroleum Company discloses a catalyst of the composition LiO-TiO₂, which is characterized by a low ethane conversion not exceeding 10%, in spite of a rather high selectivity to ethylene (92%). The major drawback of this catalyst is the high temperature of the process of oxidative dehydrogenation, which is close to or higher than 650° C.

Rather promising results were obtained for nickel-containing catalysts disclosed in United States patent no. 6,891,075, 2005 issued May 10, 2005 to Liu assigned to Symyx technologies, Inc. At 325° C the ethane conversion on the best catalyst in this series was about 20% with a selectivity of 85% (a Ni-Nb-Ta oxide catalyst).

The US patents numbers 6,624,116, issued Sept. 23, 2003 to Bharadwaj, et al. and 6,566,573 issued May 20, 2003 to Bharadwaj, et al. both assigned to Dow Global Technologies Inc. disclose Pt-Sn-Sb-Cu-Ag monolith systems that have been tested in an autothermal regime at $T > 750^{\circ}\text{C}$, the starting gas mixture contained hydrogen ($\text{H}_2 : \text{O}_2 = 2 : 1$, GHSV = 180 000 h^{-1}). The catalyst composition is different from that of the present invention and the present invention does not contemplate the use of molecular hydrogen in the feed.

US Patents numbers 4,524,236 issued June 18, 1985 to McCain assigned to Union Carbide Corporation and 4,899,003, issued February 6, 1990 to Manyik et al, assigned to Union Carbide Chemicals and Plastics Company Inc. disclose mixed metal oxide catalysts of V-Mo-Nb-Sb. At 375-400° C the ethane conversion reached 70% with the selectivity close to 71-73%. However, these parameters were achieved only at very low gas hourly space velocities less than 900 H^{-1} (i.e. 720 h^{-1}). Additionally the supported catalyst is prepared by impregnating the support and not by a dry co-communition process of the present invention.

The most efficient catalysts were described in the patents by Lopez-Nieto J.M. and coworkers.

United States Patent 7,319,179 issued January 15, 2008 to Lopez-Nieto et al. assigned to Consejo Superior de Investigaciones Cientificas and Universidad Politecnica de Valencia, discloses Mo-V-Te-Nb-O oxide catalysts that provided an ethane conversion of 50-70% and selectivity to ethylene up to 95% (at 38% conversion) at 360-400° C. The catalysts have the empirical formula $\text{MoTe}_h\text{V}_i\text{Nb}_j\text{A}_k\text{O}_x$, where A is a fifth modifying element. The catalyst is a calcined mixed oxide (at least of Mo, Te, V and Nb), optionally supported on: (i) silica, alumina and/or titania, preferably silica at 20-70 wt% of the total supported catalyst or (ii) silicon carbide. The supported catalyst is prepared by conventional methods of precipitation from solutions, drying the precipitate then calcining. The patent does not suggest co-communition of the catalyst and a support.

Similar catalysts have been also described in open publications of Lopez-Nieto and co-authors. Selective oxidation of short-chain alkanes over hydrothermally

prepared MoVTenbO catalysts is discussed by F. Ivars, P. Botella, A. Dejoz, J. M. Lopez-Nieto, P. Concepcion, and M. I. Vazquez, in Topics in Catalysis (2006), 38(1-3), 59-67.

MoVTe-Nb oxide catalysts have been prepared by a hydrothermal method and tested in the selective oxidation of propane to acrylic acid and in the oxidative dehydrogenation of ethane to ethylene. The influence of the concentration of oxalate anions in the hydrothermal gel has been studied for two series of catalysts, Nb-free and Nb-containing, respectively. Results show that the development of an active and selective active orthorhombic phase ($\text{Te}_2\text{M}_{20}\text{O}_{57}$, $\text{M} = \text{Mo}, \text{V}, \text{Nb}$) requires an oxalate/Mo molar ratio of 0.4-0.6 in the synthesis gel in both types of samples. The presence of Nb favors a higher catalytic activity in both ethane and propane oxidation and a better production of acrylic acid. Preparation of molybdenum-vanadium-tellurium-niobium catalyst useful in oxidation involves drying a slurry of a ceramic inert carrier and metal ionic precursor species; then precalcination and calcination of the slurry. This art does not suggest co-comminuting the catalyst and the carrier.

The preparation of a Mo-Te-V-Nb composition is described in WO 2005058498 A1, published 30 June, 2005 (corresponding to U.S. published application 2007149390A1). Preparation of the catalyst involves preparing a slurry by combining an inert ceramic carrier with at least one solution comprising ionic species of Mo, V, Te, and Nb, drying the slurry to obtain a particulate product, precalcining the dried product at 150-350° C in an oxygen containing atmosphere and calcining the dried product at 350-750° C under inert atmosphere. The catalyst prepared exhibits the activity and selectivity in the oxidation reaction comparable to the non-supported catalyst. Again this teaches away from the co-comminution of the catalyst and the support.

Mixed metal oxide supported catalyst composition; catalyst manufacture and use in ethane oxidation are described in Patent WO 2005018804 A1, 3 March, 2005, assigned to BP Chemicals Limited, UK. A catalyst composition for the oxidation of ethane to ethylene and acetic acid comprises (i) a support and (ii) in combination with O, the elements Mo, V and Nb, optionally W and a component Z, which is ≥ 1 metals of Group 14. Thus, $\text{Mo}_{60.5}\text{V}_{32}\text{Nb}_{7.5}\text{O}_x$ on silica was modified with 0.33 g-atom ratio Sn for ethane oxidation with good ethylene/acetic acid selectivity and product ratio 1:1.

A process for preparation of ethylene from gaseous feed comprising ethane and oxygen involving contacting the feed with a mixed oxide catalyst containing vanadium, molybdenum, tantalum and tellurium in a reactor to form effluent of ethylene is

disclosed in WO 2006130288 A1, 7 December, 2006, assigned to Celanese Int. Corp. The catalyst has a selectivity for ethylene of 50-80% thereby allowing oxidation of ethane to produce ethylene and acetic acid with high selectivity. The catalyst has the formula $\text{Mo}_1\text{V}_{0.3}\text{Ta}_{0.1}\text{Te}_{0.3}\text{O}_2$. The catalyst is optionally supported on a support selected from porous silicon dioxide, ignited silicon dioxide, kieselguhr, silica gel, porous and nonporous aluminum oxide, titanium dioxide, zirconium dioxide, thorium dioxide, lanthanum oxide, magnesium oxide, calcium oxide, barium oxide, tin oxide, cerium dioxide, zinc oxide, boron oxide, boron nitride, boron carbide, boron phosphate, zirconium phosphate, aluminum silicate, silicon nitride, silicon carbide, and glass, carbon, carbon-fiber, activated carbon, metal-oxide or metal networks and corresponding monoliths; or is encapsulated in a material (preferably silicon dioxide (SiO_2), phosphorus pentoxide (P_2O_5), magnesium oxide (MgO), chromium trioxide (Cr_2O_3), titanium oxide (TiO_2), zirconium oxide (ZrO_2) or alumina (Al_2O_3)). However, the methods of preparation of the supported compositions involve the procedures of wet chemistry (solutions are impregnated into the solid support and then the materials are dried and calcined).

The preparation of a supported catalyst usable for low temperature oxy-dehydrogenation of ethane to ethylene is disclosed in the US Patent 4,596,787 A, 24 June, 1986 assigned to UNION CARBIDE CORP. A supported catalyst for the low temperature gas phase oxydehydrogenation of ethane to ethylene is prepared by (a) preparing a precursor solution having soluble and insoluble portions of metal compounds; (b) separating the soluble portion; (c) impregnating a catalyst support with the soluble portion and (d) activating the impregnated support to obtain the catalyst. The calcined catalyst has the composition $\text{Mo}_a\text{V}_b\text{Nb}_c\text{Sb}_d\text{X}_e$. X is nothing or Li, Sc, Na, Be, Mg, Ca, Sr, Ba, Ti, Zr, Hf, Y, Ta, Cr, Fe, Co, Ni, Ce, La, Zn, Cd, Hg, Al, Tl, Pb, As, Bi, Te, U, Mn and/or W; a is 0.5-0.9, b is 0.1-0.4, c is 0.001-0.2, d is 0.001-0.1, e is 0.001-0.1 when X is an element. The patent fails to teach or suggest a co-comminution of the catalyst and the support.

Another example of the low temperature oxy-dehydrogenation of ethane to ethylene using a calcined oxide catalyst containing molybdenum, vanadium, niobium and antimony is described in the US Patent 4,524,236 A, 18 June, 1985 and 4,250,346 A, 10 February, 1981, both assigned to UNION CARBIDE CORP. The calcined catalyst contains $\text{Mo}_a\text{V}_b\text{Nb}_c\text{Sb}_d\text{X}_e$ in the form of oxides. The catalyst is prepared from a solution of soluble compounds and/or complexes and/or compounds of each of the

metals. The dried catalyst is calcined by heating at 220-550° C in air or oxygen. The catalyst precursor solutions may be supported on to a support, e.g. silica, aluminum oxide, silicon carbide, zirconia, titania or mixtures of these. The selectivity to ethylene may be greater than 65% for a 50% conversion of ethane.

The trend in the prior art is the formation of a catalyst by impregnating a porous support and then calcining. The resulting catalysts tend to have a fairly low times space yield.

The present invention seeks to provide a method of preparation of a supported active catalyst for oxidative dehydrogenation of ethane into ethylene that would exhibit a superior performance (activity, selectivity and productivity) as compared with the systems described in the prior art. The novel composite catalyst comprises the Mo-V-Nb-Te-O oxide composition containing the known in the art M1 phase and a solid support with the surface area in the range of 1-100 m²/g. The support may be silica, alumina, titania, zirconia, ceria, lanthana, magnesia, zinc oxide or a mixture thereof. The active composite catalyst is prepared by co-comminution of a mixture of the active Mo-V-Nb-Te-O oxide catalyst and a support so that the weight percent of the active phase is ranging from 10 to 99%. The resulting fine powder with the particle size ranging from 1 to 100 microns can be then pressed into pellets and crushed to collect the necessary fraction ranging from 0.1 to 1-2 mm or extrudates can be formed that can be further loaded in the plug-flow catalytic reactor.

DISCLOSURE OF INVENTION

The present invention provides a process for the preparation of an oxidative dehydrogenation catalyst of C₂₋₄ paraffins to olefins comprising comminuting:

- a) from 10 to 99 weight % of a mixed oxide catalyst of the formula $V_x Mo_y Nb_z Te_m Me_n O_p$, wherein Me is a metal selected from the group consisting of Ta, Ti, W, Hf, Zr, Sb and mixtures thereof; and:
 - x is from 0.1 to 3;
 - y is from 0.5 to 1.5;
 - z is from 0.001 to 3;
 - m is from 0.001 to 5;
 - n is from 0.001 to 2;
 - and p is a number to satisfy the valence state of the mixed oxide catalyst;
- with:

b) 90 to 1 weight % of an inert matrix selected from oxides of titanium, zirconia, aluminum, magnesium, yttria, lantana, silica and their mixed compositions or a carbon matrix;

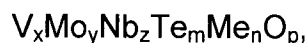
to produce particles having a size from 1 to 100 microns and forming the resulting particles into pellets having a size from 0.1 to 2 mm.

The present invention also provides the catalyst prepared by the above method and a process for the oxidative dehydrogenation of lower (C₂₋₄) alkanes to the corresponding alkene.

BEST MODE FOR CARRYING OUT THE INVENTION

In the catalyst of the present invention the mixed metal oxide is used in an amount from 10 to 99, preferably from 30 to 80, most preferably from 40 to 70 weight % of the total catalyst and the support is present in an amount from 90 to 1, preferably from 70 to 20, most preferably from 60 to 30 weight % of the total catalyst.

The mixed metal oxide has the formula:



wherein Me is a metal selected from the group consisting of Ta, Ti, W, Hf, Zr, Sb and mixtures thereof; and

x is from 0.1 to 3, preferably from 0.2 to 2;

y is from 0.5 to 1.5, preferably from 0.95 to 1.05, most preferably 1;

z is from 0.001 to 3, preferably from 0.001 to 2, most preferably from 0.01 to 1.5;

m is from 0.001 to 5, preferably from 0.2 to 2;

n is from 0.001 to 2, preferably from 0.001 to 1, most preferably from 0.01 to 0.8;

and p is a number to satisfy the valence state of the mixed oxide catalyst.

In the above formula the numbers represent the molar amounts of the components. Preferably the ratio of x:m is from 0.3 to 10, most preferably from 0.5 to 8, desirably from 0.5 to 6.

The active metal catalyst may be prepared by mixing aqueous solutions of soluble metal compounds such as hydroxides, sulphates, nitrates, halides lower (C₁₋₅) mono or di carboxylic acids, and ammonium salts or the metal acid per se. For instance, the catalyst could be prepared by blending solutions such as ammonium metavanadate, niobium oxalate, ammonium molybdate, telluric acid etc. The resulting solution is then dried typically in air at 100-150⁰ C and calcined in a flow of inert gas such as those selected from the group consisting of N₂, He, Ar, Ne and mixtures thereof

at 200-600° C, preferably at 300-500° C. The calcining step may take from 1 to 20, typically from 5 to 15 usually about 10 hours. The resulting oxide is a friable solid.

The support for the catalyst selected from oxides of titanium, zirconia, aluminum, magnesium, yttria, lantana, silica and their mixed compositions or a carbon matrix. The support should have a large surface area typically greater than about 100 m²/g, preferably greater than about 200 m²/g, most preferably from 250 m²/g to 1,000 m²/g. The support will be porous and will have a pore volume from about 0.3 to 5.0 ml/g, typically from 0.5 to 3.0 ml/g.

It is also believed titanium silicates such as those disclosed in 4,853,202 issued Aug. 1, 1989 to Kuznicki assigned to Engelhard Corporation would be useful as supports in accordance with the present invention.

It is important that the support be dried prior to use. Generally, the support may be heated at a temperature of at least 200° C for up to 24 hours, typically at a temperature from 500° C to 800° C for about 2 to 20 hours, preferably 4 to 10 hours. The resulting support will be free of adsorbed water and should have a surface hydroxyl content from about 0.1 to 5 mmol/g of support, preferably from 0.5 to 3 mmol/g.

The amount of the hydroxyl groups in silica may be determined according to the method disclosed by J. B. Peri and A. L. Hensley, Jr., in *J. Phys. Chem.*, 72 (8), 2926, **1968**, the entire contents of which are incorporated herein by reference.

The support and catalyst may be combined and then comminuted to produce a fine particulate material having a particle size ranging from 1 to 100 micron. The comminution process may be any conventional process including ball and bead mills, both rotary, stirred and vibratory, bar or tube mills, hammer mills, and grinding discs. A preferred method of comminution is a ball or bead mill.

In one embodiment of the invention the catalyst and the support are dry milled. It is also possible to wet mill the catalyst and support provided the resulting product is again dried and if necessary calcined.

The particulate material may be sieved if required to select the appropriate small particle size. The particulates may then be compacted and crushed to yield particles having a size from 0.1 to 1-2 mm. The particles or extrudates can be formed that can be further loaded in the plug-flow catalytic reactor.

The oxidative dehydrogenation reaction will typically be conducted at temperatures from 300° C to 600° C, preferably from 400° C to 600° C and pressures from 15 to 50 psig (103.4 to 344.73 kPag). The molar ratio of oxygen to feed typically

ranges from 1:2.5 to 1:10, preferably from 1:2.5 to 1:3.5. The gas hourly space velocity (GHSV) will be from 900 to 18000 h⁻¹, preferably greater than 1000 h⁻¹. The space-time yield of alkene (e.g. ethylene) (productivity) in g/hour per Kg of catalyst should be not less than 300 preferably greater than 500, most preferably greater than 950, most desirably greater than 1,000 at 380° C. It should be noted that the productivity of the catalyst will increase with increasing temperature.

While the present invention is primarily directed to the manufacture of alkenes from the corresponding alkane it may also be possible to convert the feed to carboxylic acids.

The present invention will now be illustrated by the following non limiting examples.

EXAMPLES

Example 1 (preparation of the active oxide catalyst phase no support)

2.65 g of ammonium heptamolybdate (tetrahydrate) and 0.575 g of telluric acid were dissolved in 19.5 g of distilled water at 80° C. Ammonium hydroxide (25% aqueous solution) is added to the Mo- and Te-containing solution at a pH of 7.5. Then water is evaporated under stirring at 80° C. The solid precipitate is dried at 90° C. 3.0 g of this precipitate is suspended in water (21.3 g) at 80° C and 0.9 g of vanadyl sulfate and 1.039 g of niobium oxalate were added. The mixture was stirred for 10 min and then is transferred to the autoclave with a Teflon[®] (tetrafluoroethylene) lining. Air in the autoclave was substituted with argon, the autoclave was pressurized and heated to 175° C and the system was kept for 60 hours at this temperature. Then the solid formed in the autoclave was filtered, washed with distilled water and dried at 80° C. The thus obtained active catalyst phase was calcined at 600° C (2 h) in a flow of argon. The temperature was ramped from room temperature to 600° C at 1.67° C/min. The powder was pressed then and the required mesh size particles were collected.

The catalyst was tested in oxidative dehydrogenation of ethane using a gas mixture O₂/C₂H₆ with the ratio from 1/2.5 to 1/10, preferably from 1/2.5 to 1/3/5. The mixture was fed in the plug-flow reactor with the gas hourly space velocity of 900-18000 h⁻¹ at a pressure of 1-10 atm, preferably at 1 atm.

The catalysts were tested at 320-450° C, the catalyst loading 0.13-1.3 g; fraction 0.25-0.5 mm, a flow type reactor with a stationary catalyst bed was used. The catalyst was heated to 360° C in the reaction mixture (15-75 cc/min), the catalytic activity was

measured at 380, 420, and 450° C. The data for all the catalysts are presented in the table.

Example 2 (preparation of the supported composite catalyst)

The active catalyst phase prepared in Example 1 and alpha-alumina with the specific surface area 10 m²/g were mixed and placed in the ball mill, the percentage (weight) of α -Al₂O₃ in the mixture was 50 wt %. The ball milling was carried out at room temperature for 30 min. until a fine powder with an average particle size of 3.5 micron was obtained. The obtained milled powder is pressed into pellets, crushed and the fraction having a size of 0.25-0.5 mm is collected. The obtained catalytic composite material was tested in oxidative dehydrogenation of ethane under conditions of Example 1 (see the table).

Example 3 (preparation of the supported Mo-V-Te-Nb-O mixed oxide catalyst by the wet method)

6.400 g Ammonium telluromolybdate [(NH₄)₆TeMo₆O₂₄ 7H₂O] was dissolved into 20 ml of distilled water (first solution). An aqueous solution of VOSO₄ was prepared by dissolving 2.370 g of hydrated VOSO₄ in 10 ml of distilled water (second solution). A third solution was prepared by dissolving 2.330 g hydrated niobium oxalate in 10 ml distilled water heated at 353 K. The second solution was then added to the first solution and the resulting mixture was stirred for 5 min. The third solution was finally added to the mixed solution together with α -Al₂O₃ and the resulting slurry was stirred for 10 min and then transferred to an autoclave. After 5 min of nitrogen purging, hydrothermal reaction was carried out for 48 h at 448K. The obtained powder was washed with distilled water, dried at 353 K overnight and then calcined under nitrogen flow at 873 K for 2 h. The catalyst was tested as in Example 1. The data is given in the table.

Example 4 (preparation of titania-based composite material)

This sample was prepared according to Example 2 except for the use of TiO₂ as a carrier instead of α -Al₂O₃. 50 % wt of TiO₂ (surface area 25 m²/g) was used.

TABLE 1
Catalytic Performance of the Bulk and Supported Catalysts in Oxidative
Dehydrogenation of Ethane

Catalyst (Example)	T, °C	Space-time yield of ethylene (productivity), g/h per 1 kg of catalyst	Selectivity, %
1 (bulk sample, comparative)	400	210	90-92
2 (composite catalyst with 50% α -Al ₂ O ₃)	380 420	980 2300	96.5 96
3 (supported catalyst prepared from solutions, comparative)	380 420	270 520	92 91
4 (composite catalyst with 50% TiO ₂)	380 420	1200 2500	97.5 97

It is seen from this comparison that, first, the catalysts prepared according to the invention are more active than the best catalysts known in the art, and second, the catalysts prepared by ball milling of the most active mixed oxide catalyst with an appropriate support show a dramatic enhancement of the specific activity (activity per 1 g of the active phase) as compared with the bulk catalysts.

INDUSTRIAL APPLICABILITY

The present invention provides a novel catalyst for the oxidative dehydrogenation of paraffins, particularly lower C₂₋₄ paraffins, to the corresponding olefin, preferably α -olefin.

CLAIMS

1. A process for the preparation of an oxidative dehydrogenation catalyst of C₂₋₄ paraffins to olefins comprising comminuting:
 - a) from 10 to 99 weight % of a mixed oxide catalyst of the formula $V_xMo_yNb_zTe_mMe_nO_p$, wherein Me is a metal selected from the group consisting of Ta, Ti, W, Hf, Zr, Sb and mixtures thereof; and
x is from 0.1 to 3;
y is from 0.5 to 1.5;
z is from 0.001 to 3;
m is from 0.001 to 5;
n is from 0.001 to 2
and p is a number to satisfy the valence state of the mixed oxide catalyst;
with:
 - b) 90 to 1 weight % of an inert matrix selected from oxides of titanium, zirconia, aluminum, magnesium, yttria, lantana, silica and their mixed compositions or a carbon matrix, to produce particles having a size from 1 to 100 microns and forming the resulting particles into pellets having a size from 0.1 to 2 mm.
2. The process according to claim 1 wherein the oxidative dehydrogenation catalyst has a productivity of not less than 300 g of olefin per 1 kg of the catalyst active phase per hour at a temperature from 300° C to 600° C at pressure from 1 to 10 atmospheres and a gas hourly space velocity from 900 to 1800 h⁻¹.
3. The process according to claim 2 wherein component a, is present in an amount from 30 to 80 weight %.
4. The process according to claim 3, wherein in component a, y is from 0.95 to 1.05.
5. The process according to claim 4, wherein in component a, x and m are from 0.02 to 2.
6. The process according to claim 5, wherein in component a, z is from 0.001 to 0.5.
7. The process according to claim 6, wherein in component a, n is from 0.001 and 1.
8. The process according to claim 7, wherein in the comminuting process is ball milling.

9. The process according to claim 7, wherein components a is prepared by mixing the components in a liquid phase and subsequently drying the product and dry mixing and dry ball milling components a and b.
10. The process according to claim 9, wherein component b is titania.
11. The process according to claim 8, wherein component b is magnesia.
12. The process according to claim 8, wherein component b is carbon or graphitized carbon.
13. The process according to claim 8, wherein component b is alumina.
14. A process for the oxidative dehydrogenation of ethane to ethylene using a catalyst according to claim 2 be conducted at temperatures from 300° C to 600° C and pressures from 15 to 50 psig (103.4 to 344.73 kPag) and a molar ratio of oxygen to feed from 1:2.5 to 1:10.
15. The process according to claim 14, wherein the productivity of the catalyst exceeds 1000 g of olefin per 1 kg of the catalyst active phase per hour.
16. The process according to claim 15, having a gas hourly space velocity greater than 900 h⁻¹.
17. An oxidative dehydrogenation catalyst prepared according to claim 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2010/000233

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **B01J 37/00** (2006.01), **B01J 37/04** (2006.01), **C07C 5/48** (2006.01), **C07C 11/04** (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: **B01J 37/00** (2006.01), **B01J 37/04** (2006.01), **C07C 5/48** (2006.01), **C07C 11/04** (2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)

CPD, EPOQUE, Delphion, Google Books

Search terms: oxidative, dehydrogenation, catalyst, mixed oxide, carrier, milling, comminution, preparation

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 7,319,179 B2 (Lopez Nieto et al) 15 January 2008 (15-01-2008), see entire document	1 - 17
Y	US 5,808,143 B2 (Karrer et al) 15 September 1998 (15-09-1998), see entire document	1 - 17
Y	van Bekkum, H., Flanigen, E.M., Jacobs, P.A., Jansen, J.C. "Introduction to Zeolite Science and Practice", 2nd Edition, 2001, Elsevier. ISBN: 0-444-82421-9, page 514, chapter 7.2.	1 - 17
Y	US 4,596,787 (Manyik et al) 24 June 1986 (24-06-1986), see entire document	14 - 16

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

14 May 2010 (14-05-2010)

Date of mailing of the international search report

14 May 2010 (14-05-2010)

Name and mailing address of the ISA/CA
Canadian Intellectual Property Office
Place du Portage I, C114 - 1st Floor, Box PCT
50 Victoria Street
Gatineau, Quebec K1A 0C9
Facsimile No.: 001-819-953-2476

Authorized officer

Ravi Philar
Telephone: 001-819- 953-3101

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2010/000233

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
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