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(54) Title: IMPROVED CATALYST FOR ETHANE ODH

(57) Abstract: A catalyst for oxidative dehydrogenation (ODH) of ethane with an empirical formula Mo-V-Te-Nb-Pd-O produced using a process comprising impregnation of the Pd component on the surface of the catalyst following a calcination step using a Pd compound free of halogens. The resulting catalyst can be used in both diluted and undiluted ODH processes and shows higher than expected activity without any loss of selectivity.

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IMPROVED CATALYST FOR ETHANE ODH

TECHNICAL FIELD

The present invention relates to a catalyst for oxidative dehydrogenation (ODH) of ethane comprising the elements molybdenum, vanadium, tellurium, niobium, palladium, and oxygen. The catalyst is produced in a process where incorporation of palladium into the catalyst, using a palladium compound that is free from halogens, is performed after a calcination step. The catalyst is useful for both diluted and undiluted ODH processes and shows higher activity than prior art catalysts without any concurrent loss of selectivity.

BACKGROUND ART

Conversion of paraffins (alkanes) to olefins can be achieved in a number of ways. The most widely practiced method is thermal cracking technology, where paraffins are exposed to temperatures as high as 1000°C for very short time periods, in the order of milliseconds to a few seconds, promoting the loss of hydrogen and subsequent formation of one or more unsaturated bonds characteristic of olefins. However, the current thermal cracking processes are not only cost intensive to build and operate but also energy intensive due to the substantial heat requirement for the endothermic cracking reactions. Also, significant amounts of CO_2 are produced from the operation of cracking furnaces.

Alternatively, conversion of paraffins can be accomplished using an oxidative dehydrogenation (ODH) process where a stream of one or more alkanes are passed over an oxidative dehydrogenation catalyst, in the presence of oxygen or an oxygen containing gas, at temperatures from about 300°C to 750°C. The advantages of catalytic ODH over steam cracking are that it provides higher ethane conversion and higher ethylene selectivity while using lower reaction temperatures. On the downside, the risk of thermal runaway of the reaction and consequential explosion requires extensive safety precautions. Also, developing catalysts is made difficult because olefins are more reactive than the paraffins they are derived from, creating the potential for further oxidation to unwanted byproducts. It is therefore desirable to use catalysts that are more selective for oxidation of paraffins than olefins.

Use of mixed metal oxides as catalysts for ODH is well known. US Patent No. 4,250,346 issued February 10, 1981 to Young and Thorsteinson, assigned to Union Carbide Corporation, claims a process for converting ethane to ethylene using temperatures below 550°C. The catalyst employed uses mixed metal oxides and is of the formula Mo-X-Y, where X = Cr, Mn, Nb, Ta, Ti, V and/or W and Y = Bi, Ce, Co, Cu, Fe, K, Mg, Ni, P, Pb, Sb, Si, Sn, Tl and/or U.

US Patent No. 4,524,236, issued June 18, 1985 to McCain assigned to Union Carbide Corporation, claims a process for converting ethane to ethylene using an ODH catalyst of the formula Mo-V-Nb-Sb-X, where X = 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, and W. The examples include the process for making the catalyst which includes a calcination step where the catalyst was heated to 350°C for up to five hours. When used in either the presence or absence of water the catalyst shows a selectivity of 75% for a conversion rate of 50%. Conditions for ODH using this invention included the addition of more than 85% of the inert diluent helium.

US Patent No. 8,105,971, issued January 31, 2012 to Gaffney et al., assigned to Lummus Technology Inc., claims a process for making a catalyst of the formula Mo-V-X-Y-Z-O, where X = at least one of Nb and Ta, Y = at least one of Sb and Ni, and Z = at least one of Te, Ga, Pd, W, Bi, and Al. The process requires admixing all the components followed by a pH adjustment with nitric acid before drying, calcining, and grinding the final product with acid. Claims include a requirement for selectivity of the catalyst exceeding 90% with an ethane conversion of at least 70% when used in an ODH process where molar ratios of ethane, oxygen, water, and nitrogen used are either 10/10/10/70 or 15/10/10/65. US Patent No. 8,519, 210 issued August 27, 2013 to Arnold et al., assigned to Lummus Technology Inc., provides examples that include the same catalyst and process for making said catalyst.

US Patent No. 7,718,568, issued May 18, 2010 to Gaffney et al., assigned to Rohm and Haas Company, claims a catalyst useful for conversion of an alkane, or a mixture of an alkane and an alkene, to unsaturated carboxylic acids, or in the presence of ammonia, unsaturated nitrites, of the formula Mo-V-M-Nb-X-O, where M is a group consisting of Te and Sb, and X is selected from the group consisting of Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Sc, Y, La, Ti, Zr, Hf, Ta, Cr, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, B, Ga, In, Pb, P, As, Sb, Bi, Se, F, Cl, Br, I,

Pr, Nd, Sm and Tb, provided that when M is Sb, X cannot be Sb. The patent also claims a process for making the catalyst, said process including admixing all the components in two steps, separated and followed by hydrothermal treatment. Calcination of the resulting insoluble materials is optional.

DISCLOSURE OF INVENTION

The present invention provides a highly active and selective mixed metal oxide oxidative dehydrogenation catalyst of the formula Mo-V-Nb-Te-Pd-O produced in a process whereby the Pd component is added after a calcination step. The Mo, V, Nb, and Te components are admixed together and then subjected to hydrothermal treatment followed by calcination, prior to addition of the Pd component. An oxide catalyst prepared solely with Mo, V, Nb, and Te, the four component catalyst, demonstrates lower activity than a similar catalyst containing, in addition to the same elements, small amounts of Pd impregnated onto its surface. Also, timing of addition of the Pd component is critical in that a catalyst produced by direct incorporation of the Pd component during initial admixing of all the components shows lower activity than a catalyst where the Pd component is added after the calcination step. Surprisingly, when the Pd impregnated catalyst is subjected to calcination, as is common for these catalysts, the activity is lower than a catalyst where there is no calcination after the impregnation of Pd. Furthermore, the increase of activity seen with the catalyst of the present invention is not accompanied by a decrease in selectivity for ethylene, an effect that is dependent upon the nature of the Pd compound used to impregnate the surface of the catalyst with Pd. Specifically, a catalyst produced using a Pd component containing a halogen, $PdCl_2$ for example, while maintaining high selectivity for ethylene, does not demonstrate higher activity compared to the four component catalyst. Last, the added benefit of this catalyst is that it can be used in an ODH process that does not require dilution of the reactants, oxygen and ethane, with any inert gas such as nitrogen or water. As a result, costly downstream processing for removal of excess oxygen, unwanted by products, and water are limited or not required.

Provided is a mixed metal oxide catalyst of the formula Mo-V-Nb-Te-Pd-O, in the respective relative atomic proportions of a, b, c, d, and e wherein when a=1, b=0.01 to 1.0, c=0.01 to 1.0, d=0.01 to 1, and $0.001<e\leq0.10$; where e is preferably 0.015-0.03, said catalyst produced by the process comprising:

i) admixing compounds of elements Mo, V, Te, and Nb, in a solvent comprising water;

ii) heating said first mixture in a first closed vessel at a temperature of from 100°C to 200°C for from 24 hours to 240 hours;

iii) recovering first insoluble material from steps ii) and iii);

iv) subjecting said first recovered insoluble material to calcining to produce the calcined product;

v) then, impregnating said calcined product with of a Pd compound free of halogens to form second mixture containing elements Mo, V, Te, Nb, and Pd;

vi) subjecting said second mixture to a drying step at a temperature of from 50°C to 150°C, (preferably from 110°C to 140°C, most preferably from 120°C to 130°C), for from 1 hour to 48 hours; and

vii) recovering second insoluble material to obtain a catalyst.

BEST MODE FOR CARRYING OUT THE INVENTION

Other than in the operating examples or where otherwise indicated, all numbers or expressions referring to quantities of ingredients, reaction conditions, etc. used in the specification and claims are to be understood as modified in all instances by the term "about". Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the properties that the present invention desires to obtain. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical values, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of "1 to 10" is intended to include all sub-ranges between and including the recited minimum value of 1 and the recited maximum value of 10; that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less

than 10. Because the disclosed numerical ranges are continuous, they include every value between the minimum and maximum values. Unless expressly indicated otherwise, the various numerical ranges specified in this application are approximations.

All compositional ranges expressed herein are limited in total to and do not exceed 100 percent (volume percent or weight percent) in practice. Where multiple components can be present in a composition, the sum of the maximum amounts of each component can exceed 100 percent, with the understanding that, and as those skilled in the art readily understand, that the amounts of the components actually used will conform to the maximum of 100 percent.

The present invention discloses a mixed metal oxide catalyst for the oxidative dehydrogenation of ethane into ethylene, said catalyst having the empirical formula $Mo_aV_bTe_cNb_dPd_eO_f$, wherein a, b, c, d, e and f are the relative atomic amounts of the elements Mo, V, Te, Nb, Pd and O, respectively, and when a=1, b=0.01 to 1.0, c=0.01 to 1.0, d=0.01 to 1, $0.001<e\leq0.10$ and f is dependent on the oxidation state of the other elements. The addition of small amounts of Pd into the catalyst provides an increase in activity while maintaining high selectivity for ethylene when compared to a catalyst comprised solely of Mo, V, Te, Nb, and O. The increase in activity without comprising selectivity is dependent upon the method of incorporation of Pd and the nature of the Pd compound used for incorporation into the catalyst.

The process for admixing multiple compounds in a solvent such as water for the purpose of constructing a catalyst for oxidative dehydrogenation of paraffins is well known in the art. The compounds are mixed using amounts of each compound that will result in a catalyst containing the desired relative atomic amounts of each compound. For the purposes of the present invention, aqueous solutions containing compounds with the individual elements represented in the catalyst are the preferred source material for each element.

The efficiency of the catalyst of the present invention is dependent upon the relative atomic amounts of each element, indicated by the subscripts a, b, c, d, e, f, in the formula for the catalyst, $Mo_aV_bTe_cNb_dPd_eO_f$. For all formulations the relative atomic amount of molybdenum, as represented by subscript a, is 1. The value of f, the relative atomic amount of oxygen in the catalyst, in all instances, depends on the oxidation state of all other elements present in the catalyst. In one embodiment

of the present invention b = 0.01 to 1.0, c = 0.01 to 1.0, d = 0.01 to 1.0, and $0.01 < e \leq 0.10$.

In an embodiment of the invention, the relative atomic amount of the element vanadium, indicated by subscript b, equals from 0.1 to 0.5. In another embodiment of the invention, b equals from 0.2 to 0.4. In a further embodiment of the invention b equals from 0.25 to 0.35.

In an embodiment of the invention, the relative atomic amount of the element tellurium, indicated by subscript c, equals from 0.05 to 0.4. In another embodiment of the invention, c equals from 0.08 to 0.3. In a further embodiment of the invention, c equals from 0.10 to 0.25.

In an embodiment of the invention, the relative atomic amount of the element niobium, indicated by subscript d, equals from 0.05 to 0.4. In another embodiment of the invention, c equals from 0.08 to 0.3. In a further embodiment of the invention, c equals from 0.10 to 0.25.

Hydrothermal synthesis for preparation of mixed metal oxide catalysts is known in the art, its advantages over conventional preparation methods such as solid-state reaction and dry-up are covered in Watanabe, et al., "New Synthesis Route For Mo-V-Nb-Te Mixed Metal Oxides For Propane Ammoxidation", Applied Catalysis A: General, 194-195, pp. 479-485 (2000).

The present invention comprises a hydrothermal synthesis step for preparation of the catalyst prior to addition of the Pd compound. Compounds containing elements Mo, V, Nb, and Te and a solvent are mixed to form a first mixture. The first mixture is then heated in a pressurized vessel for from 6 to 240 hours. In an embodiment of the invention the preferred solvent used for hydrothermal synthesis of the first mixture is water. Any water suitable for use in chemical syntheses can be utilized, and includes, without limitation, distilled water, de-ionized, and mineral water. The amount of solvent used is not critical for the present invention.

Preparation of the mixture is not limited to addition of all compounds of Mo, V, Nb, and Te at the same time prior to heat treatment in a first closed vessel. For example, the Mo and Te compounds may be added first, followed by the V compound and eventually the Nb compound. For a further example, the process may be reversed in that the Te and Nb compounds are combined followed by addition of a mixture of the Mo and V compounds. Other sequences of addition

would be apparent to a person skilled in the art. Sequence and timing of addition is not limited by these examples.

In an embodiment of the invention the first mixture is heated at a temperature of from 100°C to 200°C. In another embodiment of the invention, the first mixture is heated at a temperature from 130°C to 190°C. In a further embodiment of the invention, the first mixture is heated at a temperature from 160°C to 185°C.

Following hydrothermal synthesis of the first four components of the catalyst the first insoluble material is recovered from the pressurized vessel. At this point, the first insoluble material may be dried prior to calcining in order to remove any residual solvent. Any method known in the art may be used for optional drying of the first insoluble material, including, but not limited to, air drying, vacuum drying, freeze drying, and oven drying.

Methods for calcination are well known in the art. In the present invention, the calcining of the first insoluble material is conducted under an inert atmosphere. The preferred calcination vessel for the present invention is a quartz tube. The inert atmosphere may include any material that does not interact or react with the first insoluble material. Examples include, without limitation, nitrogen, argon, xenon, helium or mixtures thereof. The preferred embodiment of the present invention comprises an inert atmosphere comprising gaseous nitrogen.

Calcination methods for preparation of mixed metal oxide catalysts vary in the art. Variables include the time, temperature range, the speed of heating, use of multiple temperature stages, and the use of an oxidizing or inert atmosphere. For the present invention the speed of heating is not critical and may range from between 0.1°C/minute to around 10°C/minute. Also, the inert gas may be present statically or may be passed over the catalyst at flow rates where the loss of catalyst is minimized, i.e. carryover out of bed.

In an embodiment of the invention the said first recovered insoluble material is calcined by ramping temperature from at or about room temperature to at or about 600°C over a period of 4 to 7 hours, followed by holding at or about 600°C for from 1 hour to 4 hours.

In an embodiment of the invention the time for the calcining ranges from 1 hour to 24 hours. In another embodiment of the invention the time for the calcining

ranges from 3 hours to 15 hours. In the preferred embodiment of the invention the time for the calcining ranges from 4 hours to 12 hours.

In an embodiment of the invention the calcining takes place in an inert atmosphere at a temperature from 500°C to 700°C. In another embodiment of the invention the calcining takes place in an inert atmosphere at a temperature from 550°C to 650°C. In the preferred embodiment of the invention the calcining takes place in an inert atmosphere at a temperature of from 580°C to 620°C.

Following the calcining, the calcining product is impregnated with a Pd component free of halogens to form a second mixture. For the present invention the addition of a Pd component to the catalyst is only effective in increasing the activity of the catalyst, without significantly decreasing the selectivity, depending on the method for addition and the nature of the Pd compound used. The addition of the Pd compound must be performed following the calcining of the first insoluble material containing the four components Mo, V, Te, and Nb.

In an embodiment of the invention the Pd compound, in the form of an aqueous solution, is added dropwise to the calcining product until saturation. In another embodiment of the invention, the Pd component and the calcining product are mixed in an aqueous solution to form a slurry. In an embodiment of the invention the aqueous solution is water. Any water suitable for use in chemical syntheses can be utilized, and includes, without limitation, distilled water and de-ionized water. The amount of solvent used is not critical for the present invention.

The amount of Pd component added, either in dropwise fashion or in a slurry, will correspond roughly with 0.044 mmol Pd/$g_{ODH\ catalyst}$ to yield a final relative atomic amount of Pd, represented by the subscript e in the formula $Mo_aV_bTe_cNb_dPd_eO_f$, between 0.001 and 0.1.

The nature of the Pd compound used must be free of halogens. A catalyst produced using the present invention where the Pd component used is $PdCl_2$, fails to show any activity at all. In a preferred embodiment of the invention the Pd component used is tetra-amine Pd nitrate, chemically represented by the formula $[Pd(NH_3)_4](NO_3)_2$. In another embodiment of the invention the Pd component used is palladium (II) hydrogen carbonate, chemically represented by the formula $Pd(HCO_3)_2$. In another embodiment of the invention the Pd component used is palladium (II) acetate, chemically represented by the formula $Pd(CH_3COO)_2$

Following incorporation of the Pd component, a second insoluble material is dried and recovered for use as a catalyst. Drying steps are commonly used in the art. In an embodiment of the invention the temperature for drying the second insoluble material ranges from 50°C to 150°C. In another embodiment of the invention the temperature for drying the second insoluble material ranges from 110°C to 140°C. In a preferred embodiment of the invention the temperature for drying the second insoluble material ranges from 120°C to 130°C.

In an embodiment of the invention the time for drying the second insoluble material ranges from 1 hour to 48 hours. In another embodiment of the invention the time for drying the second insoluble material is from 8 hours to 36 hours. In a preferred embodiment of the invention the time for drying the second insoluble material is from 12 hours to 24 hours.

The dried second insoluble material is recovered and can be used directly as a catalyst for ODH, using conditions where the only atmospheric components exposed to the catalyst are oxygen and ethane. The ratios of oxygen and ethane and the temperature used for the ODH process are such that the upper explosive limit is not triggered. The ability to perform ODH using this catalyst whereby there is no dilution of the reactants with nitrogen or other inert gas or water confers a commercial advantage as costly downstream processes for the removal of excess oxygen or any unwanted byproducts are not required or are limited in nature.

EXAMPLES

Comparative Example 1 (No Pd Component)

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 and the pH adjusted to 7.5 using a 25% aqueous solution of ammonium hydroxide. The water was evaporated by stirring at 80°C, and the solid precipitate dried at 90°C. 3.0 g of the precipitate was 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 transferred to an autoclave with a Teflon® (tetrafluoroethylene) lining. Air in the autoclave was substituted with argon, the autoclave was pressurized and heated to 175°C for 60 hours. The solid formed was filtered, washed with distilled water and dried at 80°C to produce an active catalyst phase that was calcined at 600°C (2 h) in a flow of argon. The temperature for calcination was ramped from room temperature to 600°C at 1.67°C/min. The resulting powder was pressed and the

required mesh size particles were collected. The resulting catalyst comprised an atomic element ratio (oxygen not included) of $Mo_{1.0}V_{0.31}Te_{0.17}Nb_{0.16}$. – calculated by molar ratio stoichiometry of reagents.

Comparative Example 2 (Impregnation with $PdCl_2$)

The catalyst was prepared according to Comparative Example 1 with the exception that after calcining the sample at 600°C, the catalyst was ground in a mortar with a small amount of water (about 5 ml per gram of the catalyst) for 20 min. The suspension of the catalyst in water was transferred into a glass beaker (volume 50 ml) and then a solution containing 0.1 mmol of $PdCl_2$ in 10 ml of water was added to the suspension. The beaker content was stirred by a magnetic stirrer with a low rate for 2 h. The beaker was placed in a water bath at a temperature of 80°C and the content was stirred until the liquid in the beaker was fully removed. The beaker with the catalyst was transferred into a drying box and was dried overnight at 120°C. The catalyst obtained was ground in a mortar and pressed into tablets that were crashed into particles 0.8-1.0 mm. The resulting catalyst comprised an atomic element ratio (oxygen not included) of$Mo_{1.0}V_{0.31}Te_{0.17}Nb_{0.16}Pd_{0.02}$. – calculated by molar ratio stoichiometry of reagents.

Comparative Example 3 (Direct Pd Incorporation)

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 and the pH adjusted to 7.5 with a 25% aqueous solution of ammonium hydroxide. Water was evaporated by stirring at 80°C. The solid precipitate was dried at 90°C. 3.0 g of the precipitate was 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 together with palladium in the form of $[Pd(NH_3)_4](NO_3)_2]$ in amounts to produce an atomic element ratio (oxygen not included) of $Mo_{1.0}V_{0.31}Te_{0.17}Nb_{0.16}Pd_{0.02}$. The catalyst was calcined at 600°C (2 h) in a flow of argon, where the temperature was ramped from room temperature to 600°C at 1.67°C/min. The powder was pressed and the required mesh size particles were collected.

Example 1 (Pd Nitrate Incorporation)

The catalyst was prepared according to Comparative Example 1 with the exception that after calcining the sample at 600°C, the catalyst was ground in a mortar with a small amount of water (about 5 ml per gram of the catalyst) for 20 min. The suspension of the catalyst in water was transferred into a glass beaker

(volume 50 ml) and then a solution containing 0.1 mmol of $[Pd(NH_3)_4](NO_3)_2]$ in 10 ml of water was added to the suspension. The beaker content was stirred by a magnetic stirrer at a low rate for 2 h. The beaker was placed in a water bath at a temperature of 80°C and the content was stirred until the liquid in the beaker had evaporated completely. The beaker with the catalyst was transferred into a drying box and was dried overnight at 120°C. The resulting catalyst was ground in a mortar and pressed into tablets that were crushed into particles 0.8-1.0 mm. The resulting catalyst comprised an atomic element ratio (oxygen not included) of $Mo_{1.0}V_{0.31}Te_{0.17}Nb_{0.16}Pd_{0.02}$.

Example 2 (Pd Carbonate Incorporation)

The catalyst was prepared according to Example 1 with the exception that after calcining the sample at 600°C, the catalyst was treated with an aqueous solution of $Pd(HCO_3)_2$ to introduce the amount of palladium corresponding to a final atomic element ratio (oxygen not included) of $Mo_{1.0}V_{0.31}Te_{0.17}Nb_{0.16}Pd_{0.02}$.

Example 3 (Pd Acetate Incorporation)

The catalyst was prepared according to Example 1 with the exception that after calcining the sample at 600°C, the catalyst was treated with an aqueous solution of $Pd(CH_3COO)_2$ to introduce the amount of palladium corresponding to a final atomic element ration (oxygen not included) of $Mo_{1.0}V_{0.31}Te_{0.17}Nb_{0.16}Pd_{0.02}$.

ODH Testing Conditions

All catalysts were tested for ability to catalyze oxidative dehydrogenation of ethane using a gas mixture O_2/C_2H_6 with an O_2 content of 25% (outside the explosive limit). The mixture was fed into a plug-flow reactor with a gas hourly space velocity of 4500 h^{-1} at a pressure of 1atm, and a temperature that ranged from 320-440°C (preferably at 420°C). The amount of catalyst loading ranged from 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 and the catalytic activity was measured at 420°C. The data are presented in Table 1.

TABLE 1

Summary of Results

Example	Ethane Conversion %	Oxygen Conversion %	Space–Time Yield of Ethylene (Productivity). mmol/h per g of catalyst	Ethylene Selectivity %
1 (Comparative)	33	56	60	97.5
2 (Comparative)	6	17	-	96
3 (Comparative)	31	53	55	97
1	49	83	94	98
2	48	81	91	98
3	46	80	88	98

INDUSTRIAL APPLICABILITY

The invention disclosed provides a method for preparing an oxidative dehydrogenation catalyst useful for the conversion of ethane into ethylene. The catalyst displays higher than expected activity without loss of selectivity.

CLAIMS

1. An oxidative dehydrogenation catalyst comprising a mixed metal oxide having the empirical formula

$$Mo_aV_bTe_cNb_dPd_eO_f$$

wherein

a, b, c, d, e and f are the relative atomic amounts of the elements Mo, V, Te, Nb, Pd and O, respectively; and

when a=1, b=0.01 to 1.0, c=0.01 to 1.0, d=0.01 to 1.0, $0.001<e\leq0.10$ and f is dependent on the oxidation state of the other elements;

said catalyst having been produced by the process comprising:

i) admixing compounds of elements Mo, V, Te, and Nb, in a solvent comprising water to produce a first mixture;

ii) heating said first mixture in a first pressurized vessel at a temperature of from 100°C to 200°C, (preferably from 130°C to 190°C, most preferably from 160°C to 185°C), for from 6 hours to 240 hours;

iii) recovering first insoluble material from said first pressurized vessel;

iv) subjecting said first recovered insoluble material to a calcining under an inert atmosphere to produce a calcined product;

v) then, impregnating said calcined product from iv) with an aqueous solution of a Pd compound free of halogens to form second mixture;

vi) subjecting said second mixture to drying at a temperature of from 50°C to 150°C, (preferably from 110°C to 140°C, most preferably from 120°C to 130°C), for from 1 hour to 48 hours; and

vii) recovering second insoluble material from vi) to obtain a catalyst.

2. The catalyst of claim 1 wherein b equals from 0.1 to 0.5, (preferably from 0.2 to 0.4, most preferably from 0.25 to 0.35).

3. The catalyst of claim 1 wherein c equals from 0.05 to 0.4, (preferably from 0.08 to 0.3, most preferably from 0.10 to 0.25).

4. The catalyst of claim 1 wherein d equals from 0.05 to 0.4, (preferably from 0.08 to 0.3, most preferably from 0.10 to 0.25).

5. The catalyst of claim 1 wherein e equals from 0.005 to 0.10 (preferably from 0.01 to 0.05, most preferably from 0.015 to 0.03).

6. The catalyst of claim 1 wherein the inert atmosphere comprises gaseous nitrogen.

7. The catalyst of claim 1 wherein the said first recovered insoluble material is calcined at a temperature of from 500°C to 700°C, (preferably from 550°C to 650°C, most preferably from 580°C to 620°C), for from 1 hours to 8 hours.

8. The catalyst of claim 1 wherein the said first recovered insoluble material is calcined by ramping temperature from at or about room temperature to at or about 600°C over a period of 4 to 7 hours, followed by holding at or about 600°C for from 1 hour to 4 hours.

9. The catalyst of claim 1 wherein the Pd compound free of halogens is selected from one of $[Pd(NH_3)_4](NO_3)_2$, $Pd(HCO_3)_2$, $Pd(CH_3COO)_2$ and an analogous Pd containing salt.

10. The catalyst of claim 1 wherein impregnation of said calcined product is accomplished by admixing an aqueous solution of a Pd compound free of halogens.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/053428

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J23/00 B01J23/652 B01J37/10 B01J37/02 C07C5/48
ADD.

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)
B01J C07C

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KUM S S ET AL: "Performance of Pd-promoted Mo-V-Te-Nb-O catalysts in the partial oxidation of propane to acrylic acid", APPLIED CATALYSIS A: GENERAL, ELSEVIER, AMSTERDAM, NL, vol. 365, no. 1, 15 August 2009 (2009-08-15), pages 79-87, XP026319478, ISSN: 0926-860X, DOI: 10.1016/J.APCATA.2009.05.056 [retrieved on 2009-06-06] par. 2 "Experimental" -----	1-10
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 September 2017	11/10/2017

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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