

Description

Title of invention: CATALYST AND METHOD FOR MANUFACTURING SAME, AND METHOD FOR MANUFACTURING UNSATURATED HYDROCARBON

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Technical field

[0001]

The present invention relates to a catalyst and a method for producing the same, and a method for producing an unsaturated hydrocarbon.

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Background Art

[0002]

Methods for producing alkenes by dehydrogenating alkanes are generally known, and various catalysts for this dehydrogenation have been investigated.

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[0003]

For example, Patent Literature 1 describes a dehydrogenation catalyst in which nickel and tin are supported on a composite carrier formed by supporting a specific amount of zinc oxide on a specific γ -alumina carrier. Then, an example is described in which isobutane is dehydrogenated to produce isobutylene (isobutene) using this dehydrogenation catalyst.

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[0004]

In addition, Patent Literature 2 describes a catalyst in which zinc and a metal of VIIIA Group of the Periodic Table are supported on a specific zeolite carrier. And a method for producing an unsaturated hydrocarbon by dehydrogenating a hydrocarbon in the presence of this catalyst is described. As an example thereof, an example is described in which a n-butane is dehydrogenated to produce butene (1-buten, 2-buten, isobutene) using this catalyst.

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[0005]

In addition, Patent Literature 3 describes a method for producing an oxidative dehydrogenation catalyst comprising a step (a) of dispersing a silicate in water, a step (b) of adding a chromium element, a step (c) of adding a surfactant and heat-treating at a temperature of 50 to 150 °C for 1 to 20 hours after step (a) or step (b), and a step (d) of heat-treating at a temperature of 200 to 700 °C for 1 to 10 hours. Then, a method for producing an alkene from an alkane by contacting the obtained catalyst with a mixed gas containing an alkane and oxygen at a specific mixing ratio is described. As an example thereof, an example is described in which isobutylene (isobutene) is produced from isobutane using this catalyst.

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[0006]

In addition, Patent Literature 4 describes that a pretreatment is performed on a catalyst in which a transition metal is supported on a carrier in a hydrocarbon conversion process, but the time of the pretreatment is as short as 30 minutes to 90 minutes, so that the aggregation of the transition metal cannot be suppressed, and a high selectivity cannot be realized.

Citation List

Patent Literature

[0007]

- 10 Patent Literature 1: JP H09-75732A
Patent Literature 2: JP 2013-163647A
Patent Literature 3: JP 2014-140827A
Patent Literature 4: JP 2018-520858A

15 Summary of Invention

Technical Problem

[0008]

- 20 In a method for producing an unsaturated hydrocarbon by dehydrogenation of an alkane, it is desirable that the productivity is high, and for this purpose, it is required to obtain it at a higher selectivity.

[0009]

- 25 It is an object of the present invention to response to the above issue, that is, to provide a catalyst capable of producing an unsaturated hydrocarbon with high selectivity in dehydrogenation of an alkane, a method for producing the same, and a method for producing an unsaturated hydrocarbon.

Solution to Problem

[0010]

- 30 According to an aspect of the present invention, there is provided a catalyst in which a transition metal and carbon are supported on a carrier, and the carbon includes fibrous carbon.

[0011]

According to another aspect of the present invention, there is provided a method for producing a catalyst, including:
forming a catalyst precursor by mixing a solution containing a transition metal

compound and a carrier, and heating to remove a solvent,

bringing a carbon-containing gas into contact with the catalyst precursor to form a catalyst on which a transition metal and carbon are supported,

wherein in forming the catalyst, a fibrous carbon is formed and supported by bringing the carbon-containing gas into contact with the catalyst precursor.

[0012]

According to another aspect of the present invention, there is provided

a method for producing an unsaturated hydrocarbon, the method including bringing a mixed gas containing an alkane and carbon dioxide into contact with the above catalyst to produce an unsaturated hydrocarbon from the alkane.

[0013]

According to another aspect of the present invention, there is provided

a method for producing an unsaturated hydrocarbon, the method including producing a catalyst by the above method for producing a catalyst, and subsequently bringing a mixed gas containing an alkane and carbon dioxide into contact with the obtained catalyst to produce an unsaturated hydrocarbon from the alkane.

[0014]

According to another aspect of the present invention, there is provided

a method for producing an unsaturated hydrocarbon, the method including bringing a carbon-containing gas into contact with a catalyst precursor in which a transition metal compound is supported on a carrier to support carbon including fibrous carbon on the catalyst precursor, thereby forming a catalyst on which a transition metal and carbon including fibrous carbon is supported, and

bringing a mixed gas containing an alkane and carbon dioxide into contact with the obtained catalyst to produce an unsaturated hydrocarbon from the alkane.

Advantageous Effects of Invention

[0015]

According to the present invention, it is possible to provide a catalyst capable of producing an unsaturated hydrocarbon with high selectivity in dehydrogenation of an alkane, a method for producing the same, and a method for producing an unsaturated hydrocarbon.

Brief Description of Drawings

[0016]

Figure 1 is a SEM image of the catalyst of Example 2 according to the present invention.

Figure 2 is an SEM image showing a grid-shaped dividing line in the SEM image of Figure 1.

Description of Embodiments

5 [0017]

Hereinafter, a catalyst and a method for producing the same and a method for producing an unsaturated hydrocarbon (preferably an alkene) from an alkane, according to an embodiment of the present invention, will be described in detail.

[0018]

10 (Catalyst)

A catalyst according to an embodiment of the present invention is a catalyst in which carbon is supported on a carrier on which a transition metal is supported.

This catalyst is a solid catalyst having catalytic activity in a reaction of forming an unsaturated hydrocarbon by dehydrogenation of an alkane. In a method for producing an
15 unsaturated hydrocarbon from an alkane, which will be described later, it is suitable as a catalyst for a reaction for forming an unsaturated hydrocarbon (preferably an alkene) by dehydrogenation of an alkane.

[0019]

In this catalyst, the carrier on which a transition metal and carbon are supported is not
20 particularly limited, and for example, at least one selected from the group consisting of silica, alumina, zirconia, and titania can be used. One of these may be used alone or two or more thereof may be used in combination. Of these, alumina is preferable, and γ -alumina is particularly preferable.

[0020]

The particle size of the carrier can be appropriately selected, and it is preferable to
25 adjust the particle size so that the pressure loss in a catalyst layer of a reactor (e.g., a reaction tube) filled with the obtained catalyst is not excessively increased. From the viewpoint of ensuring the surface area of the catalyst while suppressing the pressure loss in the catalyst layer, it is preferable that the particle diameter of the carrier is as small as possible, and when a mesh according to the
30 Japanese Industrial Standard (JIS) is used, it is preferably 3.5 mesh (opening 5.6mm) or more, and particularly preferably 8.6 mesh (opening 2.0mm) or more. On the other hand, since the fine particle fraction is difficult to handle, and from the viewpoint of influence on reactivity due to an increase in pressure loss when filled in the reactor, it is preferably 635 mesh (opening 20 μ m) or less, and particularly preferably 280 mesh (opening 53 μ m) or less.

[0021]

The catalyst according to an embodiment of the present invention may be filled into a reactor (e.g., a reactor tube) in a powdered state. At that time, it is preferable to adjust the particle size so that the pressure loss in the catalyst layer does not become excessively large. From the viewpoint of ensuring the surface area of the catalyst while suppressing the pressure loss in the catalyst layer, it is preferable that the particle diameter of the catalyst is as small as possible. In addition, from the viewpoint of suppressing pressure loss in the catalyst layer, the catalyst may be mixed with other materials or may be filled after molding. As another material, a filler (silica ball, alumina ball) which is inert to the catalyst and does not deteriorate the catalyst performance can be used. In addition, in molding, a binder which does not deteriorate its catalytic performance can be added to the obtained catalyst, kneaded, and heated to sinter. Examples of the binder (sintering agent) include a silica-based binder, an alumina-based binder, a zirconia-based binder, and a diatomite-based binder. Examples of the shape after molding include a tablet shape, a pellet shape, a spherical shape, and an extruded shape. By molding, strength and handleability can be improved.

[0022]

As the transition metal supported on the carrier, at least one selected from the group consisting of molybdenum, tungsten, chromium, nickel, iron, noble metals (Au, Ag, Pt, Pd, Rh, Ir, Ru, Os), vanadium, manganese, and zinc may be used, and a plurality of kinds thereof may be used. Among these, nickel (Ni) is preferred from the viewpoint of cost and catalyst performance.

[0023]

The amount of the transition metal supported on the carrier is preferably 1.0% by mass or more and 30.0% by mass or less based on the carrier from the viewpoint of exhibiting good activity as a catalyst. By setting the amount of the transition metal supported on the carrier to 1.0% by mass or more, the transition metal particles present as active points tend to be retained on the surface of the carrier, so that the conversion rate of alkanes can be increased. Further, by setting the amount of the transition metal supported on the carrier to 30.0% by mass or less, it is possible to further suppress aggregation of the transition metal particles supported on the carrier, and accordingly a large surface area of the active point can be maintained, and hence the conversion of alkanes and the selectivity of alkenes corresponding to the alkanes can be increased. In the above range, the amount of the transition metal supported on the carrier is more preferably 3.0% by mass or more, still more preferably 5.0% by mass or more, particularly preferably 10.0% by mass or more, and most preferably 15.0% by mass or more, while it is more preferably 28.0% by mass or less, still more preferably 25.0% by mass or less, and particularly preferably 23.0% by

mass or less. In the present invention, the amount of the transition metal supported on the carrier can be measured by X-ray fluorescence analysis measurement.

[0024]

As described above, in the catalyst according to the present embodiment, carbon including fibrous carbon is supported in addition to the transition metal. By carrying carbon including fibrous carbon, the conversion of alkanes and the selectivity of alkenes corresponding to the alkanes in the dehydrogenation reaction of alkanes can be increased. Although the reason for this is not clear, the following reasons are conceivable.

[0025]

In ordinary metal supported catalysts, generally, as a reaction proceeds, the metal particles on the carrier aggregate to become coarse particles, resulting in a decrease in reactivity due to a decrease in the surface area of the active point, and a decrease in selectivity due to a structural change in the active point. However, by carrying carbon including a specific amount of fibrous carbon in advance in addition to the transition metal, aggregation of the transition metal particles with each other due to heat or vibration can be suppressed during the reaction due to the presence of carbon including fibrous carbon, and therefore it is probably that a good active point can be retained, and the selectivity of alkanes and the selectivity of the alkenes corresponding to the alkanes and the selectivity of unsaturated hydrocarbons are further improved. Note that, in the present invention, when observed with a scanning electron microscope (SEM), carbon elongated in a fibrous form (carbon present in a so-called elongated shape) is referred to as fibrous carbon. The cross-sectional shape (the shape of the cross-section perpendicular to the longitudinal direction) of the carbon elongated in a fibrous form may be any one of a circle, an ellipse, a triangle, a rectangle, a polygon, etc., may be an irregular shape, or may be a thin plate shape. Also, there is no particular limitation on the ratio of the length of fibrous carbon to the average diameter of the cross section. Further, the fibrous carbon may be bent or linearly extended, and may be branched.

[0026]

The amount of carbon including fibrous carbon supported on the carrier is preferably 510% by mass or more, and preferably 2500% by mass or less, based on the supported transition metal. When the amount of carbon including fibrous carbon supported on the carrier is 550% by mass or more based on the supported transition metal, an effect of immobilizing the transition metal particles can be easily obtained, so that it is easy to suppress aggregation of the transition metal particles during the reaction. As a result, the conversion of alkanes and the selectivity of the alkenes corresponding to the alkanes can be increased. It is sufficient that the carbon

supported on the carrier contains fibrous carbon, and as long as the amount of carbon including fibrous carbon is within such a range, a more sufficient above effect can be obtained. The fact that fibrous carbon is contained in the carbon supported on the carrier (the presence of fibrous carbon supported on the carrier) can be confirmed by scanning electron microscope (SEM). It is preferable that an observation image obtained by SEM is divided into twelve with a uniform lattice, and fibrous carbon is formed on the carrier to such an extent that the presence of fibrous carbon can be confirmed in each lattice.

On the other hand, if the amount of carbon including fibrous carbon supported on the carrier is 2500% by mass or less based on the supported transition metal, it is possible to further prevent the transition metal particles from being coated with an excessive amount of carbon to hinder the catalytic activity, and it is possible to increase the conversion of alkanes and the selectivity of the alkenes corresponding to the alkanes.

Among the above, the amount of carbon including fibrous carbon supported on the carrier is more preferably 700% by mass or more, particularly preferably 1000% by mass or more, based on the supported transition metal, and on the other hand, it is particularly preferably 2300% by mass or less, and particularly preferably 2000% by mass or less, based on the supported transition metal.

In the present invention, the amount of carbon including fibrous carbon supported on a carrier can be measured using simultaneous measurement of thermogravimetry and differential thermal analysis (TG-DTA) and rising to 1000 °C, and the amount of the supported carbon can be determined from the weight reduction at that time. In the examples described later, since the weight loss when heated to 200 °C is due to the desorption of adsorbed water, it was calculated assuming that the weight loss amount in the heating process from 200 °C to 1000 °C is due to the supported carbon including fibrous carbon.

[0027]

The fibrous carbon supported on the carrier on which the transition metal is supported preferably has an average diameter of the fibrous carbon of 20nm or more and 100nm or less. When the average diameter of the fibrous carbon is 20nm or more, aggregation of the transition metal particles can be further prevented during the reaction, and the conversion of alkanes and the selectivity of the alkenes corresponding to the alkanes can be further improved. On the other hand, when the average diameter of the fibrous carbon is 100nm or less, coating of the transition metal particles with the fibrous carbon can be further suppressed, and it tends to be easy to prevent the decrease in the catalytic activity. Among the above, the average diameter of the fibrous carbon is more preferably 25nm or more, particularly preferably 30nm or more, while still more preferably

95nm or less, and particularly preferably 90nm or less.

In the present invention, the average diameter of the fibrous carbon is defined as an average diameter of fibrous carbon determined by the following: an observation image obtained by a scanning electron microscope (SEM) is divided into twelve with a uniform lattice, and within
5 each lattice, a portion where the diameter of the fibrous carbon is largest and a portion where the diameter of the fibrous carbon is smallest are selected, and the selected diameter values are defined as diameter representative values, and an average value of the diameter representative values of the fibrous carbon is defined as the average diameter of the fibrous carbon.

[0028]

10 (Method for Producing Catalysts)

A method for producing a catalyst according to an embodiment of the present invention includes forming a catalyst precursor by mixing a solution containing a transition metal compound and a carrier, and heating to remove a solvent, and bringing a carbon-containing gas into contact with the catalyst precursor to form a catalyst on which a transition metal and carbon are supported.
15 By bringing the carbon-containing gas into contact with the catalyst precursor, fibrous carbon can be formed and supported.

[0029]

The step of forming the catalyst precursor may include a step of forming a solid by mixing a solution in which a transition metal compound is dissolved and a carrier, and heating to
20 evaporate a solvent, and a step of pulverizing the solid to obtain a powdery catalyst precursor.

[0030]

In the step of forming the catalyst precursor, a transition metal compound containing a transition metal to be supported is dissolved in a solvent to prepare a solution, and a carrier is added into this solution to obtain a mixed liquid containing the transition metal compound and the
25 carrier. In the present invention, addition is one kind of mixing, and it means that it may be further mixed after the addition.

[0031]

As a carrier used in the step of forming the catalyst precursor, at least one selected from the group consisting of silica, alumina, zirconia, and titania, which are described above, can be
30 used. Among these, alumina is preferable, and γ -alumina is particularly preferable.

[0032]

Subsequently, the mixed liquid containing the transition metal compound and the carrier is heated to evaporate the solvent to obtain a catalyst precursor in which the transition metal is supported on the carrier as a solid. By pulverizing the obtained catalyst precursor (solid), a

powdery catalyst precursor can be obtained.

[0033]

The obtained catalyst precursor can be subjected to a drying treatment at, for example, 20 °C or higher and 200 °C or lower, for example, 1 hours or more and 20 hours or less. The temperature of this drying treatment is more preferably 60 °C or higher, still more preferably 100 °C or higher, while more preferably 120 °C or lower. The time of this drying treatment is more preferably 5 hours or more, while more preferably 15 hours or less.

[0034]

Further, the obtained catalyst precursor may be subjected to heat treatment (calcination) at a high temperature of, for example, 300 °C or higher and 1000 °C or lower, for example, 2 hours or more and 30 hours or less. The temperature of this heat treatment (calcination) is more preferably 400 °C or higher, while more preferably 800 °C or lower. The time of this heat treatment (calcination) is more preferably 3 hours or more, while, more preferably 12 hours or less.

[0035]

The obtained powdery catalyst precursor can be filled into a reactor (e.g., a reaction tube) in a powdered state. At that time, it is preferable to adjust the particle size so that the pressure loss in the catalyst precursor phase does not become excessively large. From the viewpoint of ensuring the surface area of the catalyst precursor while suppressing the pressure loss in the catalyst precursor phase, it is preferable that the particle diameter of the catalyst precursor is as small as possible.

In addition, from the viewpoint of suppressing pressure loss in the catalyst precursor phase, the catalyst precursor may be mixed with other materials or may be filled after molding. As another material, a filler (silica ball, alumina ball) which is inert to the catalyst and does not deteriorate the catalyst performance can be used. In the molding, a binder which does not degrade the performance of the finally obtained catalyst can be added to the catalyst precursor, kneaded, and heated to sinter. Examples of the binder (sintering agent) include a silica-based binder, an alumina-based binder, a zirconia-based binder, and a diatomite-based binder. Examples of the shape after molding include a tablet shape, a pellet shape, a spherical shape, and an extruded shape. By molding, strength and handleability can be improved.

[0036]

Next, a carbon-containing gas is brought into contact with the obtained catalyst precursor. Thus, it is carbonized by an oxidation reaction of the carbon-containing gas. In addition, at the same time, by reducing the transition metal present in an oxidation state (transition metal oxide) on the catalyst precursor, carbon is supported simultaneously with reduction of the

transition metal oxide, and a catalyst (catalyst for alkane dehydrogenation) in which the transition metal and carbon are supported can be formed. At this time, since reduction of the transition metal oxide and supporting carbon can be performed simultaneously, carbon is generated between the transition metal oxides during reduction of the transition metal oxide, and aggregation of the transition metal crystallites can be suppressed.

[0037]

Regarding the crystallite diameter of the transition metal supported on the catalyst (carrier of the catalyst), a ratio of the crystallite diameter of the transition metal after bringing the carbon-containing gas into contact to the crystallite diameter of the transition metal when the carbon-containing gas is not brought into contact, or a ratio of the crystallite diameter of the transition metal when the carbon supported on the carrier includes fibrous carbon to the crystal grain diameter of the transition metal supported on the carrier when the carbon supported on the carrier does not include fibrous carbon is preferably 0.80 or less, more preferably more than 0.00 and not more than 0.60, and still more preferably 0.20 or more and 0.50 or less. It is possible to appropriately adjust the conditions shown below so as to fall within this range.

In the measurement of the crystallite diameter of the transition metal supported on the carrier, the powder X-ray analysis measurement of the catalyst is performed, and from the obtained result, it can be calculated using the sheller equation and the peak assigned to the transition metal crystallite. In the present invention, the powder X-ray analysis measurement was conducted using SmartLab/R/INP/DX (manufactured by Rigaku Corporation) was used. The measurement was carried out using Cu-K α ray as an X-ray source, at tube voltage 45kV, and a tube current 150mA. In addition, for example, when Ni is used as the transition metal, it can be calculated using the peak assigned to the (112) plane of $2\theta = 44^\circ$.

As described above, the reference of the ratio of the crystallite diameter of the transition metal supported on the catalyst (carrier of the catalyst) can be the crystallite diameter of the transition metal when the carbon-containing gas is not brought into contact with the catalyst precursor, or the crystal grain diameter of the transition metal supported on the carrier when the supported carbon does not include fibrous carbon. As the reference, it is preferable to use the crystallite diameter of the transition metal when the catalyst precursor is subjected to a hydrogen reduction treatment (contact with a pretreatment gas containing hydrogen which does not contain the carbon-containing gas). In particular, it is preferable to use as the reference the crystal grain diameter of the transition metal supported on the carrier after the catalyst precursor is subjected to the hydrogen reduction treatment (contact with the pretreatment gas containing hydrogen which does not contain the carbon-containing gas) under the conditions of Comparative Example 3

described later.

[0038]

This carbon-containing gas preferably contains a hydrocarbon as a source of carbon (carbon source) to be supported on the catalyst precursor. This hydrocarbon is preferably an alkane having 2 to 5 carbon atoms. Examples of the alkane having 2 to 5 carbon atoms include ethane, propane, n-butane, isobutane, n-pentane, and isopentane. These may be used alone or in combination of two or more thereof.

When the step of producing the catalyst and the step of dehydrogenating the alkane using the obtained catalyst to produce an unsaturated hydrocarbon are carried out continuously, the carbon source for supporting carbon and the alkane raw material for dehydrogenation reaction may be different from each other, or the same hydrocarbon may be used, but from the viewpoint of simplifying the process, the same hydrocarbon is preferable. In this case, as the carbon source and the alkane raw material, an alkane having 2 to 5 carbon atoms described above (e.g., ethane, propane, n-butane, isobutane, n-pentane, isopentane) is preferable, and isobutane is more preferable.

[0039]

This carbon-containing gas may contain an inert gas such as helium or nitrogen in addition to the carbon source.

[0040]

The concentration of the carbon source (preferably hydrocarbon) contained in the carbon-containing gas (the volume ratio of the carbon source to the carbon-containing gas) is preferably 1% by volume or more and 30% by volume or less, particularly preferably 5% by volume or more, while particularly preferably 20% by volume or less. When the concentration of the carbon source is 1% by volume or more, a sufficient amount of carbon can be supported better, and the selectivity of the unsaturated hydrocarbon can be further increased. Further, when the concentration of the carbon source is 30% by volume or less, it is possible to more easily control the support of excess carbon, and the decrease in the alkane conversion rate and the selectivity of the unsaturated hydrocarbon can be more sufficiently suppressed.

[0041]

The temperature in the step of supporting carbon on the catalyst precursor (the temperature at which the carbon-containing gas is brought into contact with the catalyst precursor) is preferably 300 °C or more and 1000 °C or less, particularly preferably 400° C or more, while more preferably 700 °C or less, and particularly preferably 600 °C or less. When the temperature of this carbon supporting step is 300 °C or higher, a more sufficient amount of supported carbon

can be obtained. Further, when the temperature of this carbon supporting step is 1000 °C or less, it is possible to more sufficiently suppress the decrease in the amount of supported carbon and the decrease in the catalytic activity due to the thermal decomposition reaction of the alkane of the carbon source.

5 [0042]

The pressure in the step of supporting carbon on the catalyst precursor (the pressure at which the carbon-containing gas is brought into contact with the catalyst precursor) can be appropriately selected depending on the type of the carbon-containing gas to be used, but is preferably 0.01MPa or more and 1MPa or less. By setting the pressure to 0.01MPa or more, it is possible to easily suppress desorption of components on the carrier under reduced pressure. Further, by setting the pressure to 1MPa or less, an increase in reactivity due to pressure can be more sufficiently prevented, and an excessive amount of carbon supported on the carrier can be prevented. Among the above, it is more preferably 0.8MPa or less, particularly preferably 0.5MPa or less, while still more preferably 0.05MPa or more. The pressure may be atmospheric pressure (0.101MPa).

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[0043]

As a method of bringing the carbon-containing gas into contact with the catalyst precursor, a fixed bed flow type reaction method in which a carbon-containing gas is flowed through a reactor (e.g., a reaction tube) filled with the catalyst precursor can be used.

20 [0044]

The W/F when the carbon-containing gas is brought into contact with the catalyst precursor is preferably 0.03g • min/ml or more and 0.5g • min/ml or less.

W is a mass (g) of the catalyst precursor filled in the reaction tube, and F is a flow rate (ml/min) of the carbon-containing gas flowing into the reaction tube filled with the catalyst precursor. In other words, W/F is a mass of the catalyst precursor filled in the reaction tube relative to a flow rate of the carbon-containing gas flowing into the reactor, and is represented by the following formula.

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[0045]

W/F = (Amount of catalyst precursor filled in the reaction tube [g]) / (Flow rate of carbon-containing gas flowing into the reaction tube [ml/min])

30

[0046]

By setting the W/F to 0.03g • min/ml or more, it is possible to prevent the amount of supported carbon from becoming insufficient. Further, by setting W/F to 0.5g • min/ml or less, it is possible to prevent the amount of supported carbon from becoming excessive. Among the

above, W/F is particularly preferably 0.05g • min/ml or more, while particularly preferably 0.2g • min/ml or less.

[0047]

(Method for producing unsaturated hydrocarbons from alkanes)

5 In the method for producing an unsaturated hydrocarbon according to an embodiment of the present invention, the catalyst according to the present invention is brought into contact with a mixed gas containing an alkane and carbon dioxide (hereinafter, also referred to as "reaction gas" as appropriate) to produce an unsaturated hydrocarbon from the alkane.

[0048]

10 The alkane raw material used in the dehydrogenation reaction of the alkane is not particularly limited, but an alkane having 2 to 5 carbon atoms is preferable. When the number of carbon atoms is 5 or less, generation of by-products having a low carbon number due to the decomposition reaction can be suppressed. Examples of the alkane having 2 to 5 carbon atoms include ethane, propane, n-butane, isobutane, n-pentane, and isopentane. These may be used
15 alone or in combination of two or more thereof. The dehydrogenation reaction mainly produces ethylene from ethane, propylene from propane, butadiene from n-butane, isobutene from isobutane, pentene from n-pentane, and isoprene from isopentane.

[0049]

In the production method according to an embodiment of the present invention, the
20 dehydrogenation reaction of the alkanes described above is performed to produce the corresponding unsaturated hydrocarbons. This dehydrogenation reaction is carried out by bringing a mixed gas (reaction gas) containing an alkane and carbon dioxide into contact with the catalyst according to the present invention. The molar ratio of carbon dioxide to alkane contained in this mixed gas (reaction gas) is preferably 0.1 or more and 1.9 or less, more preferably 0.25 or
25 more, while more preferably 1.6 or less. When this molar ratio is smaller than 0.1, since the concentration of carbon dioxide is low, the reactivity tends to decrease. On the other hand, when this molar ratio is larger than 1.9, since the concentration of carbon dioxide is high, selectivity tends to decrease.

[0050]

30 In addition to the alkane and carbon dioxide, this mixed gas (reaction gas) may contain an inert gas such as helium or nitrogen, or water vapor (water), methane, hydrogen, or the like as long as the effect of the present invention is not impaired.

[0051]

The concentration of the alkane in this mixed gas (reaction gas) is preferably 1% by

volume or more and 30% by volume or less, more preferably 1% by volume or more, still more preferably 5% by volume or more, while still more preferably 20% by volume or less. When the concentration of the alkane is 1% by volume or more, it is possible to further suppress the decrease in selectivity of the unsaturated hydrocarbon due to the increase of the conversion rate of the alkane.

5 Further, when the concentration of the alkane is 30% by volume or less, it is possible to further suppress the decrease in conversion of the alkane.

[0052]

The temperature of the dehydrogenation reaction of alkane (the temperature at which the mixed gas is brought into contact with the catalyst) is preferably 300 °C or more and 1000 °C
10 or less, more preferably 400 °C or more, while more preferably 700 °C or less, and even more preferably 600 °C or less. When the temperature of this dehydrogenation reaction is 300 °C or higher, more sufficient catalytic activity can be obtained. Further, when the temperature of this dehydrogenation reaction is 1000 °C or less, it is possible to further suppress the decrease in the selectivity of the unsaturated hydrocarbon and the decrease in the catalytic activity due to the
15 thermal decomposition reaction of the alkane.

[0053]

The pressure in the dehydrogenation reaction of the alkane can be appropriately selected depending on the type of the alkane used in the reaction, but is usually set to 1MPa or less, preferably 0.01MPa or more and 1MPa or less. Among these, the pressure is more preferably
20 0.8MPa or less, still more preferably 0.5MPa or less, while more preferably 0.05MPa or more, and still more preferably 0.1MPa or more. The pressure may be atmospheric pressure (0.101MPa). By setting the pressure to 0.01MPa or more, the active point on the catalyst and the alkane is more appropriately contacted during the reaction, and the selectivity of the alkane is easily improved. Further, by setting the pressure to 1MPa or less, it is possible to further suppress the runaway
25 reaction caused by excessive contact of the alkane in the reaction gas and the generated unsaturated hydrocarbon with the active point on the catalyst, and also the selectivity of the corresponding alkene can be increased.

[0054]

The reaction form used in the method for producing an unsaturated hydrocarbon
30 according to the embodiment of the present invention is not particularly limited, and the usual form used for catalytic reactions can be adopted. For examples, reaction types such as a fixed bed, a moving bed, and a fluidized bed. Among these, a fixed bed system can be suitably employed in view of relatively simple apparatus and easy process design. In other words, in the method for producing an unsaturated hydrocarbon according to the embodiment of the present

invention, the dehydrogenation reaction of alkane can be performed by a fixed bed flow type reaction method in which a mixed gas (reaction gas) containing an alkane of a raw material, carbon dioxide, or the like is flowed through a reactor (e.g., a reaction tube) filled with the catalyst according to the present invention.

5 [0055]

The W/F in the dehydrogenation reaction of alkane is preferably $0.001\text{ g} \cdot \text{min/ml}$ or more and $1000\text{ g} \cdot \text{min/ml}$ or less. The W/F is more preferably $0.01\text{ g} \cdot \text{min/ml}$ or more, while more preferably $100\text{ g} \cdot \text{min/ml}$ or less.

10 W is a mass (g) of the catalyst filled in the reaction tube, and F is a flow rate (ml/min) of the mixed gas (reaction gas) containing an alkane and carbon dioxide flowing into the reaction tube filled with the catalyst. In other words, W/F is a mass of the catalyst filled in the reaction tube relative to a flow rate of the mixed gas (reaction gas) flowing into the reaction tube, and is represented by the following formula.

[0056]

15
$$W/F = (\text{Amount of catalyst filled in the reaction tube [g]}) / (\text{Flow rate of the mixed gas flowing into the reaction tube [ml/min]})$$

[0057]

When the W/F is $0.001\text{ g} \cdot \text{min/ml}$ or more, the reaction time of the alkane with respect to the catalyst can be further secured, and the conversion rate of the alkane can be improved. 20 Further, when the W/F is $1000\text{ g} \cdot \text{min/ml}$ or less, it is possible to further prevent the reaction time of the alkane with respect to the catalyst from becoming excessive, and it is possible to further prevent a decrease in selectivity due to the generated alkene reacting on the catalyst to become carbon dioxide.

25 Examples

[0058]

Hereinafter, the present invention will be described in detail by way of Examples and Comparative Examples, but the present invention is not limited to these Examples.

[0059]

30 (Example 1)

First, a catalyst (Ni-C/ γ - Al_2O_3 catalyst) was prepared as follows.

To 15 parts by mass of water, 3.89 parts by mass of nickel nitrate hexahydrate (Wako Pure Chemical Industries, Ltd.) was added and dissolved to obtain an aqueous solution so that the charge amount of Ni to γ - Al_2O_3 became 20% by mass.

Afterwards, 4 parts by weight of γ - Al_2O_3 (Nippon Light Metal Co., Ltd.) was added to the aqueous solution and mixed. The mixture was then heated and the water evaporated to give a solid. The resulting solid was pulverized and dried in vacuo at 110 °C for 12 hours.

The pulverized solid was further calcined for one hour at 550 °C (heating rate 1 °C/min).

- 5 The obtained solid was pulverized again to obtain a powdery catalyst precursor 1 (γ - Al_2O_3 on which nickel was supported).

[0060]

- 10 The obtained catalyst precursor 1 was packed in a quartz reaction tube having a diameter of 9mm and a length of 35mm, which was installed in a fixed bed flow type reactor, and heated to 550 °C while flowing helium. Thereafter, each condition was set so that W/F of the pretreatment gases containing 85.8% by volume of helium and 14.2% by volume of isobutane became 0.12g • min/ml. In this way, the pretreatment gas was flowed through the reaction tube for 3 hours to obtain a Ni-C/ γ - Al_2O_3 catalyst in which carbon was supported on the catalyst precursor 1.

- 15 In addition, powder X-ray analysis measurement of the obtained catalysts (Ni-C/ γ - Al_2O_3 catalysts) was measured. For the powder X-ray analysis measurement, SmartLab/R/INP/DX (manufactured by Rigaku Corporation) was used. The measurement was carried out using Cu-K α ray as an X-ray source, at tube voltage 45kV, and a tube current 150mA. The crystallite diameter of Ni was calculated using the peak assigned to the (112) plane of $2\theta =$
20 44 °.

[0061]

Next, isobutene was produced from isobutane using this catalyst in the following manner.

- 25 A reaction gas adjusted to 73.7% by volume of helium, 14.2% by volume of isobutane, and 12.1% by volume of carbon dioxide was flowed in a state in which the catalyst obtained as described above was filled in the reaction tube as it was. At that time, each condition was set so that the W/F was 0.017g • min/ml.

- 30 The reaction tube outlet gas at 6 hours after starting the flow of the reaction gas was measured by gas chromatography to determine isobutane conversion rate, isobutene selectivity and isobutene yield. The results are shown in Table 1.

[0062]

"W/F" is represented by the following formula.

W/F = Amount of catalyst precursor or catalyst filled in the reaction tube (g) / Feed rate of carbon-containing gas or reaction gas supplied into the reaction tube (ml/min)

[0063]

In addition, isobutane conversion rate, isobutene selectivity and isobutene yield are represented by the following formulas.

Isobutane conversion rate (%) = (number of moles of reacted isobutane) / (number of
5 moles of supplied isobutane)

Isobutene selectivity (%) = (number of moles of produced isobutene) / (number of
moles of reacted isobutane)

Isobutene yield (%) = (number of moles of isobutene produced) / (number of moles of
supplied isobutane)

10 [0064]

(Example 2)

A catalyst (Ni-C/ γ -Al₂O₃ catalyst) was prepared by the same method as in Example 1, except that the flow time of the pretreatment gas was changed to 5 hours, and subsequently isobutene was produced by the same method as in Example 1.

15 Further, by using simultaneous measurement of thermogravimetry and differential thermal analysis (TG-DTA), the obtained catalyst (Ni-C/ γ -Al₂O₃ catalyst) was heated to 1000 °C, and the amount of supported carbon was measured from the weight reduction at that time. In the weight change at this time, since the weight loss when heated to 200 °C was due to the desorption of adsorbed water, it was calculated assuming that the weight loss amount in the heating process
20 from 200 °C to 1000 °C is due to the supported carbon including fibrous carbon. Subsequently, it was confirmed by using a scanning electron microscope (SEM) that the carbon of the catalyst was fibrous carbon (SEM images are shown in Figs. 1 and 2). The average diameter of the fibrous carbon was 41.9nm. The results are shown in Table 1.

[0065]

25 (Example 3)

A catalyst (Ni-C/ γ -Al₂O₃ catalyst) was prepared by the same method as in Example 1, except that the flow time of the pretreatment gas was changed to 7 hours, and subsequently isobutene was produced by the same method as in Example 1. The results are shown in Table 1.

[0066]

30 (Comparative Example 1)

A Ni/ γ -Al₂O₃ catalyst was prepared by the same method as in Example 1, except that the pretreatment gas was not flowed, and subsequently isobutene was produced by the same method as in Example 1. The results are shown in Table 1.

[0067]

(Comparative Example 2)

A Ni/ γ -Al₂O₃ catalyst was prepared by the same method as in Example 1, except that the pretreatment gas was changed to a gas containing 80.0% by volume of helium and 20.0% by volume of hydrogen, and each condition was changed so that W/F was 0.0042g • min/ml and the flow time of the pretreatment gas was 1 hours, and subsequently isobutene was produced by the same method as in Example 1. The results are shown in Table 1.

[0068]

(Comparative Example 3)

A Ni/ γ -Al₂O₃ catalyst was prepared by the same method as in Comparative Example 2, except that the flow time of the pretreatment gas was changed to 5 hours, and subsequently isobutene was produced by the same method as in Example 1. The results are shown in Table 1.

[0069]

(Comparative Example 4)

A Ni/ γ -Al₂O₃ catalyst was prepared by the same method as in Example 1, except that the flow time of the pretreatment gas was changed to 1 hours, and subsequently isobutene was produced by the same method as in Example 1. The results are shown in Table 1.

[0070]

[Table 1]

(Table 1)	Flow time of pretreatment gas [hr]	Composition of pretreatment gas [% by volume]	W/F of pretreatment gas ($\text{g} \cdot \text{min}/\text{ml}$)	W/F of reaction gas ($\text{g} \cdot \text{min}/\text{ml}$)	Flow time of reaction gas [hr]	Isobutane conversion rate [%]	Isobutene selectivity [%]	Isobutene yield [%]	Carbon amount of catalyst [% by mass]	Carbon structure of catalyst	Crystallite diameter of Ni after pretreatment (μm)	Ratio of crystallite diameter of Ni
Example 1	3	helium : 85.8 isobutane : 14.2	0.12	0.0017	6	33.13	49.54	16.41			30	0.32
Example 2	5	helium : 85.8 isobutane : 14.2	0.12	0.0017	6	32.03	58.02	18.58	1649	Including fibrous carbon	29	0.31
Example 3	7	helium : 85.8 isobutane : 14.2	0.12	0.0017	6	31.07	51.13	15.89			39	0.42
Comparative Example 1	0	—	—	0.0017	6	33.8	23.49	7.94	0	non	90	0.97
Comparative Example 2	1	helium : 80.0 hydrogen : 20.0	0.0042	0.0017	6	52.09	10.06	5.24	0	non		
Comparative Example 3	5	helium : 80.0 hydrogen : 20.0	0.0042	0.0017	6	14.41	26.78	3.86	0	non	93	1.00
Comparative Example 4	1	helium : 85.8 isobutane : 14.2	0.12	0.0017	6	49.0	18.6	9.1	504		75	0.81

Claims

[Claim 1]

A catalyst for alkane dehydrogenation, wherein a transition metal and carbon are supported on a carrier, and the carbon comprises fibrous carbon,

5 the transition metal is Ni,

an amount of the carbon based on the transition metal is 1000% by mass or more and 2500% by mass or less, and

a ratio of a crystallite diameter of the transition metal when the carbon comprises the fibrous carbon to a crystallite diameter of the transition metal supported on the carrier when the carbon supported on the carrier does not comprise fibrous carbon is 0.80 or less.

[Claim 2]

The catalyst according to claim 1, wherein a ratio of a crystallite diameter of the transition metal when the carbon comprises the fibrous carbon to a crystallite diameter of the transition metal supported on the carrier when the carbon supported on the carrier does not comprise fibrous carbon is 0.20 or more and 0.50 or less.

[Claim 3]

The catalyst according to claim 1 or 2, wherein an amount of the carbon based on the transition metal is 1000% by mass or more and 2300% by mass or less.

[Claim 4]

The catalyst according to claim 1, wherein an amount of the carbon based on the transition metal is 1000% by mass or more and 2000% by mass or less.

[Claim 5]

The catalyst according to any one of claims 1 to 4, wherein the carrier is at least one selected from the group consisting of silica, alumina, zirconia, and titania.

[Claim 6]

The catalyst according to any one of claims 1 to 4, wherein the carrier is γ -alumina.

[Claim 7]

A method for producing a catalyst, comprising:

forming a catalyst precursor by mixing a solution containing a transition metal compound and a carrier, and heating to remove a solvent,

bringing a carbon-containing gas into contact with the catalyst precursor to form a catalyst on which a transition metal and carbon are supported,

5 wherein in forming the catalyst, a fibrous carbon is formed and supported by bringing the carbon-containing gas into contact with the catalyst precursor,

the transition metal is Ni,

a ratio of a crystallite diameter of the transition metal supported on the catalyst to a crystallite diameter of the transition metal on the catalyst precursor when the carbon-containing
10 gas is not brought into contact is 0.80 or less, and

the catalyst is a catalyst for producing an unsaturated hydrocarbon by bringing a mixed gas comprising an alkane and carbon dioxide into contact with the catalyst.

[Claim 8]

15 The method for producing a catalyst according to claim 7, wherein the step of forming the catalyst precursor comprises a step of forming a solid by mixing a solution in which a transition metal compound is dissolved and a carrier, and heating to evaporate a solvent, and a step of pulverizing the solid to obtain a powdery catalyst precursor.

20 [Claim 9]

The method for producing a catalyst according to claim 7 or 8, wherein the carbon-containing gas comprises a hydrocarbon.

[Claim 10]

25 The method for producing a catalyst according to claim 9, wherein the hydrocarbon is an alkane having 2 to 5 carbon atoms.

[Claim 11]

30 The method for producing a catalyst according to claim 9, wherein the hydrocarbon is isobutane.

[Claim 12]

The method for producing a catalyst according to any one of claims 9 to 11, wherein a volume ratio of the hydrocarbon to the carbon-containing gas is 1% by volume or more and 30%

by volume or less.

[Claim 13]

The method for producing a catalyst according to any one of claims 7 to 12, wherein a
5 temperature at which the carbon-containing gas is brought into contact with the catalyst precursor
is 300 °C or more and 1000 °C or less.

[Claim 14]

The method for producing a catalyst according to any one of claims 7 to 13, wherein a
10 ratio (W/F) of an amount of the catalyst precursor to a feed rate of the carbon-containing gas when
the carbon-containing gas is brought into contact with the catalyst precursor is 0.03g • min/ml or
more and 0.5g • min/ml or less.

[Claim 15]

15 The method for producing a catalyst according to any one of claims 7 to 14, wherein
the carrier is at least one selected from the group consisting of silica, alumina, zirconia, and titania.

[Claim 16]

20 The method for producing a catalyst according to any one of claims 7 to 14, wherein
the carrier is γ -alumina.

[Claim 17]

The method for producing a catalyst according to any one of claims 7 to 16, wherein a
ratio of a crystallite diameter of the transition metal supported on the catalyst to a crystallite
25 diameter of the transition metal on the catalyst precursor when the carbon-containing gas is not
brought into contact is 0.20 or more and 0.50 or less.

[Claim 18]

30 A method for producing an unsaturated hydrocarbon, the method comprising bringing
a mixed gas comprising an alkane and carbon dioxide into contact with the catalyst according to
any one of claims 1 to 6 to produce an unsaturated hydrocarbon from the alkane.

[Claim 19]

The method for producing an unsaturated hydrocarbon according to claim 18, wherein

in the mixed gas, a molar ratio of the carbon dioxide to the alkane is 0.1 or more and 1.9 or less.

[Claim 20]

The method for producing an unsaturated hydrocarbon according to claim 18 or 19,
5 wherein the alkane is an alkane having 2 to 5 carbon atoms.

[Claim 21]

The method for producing an unsaturated hydrocarbon according to claim 18 or 19,
10 wherein the alkane is isobutane.

[Claim 22]

The method for producing an unsaturated hydrocarbon according to any one of claims
18 to 21, wherein a temperature at which the mixed gas is brought into contact with the catalyst is
300 °C or more and 1000 °C or less.

[Claim 23]

The method for producing an unsaturated hydrocarbon according to any one of claims
18 to 22, wherein a ratio (W/F) of an amount of the catalyst to a feed rate of the mixed gas when
the mixed gas is brought into contact with the catalyst is 0.001g • min/ml or more and 1000g •
20 min/ml or less.

[Claim 24]

A method for producing an unsaturated hydrocarbon, the method comprising producing
a catalyst by the production method according to any one of claims 7 to 17, and subsequently
25 bringing a mixed gas comprising an alkane and carbon dioxide into contact with the obtained
catalyst to produce an unsaturated hydrocarbon from the alkane.

[Claim 25]

The method for producing an unsaturated hydrocarbon according to claim 24, wherein
30 in the mixed gas, a molar ratio of the carbon dioxide to the alkane is 0.1 or more and 1.9 or less.