

## DESCRIPTION

PRODUCTION METHOD FOR  $\epsilon$ -CAPROLACTAM

## 5     Technical Field

[0001]

The present invention relates to a method of producing  $\epsilon$ -caprolactam, the method including conducting a gas phase reaction using a solid catalyst to convert cyclohexanone oxime into  $\epsilon$ -caprolactam.

10             Priority is claimed on Japanese Patent Application No. 2011-228142, filed October 17, 2011, the content of which is incorporated herein by reference.

## Background Art

[0002]

15              $\epsilon$ -Caprolactam is an important key chemical raw material as a raw material for producing nylon. As a method of producing  $\epsilon$ -caprolactam, a method including a step in which a gas phase reaction is conducted using a solid catalyst such that cyclohexanone oxime is subjected to rearrangement reaction (i.e., Beckmann rearrangement reaction) has been well known. A method is disclosed, in which the conversion of cyclohexanone  
20             oxime, the selectivity of  $\epsilon$ -caprolactam and the lifetime of catalyst can be improved by conducting the rearrangement reaction in the presence of a lower alcohol (see Patent Document 1). According to the method, even in a condition where the conversion of cyclohexanone oxime is virtually in the vicinity of 100%, both  $\epsilon$ -caprolactam can be obtained with extremely high selectivity and the lifetime of catalyst can be improved.

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## Citation List

## Patent Document

[0003]

[Patent Document 1] Japanese Patent No. 2616088

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## Summary of Invention

Problems To Be Resolved By the Invention [0004]

In the production method described in Patent Document 1, the lower alcohol used in the rearrangement reaction can be recycled after the reaction so as to be reused. It is an important step in the production of  $\epsilon$ -caprolactam with a low cost.

On the other hand, to improve the yield of  $\epsilon$ -caprolactam, it is important to reduce the amount of impurities mixed during the rearrangement reaction so as to improve the conversion and the selectivity. For example, the lower alcohol which has been recycled to be reused may cause the contamination of a reaction system due to impurities. Therefore, the amount of impurities needs to be reduced. By reducing the amount of impurities, the yield of  $\epsilon$ -caprolactam can be further improved.

[0005]

The present invention was achieved under such circumstances, and an object of the present invention is to provide a method of producing  $\epsilon$ -caprolactam, which exhibits excellent conversion and excellent selectivity in the rearrangement reaction of cyclohexanone oxime.

Means Of Solving the Problems [0006]

In order to solve the problems described above, the present invention provides a method of producing  $\epsilon$ -caprolactam, in which a gas phase reaction with a solid catalyst is conducted in the presence of a lower alcohol to convert cyclohexanone oxime into  $\epsilon$ -caprolactam, the lower alcohol contains a recycled lower alcohol which is recovered from a reaction mixture of the gas phase reaction, and the method includes adjusting the amount of water, ammonia and amines in a gas phase reaction system to the following values (1) to (3).

(1)  $0 \leq \{[\text{the amount of ammonia (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 14$

(2)  $0 < \{[\text{the amount of water (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 11$

(3)  $0 \leq \{[\text{the amount of amines (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 7.5$

In the method of producing  $\epsilon$ -caprolactam according to the present invention, a distilled lower alcohol is preferably used as part of the recycled lower alcohol, the distilled lower alcohol is obtained by distilling the reaction mixture to separate gas

mainly containing the lower alcohol, then cooling and condensing part of the gas to obtain a liquid mixture, and then distilling the liquid mixture to obtain the distilled lower alcohol.

In the method of producing  $\epsilon$ -caprolactam according to the present invention,  
5 the solid catalyst is preferably zeolite.

#### Advantageous Effects of Invention

[0007]

According to the present invention, a method of producing  $\epsilon$ -caprolactam, which  
10 exhibits excellent conversion and excellent selectivity in the rearrangement reaction of cyclohexanone oxime may be provided.

By reusing the recycled lower alcohol, the amount of industrial waste may be reduced, and the burden on the environment may be reduced.

#### 15 Brief Description of Drawings

[0008]

FIG. 1 is a flow diagram for illustrating the production process in the method of producing  $\epsilon$ -caprolactam according to an embodiment of the present invention.

#### 20 Description of Embodiments

[0009]

The method of producing  $\epsilon$ -caprolactam related to the present invention is a method including conducting a gas phase reaction with a solid catalyst in the presence of a lower alcohol to convert cyclohexanone oxime into  $\epsilon$ -caprolactam. The lower alcohol  
25 existing in the reaction system contains a lower alcohol which has been recovered from the reaction mixture of the gas phase reaction (hereafter, sometimes referred to as “recycled lower alcohol”). The method includes adjusting the amount of water, ammonia and amines in a gas phase reaction system to the following values.

(1)  $0 \leq \{[\text{the amount of ammonia (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 14$

(hereafter, sometimes referred to as “mole percent (a)”) )

(2)  $0 < \{[\text{the amount of water (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 11$

(hereafter, sometimes referred to as “mole percent (b)”)

(3)  $0 \leq \{[\text{the amount of amines (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 7.5$

(hereafter, sometimes referred to as “mole percent (c)”)

5 In the gas phase reaction, a rearrange reaction of cyclohexanone oxime (i.e., Beckmann rearrangement reaction) proceeds.

[0010]

That is, the present invention relates to the followings.

[0011]

10 [1] A method of producing  $\epsilon$ -caprolactam, including:

conducting a gas phase reaction in which cyclohexanone oxime is allowed to come into contact with a solid catalyst in the presence of a lower alcohol, and then cyclohexanone oxime is converted into  $\epsilon$ -caprolactam, and

15 adjusting the amount of water, ammonia and amines in a gas phase reaction system to the following values (1) to (3), wherein

the lower alcohol contains a recycled lower alcohol which is recovered from a reaction mixture obtained by a gas phase reaction.

(1)  $0 \leq \{[\text{the amount of ammonia (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 14$

20 (2)  $0 < \{[\text{the amount of water (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 11$

(3)  $0 \leq \{[\text{the amount of amines (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 7.5$

[0012]

25 [2] The method of producing  $\epsilon$ -caprolactam according to [1], wherein the recycled lower alcohol contains a distilled lower alcohol, and wherein the distilled lower alcohol is obtained by a method which includes distilling the reaction mixture obtained by a gas phase reaction to separate gas mainly containing the lower alcohol, then

30 cooling and condensing part of the gas to obtain a liquid mixture mainly containing the lower alcohol, and then

distilling the liquid mixture to obtain the distilled lower alcohol.

[0013]

[3] The method of producing  $\epsilon$ -caprolactam according to [1] or [2], wherein the solid catalyst is zeolite.

[0014]

[4] A method of producing  $\epsilon$ -caprolactam, including:

5 a vaporization step of vaporizing cyclohexanone oxime in the presence of an inert gas and a lower alcohol to obtain raw material gas containing cyclohexanone oxime, the inert gas and the lower alcohol;

a reaction step of contacting the raw material gas with a solid catalyst to conduct a gas phase reaction, and then converting cyclohexanone oxime into  $\epsilon$ -caprolactam to  
10 obtain a reaction gas containing  $\epsilon$ -caprolactam, the lower alcohol and the inert gas;

a first distillation step of cooling the reaction gas to obtain a reaction solution, and then separating a high-boiling component from the reaction solution to obtain a mixed gas containing  $\epsilon$ -caprolactam, the lower alcohol and the inert gas;

a lower alcohol separation step of separating a crude lower alcohol mixture  
15 containing a lower alcohol and the inert gas, and a crude  $\epsilon$ -caprolactam mixture containing  $\epsilon$ -caprolactam from the mixed gas;

a second distillation step of separating a low-boiling component and a high-boiling component from the crude  $\epsilon$ -caprolactam mixture to obtain  $\epsilon$ -caprolactam mixture; and

20 a lower alcohol recycle step of purifying part or all of the crude lower alcohol mixture to obtain the recycled lower alcohol, wherein

the method of producing  $\epsilon$ -caprolactam further includes adjusting the amount of water, ammonia and amines in the gas phase reaction to the following values (1) to (3).

(1)  $0 \leq \{[\text{the amount of ammonia (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 14$   
25

(2)  $0 < \{[\text{the amount of water (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 11$

(3)  $0 \leq \{[\text{the amount of amines (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 7.5$

30 [0015]

[5] The method of producing  $\epsilon$ -caprolactam according to [4], wherein the solid catalyst is zeolite.

[0016]

Hereinafter, with reference to the drawings, the method of producing  $\epsilon$ -caprolactam according to the present invention will be described. FIG. 1 is a flow diagram for illustrating the production process in the method of producing  $\epsilon$ -caprolactam according to an embodiment of the present invention.

5 [0017]

This embodiment includes: a vaporization step (1) in which cyclohexanone oxime 7 is vaporized in the presence of an inert gas 8, a lower alcohol 9 and water 10; a reaction step (2) in which cyclohexanone oxime 7 is subjected to Beckmann rearrangement reaction in the presence of a solid catalyst; a first distillation step (3) in  
10 which the resulting reaction gas 12 is cooled and a high-boiling component 13 is separated from the reaction solution to obtain a mixed gas 14 containing  $\epsilon$ -caprolactam, a lower alcohol and an inert gas; a lower alcohol separation step (4) in which the lower alcohol and the inert gas are separated from the mixed gas 14 to obtain a crude lower alcohol mixture 15 containing the inert gas, and a crude  $\epsilon$ -caprolactam mixture 18  
15 containing a crude  $\epsilon$ -caprolactam as main components; a second distillation step (5) in which a low-boiling component 20 and a high-boiling component 19 are separated from the crude  $\epsilon$ -caprolactam mixture 18; and a lower alcohol recycle step (6) in which part or all of the crude lower alcohol mixture 15 is purified.

That is, this embodiment includes: a vaporization step (1) of vaporizing  
20 cyclohexanone oxime in the presence of an inert gas 8, a lower alcohol 9 and water 10, to obtain raw material gas containing cyclohexanone oxime 7, the inert gas 8, the lower alcohol 9 and water 10; a reaction step (2) of contacting the raw material gas with a solid catalyst to conduct a gas phase reaction so as to convert cyclohexanone oxime 7 into  $\epsilon$ -caprolactam to obtain a reaction gas 12 containing  $\epsilon$ -caprolactam, the lower alcohol  
25 and the inert gas; a first distillation step (3) of cooling the reaction gas 12 to obtain a reaction solution, and then separating a high-boiling component 13 from the reaction solution to obtain a mixed gas 14 containing  $\epsilon$ -caprolactam, the lower alcohol and the inert gas; a lower alcohol separation step (4) of separating a crude lower alcohol mixture 15 containing a lower alcohol and the inert gas, and a crude  $\epsilon$ -caprolactam  
30 mixture 18 containing  $\epsilon$ -caprolactam from the mixed gas 14; a second distillation step (5) of separating a low-boiling component 20 and a high-boiling component 19 from the crude  $\epsilon$ -caprolactam mixture 18; and a lower alcohol recycle step (6) of purifying part or all of the crude lower alcohol mixture 15 to obtain the recycled lower alcohol.

The second distillation step (5) may be composed of a plurality of distillation steps. Specific examples will be described as follows.

[0018]

5 In the vaporization step (1), cyclohexanone oxime 7, an inert gas 8, a lower alcohol 9, and water 10 are supplied to an evaporator 1. Then, cyclohexanone oxime 7 is vaporized by heating in the presence of the lower alcohol 9 and water 10 to obtain a raw material gas 11 containing cyclohexanone oxime 7, a lower alcohol 9, and water 10. Here, water may be mixed with cyclohexanone oxime in advance.

[0019]

10 Next, in the reaction step (2), the raw material gas 11 obtained in the vaporization step (1) is supplied to a reactor vessel 2, and is allowed to come into contact with a solid catalyst to conduct a gas phase reaction (i.e., Beckmann rearrangement reaction) so as to convert cyclohexanone oxime into  $\epsilon$ -caprolactam, thereby obtaining a reaction gas 12 (hereafter, sometimes referred to as reaction mixture).  
15 The reaction gas 12 contains  $\epsilon$ -caprolactam, the lower alcohol and the inert gas.

In the present specification, the term “gas phase reaction” refers to a reaction in which a raw material gas containing cyclohexanone oxime 7, a lower alcohol 9 and water 10 is allowed to come into contact with a solid catalyst to effect a rearrangement reaction, and has a concept that is different from that of liquid-phase reaction.

20 [0020]

Next, in the first distillation step (3), the reaction gas 12 obtained in the reaction step (2) is supplied to a first distillation column 3 and then cooled to obtain a reaction solution. A high-boiling component 13 is separated from the reaction solution obtained after cooling, thereby obtaining a mixed gas 14 containing  $\epsilon$ -caprolactam, the lower  
25 alcohol and the inert gas.

Here, examples of the inert gas include nitrogen, argon, carbon dioxide, and the like.

[0021]

30 Next, in the lower alcohol separation step (4), the mixed gas 14 obtained in the first distillation step (3) is supplied to a lower alcohol-collecting column 4. Then, each of a crude lower alcohol mixture 15 containing a lower alcohol and the inert gas and a crude  $\epsilon$ -caprolactam mixture 18 containing  $\epsilon$ -caprolactam are separated from the mixed gas 14. Here, the amount of moisture contained in the crude lower alcohol mixture 15

containing an inert gas can be controlled depending on distillation conditions.

[0022]

In the second distillation step (5), the crude  $\epsilon$ -caprolactam mixture 18 obtained in the lower alcohol separation step (4) is supplied to a second distillation column 5.

5 Then a low-boiling component 20 and a high-boiling component 19 as impurities are separated from the crude  $\epsilon$ -caprolactam mixture 18 to obtain a crude  $\epsilon$ -caprolactam 21.

Here, the low-boiling component refers a component having a lower boiling point than that of  $\epsilon$ -caprolactam.

10 The high-boiling component refers a component having a higher boiling point than that of  $\epsilon$ -caprolactam.

[0023]

In the lower alcohol recycle step (6), part or all of the crude lower alcohol mixture 15 obtained in the lower alcohol separation step (4) is supplied to a lower alcohol-purification apparatus 6. Then, the part or all of the crude lower alcohol  
15 mixture 15 is purified by removing impurities 16 such as ammonia and amines, thereby obtaining a recycled lower alcohol (i.e., purified lower alcohol) containing the inert gas 17. The recycled lower alcohol 17 is supplied to an evaporator 1 and reused in any step after the vaporization step (1).

[0024]

20 It should be noted that the production process shown in Fig. 1 is merely an example, and the present invention is not intended to be limited to Fig. 1. Hereinafter, the present invention, in particular, a recycled lower alcohol and a gas phase reaction using a solid catalyst in the presence of a lower alcohol will be described.

[0025]

25 The solid catalyst is a catalyst for producing  $\epsilon$ -caprolactam, which is used in Beckmann rearrangement reaction in a gas phase to convert cyclohexanone oxime into  $\epsilon$ -caprolactam. As such a solid catalyst, various catalysts have been conventionally proposed. Among these, zeolite is preferable, pentasil-type zeolite is more preferable, and MFI zeolite is particularly preferable.

30 [0026]

As zeolite, a crystalline silica in which the skeleton thereof is essentially composed of silica and oxygen, and a crystalline metallocosilicate which further contains an element other than silica and oxygen, such as a metal element, as a component for

constituting the skeleton can be mentioned. Examples of the element other than silica and oxygen include Be, B, Al, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Ga, Ge, Zr, Nb, Sb, La, Hf, and Bi, and if necessary two or more these elements may be used in combination. The atom ratio of silica relative to the elements is preferably 50 or more, and more preferably 500 or more.

[0027]

Zeolite can be appropriately prepared by conducting a hydrothermal synthesis using raw materials such as a silica compound, a quaternary ammonium compound, water, and if necessary, a metal compound; drying and calcining the obtained crystal; conducting a contact treatment using ammonia or an ammonium salt; and drying.

[0028]

The particle diameter of the solid catalyst is preferably 0.0001 to 5mm, more preferably 0.001 to 3mm. The solid catalyst may be a molded article which is essentially composed of a catalyst component, or a material in which a catalyst component has been supported on a support.

[0029]

The lower alcohol preferably has 6 or less carbon atoms. Specific examples thereof include methanol, ethanol, 1-propanol (n-propyl alcohol), 2-propanol (isopropyl alcohol), 1-butanol (n-butyl alcohol), 2-butanol (sec-butyl alcohol), 2-methyl-1-propanol (isobutyl alcohol), 1-pentanol (n-pentyl alcohol), 1-hexanol (n-hexyl alcohol), and 2,2,2-trifluoroethanol. Among these, in terms of selectivity of  $\epsilon$ -caprolactam and improvement in the lifetime of catalyst, methanol, ethanol, 1-propanol, 2-propanol and 1-butanol are preferable, and methanol and ethanol are more preferable. Methanol and ethanol are most preferable from an industrial viewpoint.

Here, the term "selectivity" refers to the production ratio of  $\epsilon$ -caprolactam in the reaction product.

[0030]

As a lower alcohol used to be present in the reaction system, one kind of lower alcohol or two or more kinds of lower alcohols may be used. When two or more kinds are used, the combination and the ratio are arbitrarily selected. In view of the handling, one kind of lower alcohol is preferably used.

[0031]

In the present invention, a gas phase reaction is conducted, and then a lower

alcohol is recycled from the obtained reaction mixture (for example, reaction gas 12 described in Fig. 1). The recycled lower alcohol (for example, recycled lower alcohol 17 described in Fig. 1) is reused in a gas phase reaction.

That is, the lower alcohol used to be present in a gas phase reaction contains the recycled lower alcohol.

As the recycled lower alcohol, any kinds of lower alcohol classified in relation to the recycle method may be used. One kind of recycled lower alcohol may be used, or two or more kinds of recycled lower alcohols may be used in combination. When two or more kinds of recycled lower alcohols are used, the combination and the ratio are arbitrarily selected.

[0032]

As the lower alcohol used to be present in the reaction system, only the recycled lower alcohol may be used, or a combination with a lower alcohol which is not a recycled lower alcohol (for example, lower alcohol 9 described in Fig. 1, hereafter sometimes referred to as “non-recycled lower alcohol”) may be used. Although depending on the purity of the recycled lower alcohol, even when only the recycled lower alcohol is used, the amount of impurities can be easily reduced within the range of the intended amount by using at least part of the recycled lower alcohol after purification. On the other hand, the recycled lower alcohol generally contains a larger amount of impurities than that of a non-recycled lower alcohol. Therefore, there may be a case where a large number of steps for purification are required to reduce the amount of impurities. However, by using the recycled lower alcohol with the non-recycled alcohol in combination, even when the number of steps for purifications is omitted or reduced, the amount of impurities in a gas phase reaction may be easily reduced.

[0033]

The recycled lower alcohol can be obtained by separating a gas containing a lower alcohol as a main component (for example, crude lower alcohol mixture 15 described in Fig. 1) from a reaction mixture obtainable in a gas phase reaction. The gas containing a lower alcohol as a main component can be separated by distillation from the reaction mixture. The lower alcohol obtainable by distillation is sometimes referred to as a distilled lower alcohol 15.

The term “gas phase reaction” refers to a gas phase reaction in which cyclohexanone oxime is allowed to come into contact with a solid catalyst in the

presence of a recycled lower alcohol or a lower alcohol mixture containing a recycled lower alcohol to convert cyclohexanone oxime into  $\epsilon$ -caprolactam in the case of an operation method in which a reaction solution 12 is ejected in a continuous manner while supplying a raw material gas 11 in a continuous manner using one reactor vessel, or a gas phase reaction in which cyclohexanone oxime is allowed to come into contact with a solid catalyst in the presence of a recycled lower alcohol or a lower alcohol mixture containing a recycled lower alcohol to convert cyclohexanone oxime into  $\epsilon$ -caprolactam in the case of another production process of  $\epsilon$ -caprolactam using another reaction vessel. The separated gas (i.e., gas containing a lower alcohol as a main component) may be used without modification, or part or all of them which have been purified by a conventional method may be used. Generally, part of them after purification is preferably used.

The gas 15 containing a lower alcohol as a main component can be purified by supplying the gas to a gas absorption column and cooling to condense the gas, followed by distilling to reduce impurities. The term "to condense" refers to convert the gas containing a lower alcohol as a main component into a liquid mixture containing a lower alcohol as a main component.

The recycled lower alcohol mixture 15 may be used in combination with the purified lower alcohol 17 obtainable by condensing and distilling in the same manner as above.

The purified lower alcohol is preferably produced by distilling a reaction mixture obtainable in a gas phase reaction to separate a gas containing a lower alcohol as a main component, cooling part of the obtained gas to condense the gas and thereby obtaining a liquid mixture containing a low alcohol as a main component, and distilling the liquid mixture to obtain a distilled lower alcohol.

[0034]

In the present invention, it is preferable that a lower alcohol is used as part of a recycled lower alcohol, which is obtainable by distilling a reaction mixture obtainable in a gas phase reaction to separate a gas containing a lower alcohol as a main component, cooling part of the obtained gas to condense the gas, followed by distilling.

[0035]

The lower alcohol is preferably present in the reaction system within the weight ratio relative to cyclohexanone oxime (i.e., the weight ratio represented by [the amount

of lower alcohol (weight) / the amount of cyclohexanone oxime (weight)] of 0.1 to 20, more preferably 0.1 to 10, and particularly preferably 0.3 to 8.

[0036]

The mole percent (a) of ammonia in a reaction system during a gas phase  
5 reaction, represented by [the amount of ammonia (number of moles) / the amount of the lower alcohol (number of moles)  $\times$  100] is 0 to less than 14, and more preferably 13 or less.

[0037]

The mole percent (b) of water in a reaction system during a gas phase reaction,  
10 represented by [the amount of water (number of moles) / the amount of the lower alcohol (number of moles)  $\times$  100] is 0 to less than 11, and more preferably 10 or less.

Water is an essential component to effect the rearrangement reaction smoothly. From such a viewpoint, the amount of water in a reaction system during a gas phase reaction is preferably 0.06 moles or more, relative to 1 mole of cyclohexanone oxime.

15 [0038]

The amines refer to compounds in which a hydrogen atom of ammonia ( $\text{NH}_3$ ) has been substituted with a hydrocarbon group. The amines may be primary amines, secondary amines or tertiary amines, and may be a monoamines or polyamines. As typical amines, monomethylamine as a primary amine, dimethylamine as a secondary  
20 amine, and triethylamine as a tertiary amine can be mentioned.

Here, it is presumed that ammonia is generated in hydrolysis of cyclohexanone oxime, and amines are generated by reaction between ammonia and a lower alcohol.

[0039]

The mole percent (c) of amines in a reaction system during a gas phase reaction,  
25 represented by [the amount of amines (number of moles) / the amount of the lower alcohol (number of moles)  $\times$  100] is 0 to less than 7.5, and more preferably 7 or less.

[0040]

As a main contamination source of water, ammonia and amines, a recycled lower alcohol can be mentioned. Therefore, by controlling the amount of the recycled  
30 lower alcohol and the purity thereof, the amount of water, ammonia and amines can be easily controlled.

It is preferable that the mixing ratio of a recycled lower alcohol and a non-recycled lower alcohol (i.e., the mixing ratio represented by [the amount of the

recycled lower alcohol (% by weight)] : [the amount of the non-recycled lower alcohol (% by weight)] is controlled within the range of 10:0 to 10:10, and it is more preferable that the mixing ratio is controlled within the range of 10:0 to 10:2.

As a method of controlling the amount of water, ammonia and amines, a method  
5 in which the amount of water, ammonia and amines are controlled by supplying a non-recycled lower alcohol in a reaction system, while the amount of water, ammonia and amines are detected in a gas phase reaction, can be mentioned.

The amount of water can be measured by a conventional method such as Karl  
Fischer's method, and the amount of ammonia and amines can be measured by an ion  
10 chromatography method.

[0041]

In the present invention, a molecular oxygen-containing gas may be present in a reaction system. As a molecular oxygen-containing gas, air is preferable in economic terms. The concentration of the molecular oxygen is preferably out of an explosion  
15 composition range.

[0042]

The amount of the molecular oxygen in a reaction system during a gas phase reaction is preferably 0.1 to 10 moles, and more preferably 0.3 to 5 moles, relative to 1 mole of cyclohexanone oxime.

20 [0043]

A gas phase reaction can be generally conducted as a gas phase catalytic reaction in a fixed bed system, a fluidized bed system or a moving bed system. Cyclohexanone oxime as a raw material is reacted in a gas state by being allowed to come into contact with a catalyst layer. A lower alcohol may be mixed with cyclohexanone oxime in  
25 advance in a gas state, or may be supplied separately from cyclohexanone oxime. In the case of a fixed bed system, it is preferable that a mixture in which cyclohexanone oxime and a lower alcohol have been mixed well is passed through a catalyst layer. On the other hand, in the case of a fluidized bed system, there is no need to mix cyclohexanone oxime and a lower alcohol in advance, and cyclohexanone oxime and a lower alcohol may  
30 be supplied separately to a reactor vessel. Alternatively, the lower alcohol may be supplied in several batches. In the case of a fluidized bed system, a lower alcohol may be supplied on upper stream side relative to cyclohexanone oxime.

[0044]

In the case of molecular oxygen-containing gas is used, the molecular oxygen can be supplied as a mixture with a lower alcohol and cyclohexanone oxime, or as a mixture with a lower alcohol. The molecular oxygen may be supplied to upper stream in the reaction system than that of cyclohexanone oxime.

5 [0045]

A gas phase reaction may be conducted either in the presence of vapor of a compound which is inactive in the reaction, such as benzene, cyclohexane, toluene, and the like, as a dilution gas, or in the presence of inert gas such as nitrogen, carbon dioxide, and the like.

10 [0046]

A gas phase reaction is preferably conducted under atmospheric pressure or a reduced pressure of less than atmospheric pressure.

[0047]

The reaction temperature during a gas phase reaction is preferably 250 to 500°C, and more preferably 300 to 450°C, and particularly preferably 300 to 400°C. When the reaction temperature is no less than the lower limit of the above-mentioned range, the rate of reaction can be improved, and selectivity of  $\epsilon$ -caprolactam can be further improved.

When the reaction temperature is no more than the upper limit of the above-mentioned range, heat decomposition of cyclohexanone oxime can be suppressed, and selectivity of  $\epsilon$ -caprolactam can be further improved.

[0048]

The space velocity WHSV ( $\text{h}^{-1}$ ) of cyclohexanone oxime during a gas phase reaction is preferably 0.1 to 40  $\text{h}^{-1}$  (that is, the supply rate of cyclohexanone oxime per 1 kg of a catalyst is 0.1 to 40  $\text{h}^{-1}$ ), more preferably 0.2 to 20  $\text{h}^{-1}$ , and particularly preferably 0.5 to 10  $\text{h}^{-1}$ .

[0049]

$\epsilon$ -Caprolactam produced in a gas phase reaction (i.e., rearrangement reaction) can be separated from a reaction mixture by a conventional method. For example, by condensation of gas generated in the reaction, followed by extraction, distillation or crystallization to separate  $\epsilon$ -caprolactam, purified  $\epsilon$ -caprolactam can be obtained.

[0050]

On a solid catalyst, carbonaceous materials deposited thereon during a gas phase

reaction can be burned off (calcining) using oxygen-containing gas at 200 to 600°C.

After calcining, and it can be easily reactivated, and therefore, it can be reused repeatedly.

The burning off process of carbonaceous materials may be conducted in the presence of an alcohol in addition to oxygen containing-gas.

5 [0051]

The burning off process using the oxygen containing-gas may be conducted at 200 to 600°C, by fixing the temperature or by increasing the temperature in a multistep procedure.

[0052]

10 As the oxygen containing-gas, in general, air is preferably used, and gases obtainable by dilution of air or oxygen with inert gas such as argon, carbon dioxide, and the like may be used.

The concentration of oxygen in oxygen-containing gas is preferably 1 to 30% by volume, and more preferably 5 to 25% by volume.

15 [0053]

The present invention has a concept in that recycled materials obtainable from a reaction product in a rearrangement reaction are reused as raw materials of a rearrangement reaction of cyclohexanone oxime. By focusing on impurities generated during a rearrangement reaction of cyclohexanone oxime, and by identifying ammonia, 20 water and amines as impurities which may inhibit the rearrangement reaction in the case where the excess amount of impurities is present in a reaction system, the contamination amount of these impurities in a reaction system are controlled within the limited range. The conventional method of producing  $\epsilon$ -caprolactam, in which a rearrangement reaction of cyclohexanone oxime is conducted, is an industrially excellent method in terms of 25 high yield. However, according to the present invention, the conversion and selectivity in a rearrangement reaction of cyclohexanone oxime can be maintained in an extremely high level, and the used catalyst can be recycled, and therefore, it may be possible to increase the yield of  $\epsilon$ -caprolactam with a low cost.

30 Examples

[0054]

Hereinafter, the present invention will be described in more detail based on specific Examples. However, the present invention is not intended to be limited to the

Examples described below.

Hereafter, space velocity WHSV ( $\text{h}^{-1}$ ) was calculated by dividing the supply rate of cyclohexanone oxime ( $\text{g/h}$ ) by the weight of the catalyst ( $\text{g}$ ). Analyses of cyclohexanone oxime and  $\epsilon$ -caprolactam were conducted using gas chromatography.

- 5 The conversion of cyclohexanone oxime and the selectivity of  $\epsilon$ -caprolactam were calculated by the following formulae in which X is the number of moles of supplied cyclohexanone oxime, Y is the number of moles of unreacted cyclohexanone oxime, and Z is the number of moles of produced  $\epsilon$ -caprolactam.

$$\text{Conversion of cyclohexanone oxime (\%)} = [(X-Y)/X] \times 100$$

10  $\text{Selectivity of } \epsilon\text{-caprolactam (\%)} = [Z/(X-Y)] \times 100$

[0055]

[Example 1]

- Particles which had a particle diameter of 0.3 mm or less and contained MFI zeolite composed of crystalline silica (Si/Al atom ratio: 14,700) as a main component were used as a solid catalyst. 0.75 g of the catalyst was filled in a quartz glass reaction tube having an inner diameter of 1 cm to form a catalyst layer, followed by pre-heating for 1 hour at 340°C while allowing nitrogen gas to flow at 0.72 L/h. Subsequently, while allowing nitrogen gas to flow at 0.72 L/h, a mixture of methanol/cyclohexanone oxime = 1.3/1 (weight ratio) was supplied to the reaction tube at a supply rate of 6.9 g/h (WHSV of cyclohexanone oxime:  $4 \text{ h}^{-1}$ ), and reaction was effected for 10 hours while maintaining the temperature of the catalyst layer of 380°C. The amount of impurities in the reaction system was controlled to fulfill the following relationships.
- 15
- 20

(a)  $\{[\text{the amount of ammonia (number of moles) / the amount of methanol (number of moles)} \times 100]\} = 0$

25 (b)  $\{[\text{the amount of water (number of moles) / the amount of methanol (number of moles)} \times 100]\} = 6.4$

(c)  $\{[\text{the amount of amines (number of moles) / the amount of methanol (number of moles)} \times 100]\} = 0$

[0056]

- 30 The reaction solution obtainable up to 10 hours from the start of the reaction was collected, and with respect to the collected reaction solution, the conversion of cyclohexanone oxime and the selectivity of  $\epsilon$ -caprolactam were calculated. The results are shown in Table 1.

The yield of  $\epsilon$ -caprolactam in this example was 94.9%.

[0057]

[Example 2]

5  $\epsilon$ -Caprolactam was produced in the same manner as in Example 1 except that the value of mole percent (a) of ammonia was adjusted to 5.9 instead of 0 as shown in Table 1.

The yield of  $\epsilon$ -caprolactam in this example was 95.0%.

[0058]

[Example 3]

10  $\epsilon$ -Caprolactam was produced in the same manner as in Example 1 except that the value of mole percent (a) of ammonia was adjusted to 8.7 instead of 0 as shown in Table 1.

The yield of  $\epsilon$ -caprolactam in this example was 95.1%.

[0059]

15 [Comparative Example 1]

$\epsilon$ -Caprolactam was produced in the same manner as in Example 1 except that the value of mole percent (a) of ammonia was adjusted to 18 instead of 0 as shown in Table 1.

The yield of  $\epsilon$ -caprolactam in this example was 93.2%.

20 [0060]

[Example 4]

In the same manner as in Example 1, 0.75 g of the catalyst was filled in a quartz glass reaction tube having an inner diameter of 1 cm to form a catalyst layer, followed by pre-heating for 1 hour at 340°C while allowing nitrogen gas to flow at 0.72 L/h.

25 Subsequently, while allowing nitrogen gas to flow at 0.72 L/h, a mixture of methanol/cyclohexanone oxime = 1.3/1 (weight ratio) was supplied to the reaction tube at a supply rate of 6.9 g/h (WHSV of cyclohexanone oxime: 4 h<sup>-1</sup>), and reaction was effected for 2 hours while maintaining the temperature of the catalyst layer of 380°C. The amount of impurities in the reaction system was controlled to fulfill the following  
30 relationships.

(a) [the amount of ammonia (number of moles) / the amount of methanol (number of moles) × 100] = 0

(b) {[the amount of water (number of moles) / the amount of methanol (number

of moles)  $\times 100$ ] = 6.4

(c) {[the amount of amines (number of moles) / the amount of methanol (number of moles)  $\times 100$ ]} = 0

After 2 hours from the start of the reaction, the conversion of cyclohexanone oxime and the selectivity of  $\epsilon$ -caprolactam were calculated in the same manner as in Example 1.

The yield of  $\epsilon$ -caprolactam in this example was 95.6%.

[0061]

[Example 5]

$\epsilon$ -Caprolactam was produced in the same manner as in Example 4 except that the value of mole percent (b) of water was adjusted to 8.3 instead of 6.4 as shown in Table 1.

The yield of  $\epsilon$ -caprolactam in this example was 95.3%.

[0062]

[Comparative Example 2]

$\epsilon$ -Caprolactam was produced in the same manner as in Example 4 except that the value of mole percent (b) of water was adjusted to 14 instead of 6.4 as shown in Table 1.

The yield of  $\epsilon$ -caprolactam in this example was 94.6%.

[0063]

[Example 6]

In the same manner as in Example 1, 0.75 g of the catalyst was filled in a quartz glass reaction tube having an inner diameter of 1 cm to form a catalyst layer, followed by pre-heating for 1 hour at 340°C while allowing nitrogen gas to flow at 0.72 L/h.

Subsequently, while allowing nitrogen gas to flow at 0.72 L/h, a mixture of methanol/cyclohexanone oxime = 1.3/1 (weight ratio) was supplied to the reaction tube at a supply rate of 6.9 g/h (WHSV of cyclohexanone oxime: 4 h<sup>-1</sup>), and reaction was effected for 2 hours while maintaining the temperature of the catalyst layer of 380°C. The amount of impurities in the reaction system was controlled to fulfill the following relationships.

(a) [the amount of ammonia (number of moles) / the amount of methanol (number of moles)  $\times 100$ ] = 0

(b) {[the amount of water (number of moles) / the amount of methanol (number

of moles)  $\times 100$ ]} = 6.4

(c) {[the amount of amines (number of moles) / the amount of methanol (number of moles)  $\times 100$ ]} = 0

After 6 hours from the start of the reaction, the conversion of cyclohexanone oxime and the selectivity of  $\epsilon$ -caprolactam were calculated in the same manner as in Example 1.

The yield of  $\epsilon$ -caprolactam in this example was 95.8%.

[0064]

[Example 7]

$\epsilon$ -Caprolactam was produced in the same manner as in Example 6 except that trimethylamine was used as an amine and the value of mole percent (c) of triethylamine was adjusted to 3.6 instead of 0 as shown in Table 1.

The yield of  $\epsilon$ -caprolactam in this example was 95.6%.

[0065]

[Comparative Example 3]

$\epsilon$ -Caprolactam was produced in the same manner as in Example 6 except that trimethylamine was used as an amine and the value of mole percent (c) of triethylamine was adjusted to 7.5 instead of 0 as shown in Table 1.

The yield of  $\epsilon$ -caprolactam in this example was 95.5%.

[0066]

[Reference Example 1]

Part or all distilled lower alcohol obtained in a lower alcohol separation step (4) was cooled to 7 to 30°C to be liquefied. The liquefied lower alcohol was distilled at 80°C, at 175 kPaA, thereby recycled lower alcohol 17 was obtained.

Methanol obtained as above contained 0.49% of water, 0.01% of ammonia, and 1.4% of trimethylamine. Water was added to the obtained methanol to adjust the moisture content of 4.0%. The resulting solution was mixed with cyclohexanone oxime to prepare a mixture of methanol/cyclohexanone oxime = 1.3/1 (weight ratio), and the obtained mixture was used in a reaction.

[Example 8]

In the same manner as in Example 1, 0.75 g of the catalyst was filled in a quartz glass reaction tube having an inner diameter of 1 cm to form a catalyst layer, followed by pre-heating for 1 hour at 340°C while allowing nitrogen gas to flow at 0.72 L/h.

Subsequently, while allowing nitrogen gas to flow at 0.72 L/h, a mixture of methanol/cyclohexanone oxime = 1.3/1 (weight ratio), which was prepared in the Reference Example 1, was supplied to the reaction tube at a supply rate of 6.9 g/h (WHSV of cyclohexanone oxime: 4 h<sup>-1</sup>), and reaction was effected for 10 hours while maintaining the temperature of the catalyst layer of 380°C. The amount of impurities in the reaction system was controlled to fulfill the following relationships.

(a) [the amount of ammonia (number of moles) / the amount of methanol (number of moles) × 100]} = 0.02

(b) {[the amount of water (number of moles) / the amount of methanol (number of moles) × 100]} = 7.2

(c) {[the amount of amines (number of moles) / the amount of methanol (number of moles) × 100]} = 0.77

The reaction solution obtainable up to 10 hours from the start of the reaction was collected, and with respect to the collected reaction solution, the conversion of cyclohexanone oxime and the selectivity of ε-caprolactam were calculated as in the same manner in Example 1.

The yield of ε-caprolactam in this example was 95.3%.

[Table 1]

|                          | (A)<br>MeOH/O<br>x<br>(w/w) | (a)<br>NH <sub>3</sub> /MeO<br>H<br>(mol/mol)×<br>100 | (b)<br>H <sub>2</sub> O/MeO<br>H<br>(mol/mol)×<br>100 | (a)<br>Amines/<br>MeOH<br>(mol/mol)<br>×<br>100 | Conversion<br>(%) | Selectivity<br>(%) |
|--------------------------|-----------------------------|-------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------|-------------------|--------------------|
| Example 1                | 1.3                         | 0                                                     | 6.4                                                   | 0                                               | 99.9              | 95.0               |
| Example 2                | 1.3                         | 5.9                                                   | 6.4                                                   | 0                                               | 99.9              | 95.1               |
| Example 3                | 1.3                         | 8.7                                                   | 6.4                                                   | 0                                               | 99.9              | 95.2               |
| Comparative<br>Example 1 | 1.3                         | 18                                                    | 6.4                                                   | 0                                               | 99.9              | 93.3               |
| Example 4                | 1.3                         | 0                                                     | 6.4                                                   | 0                                               | 100               | 95.6               |
| Example 5                | 1.3                         | 0                                                     | 8.3                                                   | 0                                               | 99.9              | 95.4               |
| Comparative<br>Example 2 | 1.3                         | 0                                                     | 14                                                    | 0                                               | 99.9              | 94.7               |
| Example 6                | 1.3                         | 0                                                     | 6.4                                                   | 0                                               | 99.9              | 95.9               |
| Example 7                | 1.3                         | 0                                                     | 6.4                                                   | 3.6                                             | 99.9              | 95.7               |
| Comparative<br>Example 3 | 1.3                         | 0                                                     | 6.4                                                   | 7.5                                             | 99.9              | 95.6               |
| Example 8                | 1.3                         | 0.02                                                  | 7.2                                                   | 0.77                                            | 99.9              | 95.3               |

[0067]

From the results shown above, the following points could be confirmed.

- 5 It was confirmed that Examples 1 to 7 exhibited a high level of selectivity and high level of conversion, and excellent catalyst activity.

On the other hand, it was confirmed that, by increasing the value of mole percent (a) of ammonia, Comparative Example 1 exhibited excellent conversion, but selectivity was lower than that of Examples 1 to 3 and yield was deteriorated.

- 10 It was confirmed that, by increasing the value of mole percent (b) of water, Comparative Example 2 exhibited excellent conversion, but selectivity was deteriorated as compared to Examples 4 and 5.

- It was confirmed that, by increasing the value of mole percent (c) of amines, Comparative Example 3 exhibited excellent conversion, but selectivity was deteriorated as compared to Examples 6 and 7.
- 15

As shown above, it was confirmed that, by selecting ammonia, water and amines as impurities whose amount is to be controlled in the reaction system and by controlling the amount of these impurities within the limited range, conversion and selectivity in a rearrangement reaction of cyclohexanone oxime can be maintained in an extremely high

level.

### Industrial Applicability

[0068]

5           The present invention can be used in production of  $\epsilon$ -caprolactam by a gas phase reaction in the presence of a solid catalyst.

          According to the present invention, a method of producing  $\epsilon$ -caprolactam, which exhibits excellent selectivity in the rearrangement reaction of cyclohexanone oxime may be provided.

10           By reusing the recycled lower alcohol, the amount of industrial waste may be reduced, and the burden on the environment may be reduced.

### Reference Signs List

[0069]

15           1: Evaporator, 2: Reactor vessel, 3: First distillation column, 4: Lower alcohol-collecting column, 5: Second distillation column, 6: Lower alcohol-purification apparatus, 7: Cyclohexanone oxime, 8: Inert gas, 9: Lower alcohol, 10: Water, 11: Raw material gas, 12: reaction gas, 13: High-boiling component, 14: Mixed gas containing  $\epsilon$ -caprolactam, lower alcohol and inert gas, 15: Crude lower alcohol mixture (including  
20           inert gas), 16: Impurities such as ammonia and amines, 17: Purified lower alcohol (containing recycled lower alcohol and inert gas), 18: Crude  $\epsilon$ -caprolactam mixture, 19: High-boiling component, 20: Low-boiling component, 21: Crude  $\epsilon$ -caprolactam

## CLAIMS

1. A method of producing  $\epsilon$ -caprolactam, comprising:  
conducting a gas phase reaction in which cyclohexanone oxime is allowed to  
5 come into contact with a solid catalyst in the presence of a lower alcohol, and then  
cyclohexanone oxime is converted into  $\epsilon$ -caprolactam, and  
adjusting the amount of water, ammonia and amines in a gas phase reaction  
system to the following values (1) to (3), wherein  
the lower alcohol comprises a recycled lower alcohol which is recovered from a  
10 reaction mixture obtained by a gas phase reaction.  
(1)  $0 \leq \{[\text{the amount of ammonia (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 14$   
(2)  $0 < \{[\text{the amount of water (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 11$   
15 (3)  $0 \leq \{[\text{the amount of amines (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 7.5$
2. The method of producing  $\epsilon$ -caprolactam according to claim 1, wherein  
the recycled lower alcohol contains a distilled lower alcohol, and wherein  
20 the distilled lower alcohol is obtained by a method which comprises  
distilling the reaction mixture obtained by a gas phase reaction to separate gas  
mainly containing the lower alcohol, then  
cooling and condensing part of the gas to obtain a liquid mixture mainly  
containing the lower alcohol, and then  
25 distilling the liquid mixture to obtain the distilled lower alcohol.
3. The method of producing  $\epsilon$ -caprolactam according to claim 1 or 2, wherein  
the solid catalyst is zeolite.
- 30 4. A method of producing  $\epsilon$ -caprolactam, comprising:  
a vaporization step of vaporizing cyclohexanone oxime in the presence of an  
inert gas and a lower alcohol to obtain raw material gas comprising cyclohexanone oxime,  
the inert gas and the lower alcohol;

a reaction step of contacting the raw material gas with a solid catalyst to conduct a gas phase reaction, and then converting cyclohexanone oxime into  $\epsilon$ -caprolactam to obtain a reaction gas comprising  $\epsilon$ -caprolactam, the lower alcohol and the inert gas;

5 a first distillation step of cooling the reaction gas to obtain a reaction solution, and then separating a high-boiling component from the reaction solution to obtain a mixed gas comprising  $\epsilon$ -caprolactam, the lower alcohol and the inert gas;

a lower alcohol separation step of separating a crude lower alcohol mixture containing a lower alcohol and the inert gas, and a crude  $\epsilon$ -caprolactam mixture containing  $\epsilon$ -caprolactam from the mixed gas;

10 a second distillation step of separating a low-boiling component and a high-boiling component from the crude  $\epsilon$ -caprolactam mixture to obtain  $\epsilon$ -caprolactam mixture; and

a lower alcohol recycle step of purifying part or all of the crude lower alcohol mixture to obtain the recycled lower alcohol, wherein

15 the method of producing  $\epsilon$ -caprolactam further comprises adjusting the amount of water, ammonia and amines in the gas phase reaction to the following values (1) to (3).

(1)  $0 \leq \{[\text{the amount of ammonia (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 14$

20 (2)  $0 < \{[\text{the amount of water (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 11$

(3)  $0 \leq \{[\text{the amount of amines (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 7.5$

5. The method of producing  $\epsilon$ -caprolactam according to claim 4, wherein  
25 the solid catalyst is zeolite.