

SPECIFICATION

PROCESS FOR PRODUCING CYCLOHEXANONE OXIME

BACKGROUND OF THE INVENTION

5 Technical Field

[0001] The present invention relates to a process for producing cyclohexanone oxime by ammoximation of cyclohexanone.

10 Description of the related art

[0002] A process for producing cyclohexanone oxime wherein cyclohexanone is ammoximated with hydrogen peroxide and ammonia using a titanasilicate catalyst has been known (see, for example, USP 4,745,221, USP 4,794,198, USP 15 5,312,987, and USP 5,227,525). In this ammoximation, the catalyst activity of the titanasilicate is usually lowered over time. Therefore, it is necessary to replace the titanasilicate in order to maintain a conversion rate of cyclohexanone at a predetermined value or greater. If a 20 frequency of the replacement is high, it may cause the problem in terms of catalyst cost. For this reason, US-A-2004/0002619 suggests that a silicone compound other than the titanasilicate coexists with titanasilicate so as to suppress deterioration of the catalyst activity of the 25 titanasilicate.

SUMMARY OF THE INVENTION

[0003] However, it is difficult to completely suppress the deterioration of the catalyst activity of the titanosilicate and the replacement of the titanosilicate is still required, whereby a spent titanosilicate is left as a spent catalyst. The inventors have intensively studied for the purpose of further reducing the catalyst cost by activation and reuse of the spent titanosilicate. As a result, the inventors have found that when the silicon compound other than the titanosilicate coexists with the titanosilicate, the catalyst activity of the spent titanosilicate is more effectively recovered by calcination with an oxygen-containing gas compared with the titanosilicate without coexistence of the silicon compound, to complete the present invention.

[0004] The present invention provides a process for producing cyclohexanone oxime which includes the steps of:

(1) subjecting cyclohexanone to ammoximation with hydrogen peroxide and ammonia in the presence of a titanosilicate and a silicon compound other than the titanosilicate; and

(2) calcinating the titanosilicate which has been used in the step (1), in the atmosphere of an oxygen-containing gas,

wherein the titanasilicate calcinated in the step (2) is used in the step (1).

[0005] The present invention makes it possible to reduce the catalyst cost for ammoximation of cyclohexanone, whereby cyclohexanone oxime can be produced at a low cost.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0006] The present invention is described in detail below. A titanasilicate used as the catalyst in the present invention contains titanium, silicon and oxygen as elements which form a framework. The framework of the titanasilicate may be composed of only titanium, silicon and oxygen or may further contain another element for constituting the framework. It is preferable to use the titanasilicate having an atomic ratio of silicon/titanium of from 10 to 1000. Further, the titanasilicate may be in a form of fine powders. Alternatively, it may be molded into pellets optionally using a binder or it may be carried by a carrier. Representative examples of the titanasilicate include TS-1 (MFI type), TS-2 (MEL type), Ti-MCM-22 (MWW type) and Ti-MCM-41.

[0007] Cyclohexanone oxime is produced by ammoximation of cyclohexanone with hydrogen peroxide and ammonia using, as the catalyst, the titanasilicate described above (the step (1)). This ammoximation may be carried out as a

solid-phase catalyst reaction wherein the titanasilicate as the catalyst is dispersed as a solid phase in a reaction mixture. An amount of the titanasilicate in a reaction system is usually 1g/L to 200g/L, wherein the unit
5 corresponds to a weight per volume of the reaction mixture (solid phase + liquid phase).

[0008] Cyclohexanone as a raw material may be obtained by oxidizing cyclohexane or may be obtained by hydrating cyclohexene followed by dehydrogenation or may be obtained
10 by hydrogenating phenol.

[0009] The amount of hydrogen peroxide is usually from 0.5 times to 3 times by mol based on cyclohexanone, preferably 0.5 times to 1.5 times by mol. Hydrogen peroxide is usually produced by a so-called anthraquinone
15 method. In general, hydrogen peroxide is commercially available as an aqueous solution with a concentration of 10% to 70% by weight. This aqueous solution can be employed. A stabilizer may be added to hydrogen peroxide. The stabilizer is, for example, a phosphate such as sodium
20 phosphate, polyphosphate such as sodium pyrophosphate and sodium tripolyphosphate, pyrophosphoric acid, ascorbic acid, ethylenediaminetetraacetic acid, or diethylenetriaminepentaacetic acid.

[0010] The amount of ammonia is usually 1 or more times
25 by mol and preferably 1.5 or more times by mol based on

cyclohexanone. Further, it is preferable to use ammonia in an excess amount compared to hydrogen peroxide so that ammonia remains in the reaction mixture. Gaseous ammonia may be used or a liquid ammonia may be used. Alternatively, an aqueous or an organic solution of ammonia may be used.

[0011] The ammoximation is usually carried out using water and/or an organic solvent as a reaction solvent. The examples of organic solvent include an alcohol such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol and tert-amyl alcohol, an aromatic hydrocarbon such as benzene, toluene, xylene and ethylbenzene, and an ether such as tetrahydrofuran, dioxane, di-isopropyl ether, and tert-butyl methyl ether.

[0012] In the present invention, the silicon compound other than the titanasilicate (this compound may be merely referred to as the "silicon compound" hereinafter) coexists with the titanasilicate as the catalyst in the ammoximation, as described in US-A-2004/0002619. This recipe can suppresses the deterioration of the catalyst activity of the titanasilicate, whereby the frequency of the replacement of the titanasilicate is reduced leading to reduction in the cost for the catalyst. Further, the amount of the titanasilicate in the reaction system can be reduced, which also can reduce the cost for the catalyst.

[0013] It is presumed that the deterioration of the catalyst activity of the titanosilicate arises by break of active points due to elution of silicon, or poisoning of active point due to attachment of impurities. The reason why the deterioration of the catalyst activity of the titanosilicate is suppressed by the coexistence of the silicon compound seems to be that the elution of silicon from the silicon compound suppresses the elution of silicon from the titanosilicate by just that much and the impurity adsorption by the silicon compound suppresses the impurity adsorption by the titanosilicate by just that much.

Therefore, the silicon compound from which silicon is liable to be eluted or the silicon compound on which the impurities is liable to be adsorbed is preferably employed.

When the silicon compound in a form of solid is used, one having a larger surface area or one in a form of particles having a smaller diameter is preferably used.

[0014] The silicon compound containing silicon and oxygen is preferably used, and the silicon compound containing a silicon-oxygen bond is particularly preferable. For example, silica, silicic acid, a silicate salt and a silicate ester may be exemplified. A mixture of two or more silicon compounds may be used as the silicon compound may be. The silica may be crystalline silica such as silicalite or amorphous silica such as a fumed silica or a

silica gel. The silicic acid or the salt thereof may be orthosilicic acid or a poly-acid thereof or the salts of these acids, or may be a crystalline or an amorphous.

Metillosilicate other than the titanosilicate may be used.

5 Tetraalkyl orthosilicate is preferably used as the silicate ester. The alkyl group of tetraalkyl orthosilicate usually has from one to four carbon atoms.

[0015] The amount of the silicon compound in the reaction system may be adjusted optimally depending the
10 characteristics of the silicon compound and the introduction way of the silicon compound into the reaction system. For example, when the silicon compound in the form of solid is directly introduced or a dispersion such as sol wherein the solid silicon compound is dispersed in an
15 organic solvent or water is introduced, the amount of the silicon compound in the reaction system is usually from 0.1 times to 20 times by weight based on the titanosilicate. In that case, it is preferable to disperse the silicon compound as the solid phase in the reaction mixture. When
20 the silicon compound in the form of liquid is directly introduced or a solution wherein the solid or the liquid silicon compound is dissolved in the organic solvent or water is introduced, the amount of the silicon compound in the reaction system is usually from 0.0001 times to 0.5
25 times by weight based on the titanosilicate. In that case,

it is preferable to avoid the deposition of the silicon compound in the reaction mixture.

[0016] The ammoximation may be carried out in a batch operation, or may be carried out in a continuous operation.

5 The continuous operation is preferable from the viewpoints of productivity and operability. The introduction recipe of raw materials may be appropriately selected. In the case of the batch operation, the introduction may be carried out by charging cyclohexanone, ammonia, the
10 titanasilicate, the silicon compound and a solvent in a reactor and then providing hydrogen peroxide herein, or may be carried out by charging cyclohexanone, the titanasilicate, the silicon compound and the solvent in the reactor and then providing hydrogen peroxide and ammonia
15 herein, or may be carried by charging the titanasilicate, the silicon compound and the solvent and then providing cyclohexanone, hydrogen peroxide and ammonia herein.

[0017] In the case of the continuous operation, when the silicon compound is dispersed as the solid phase in the
20 reaction mixture, it is preferable that a predetermined amount of the reaction mixture with the titanasilicate and the silicon compound dispersed therein is retained in the reactor and cyclohexanone, hydrogen peroxide, ammonia and the solvent are provided herein, while the reaction mixture
25 is drawn in an amount substantially equal to the total

amount of these raw materials. In this operation, the reaction mixture is preferably drawn through a filter so that only the liquid phase is drawn and the titanasilicate and the silicon compound of the solid phase stay in the reactor. Alternatively, when the silicon compound which is soluble as a solute in the reaction mixture is employed, it is preferable that a predetermined amount of the reaction mixture with the titanasilicate dispersed therein is retained in the reactor and cyclohexanone, hydrogen peroxide, ammonia, silicon compound and solvent are provided herein, while the reaction mixture is drawn in an amount substantially equal to the total amount of the raw materials. In this operation, the reaction mixture is preferably drawn through a filter so that only the liquid phase is drawn and the titanasilicate of the solid phase stays in the reactor, as described above. The reactor is preferably lined with a fluorine resin or glass, or made of stainless steel from the viewpoint of prevention of the decomposition of hydrogen peroxide.

[0018] The reaction temperature of the ammoximation is usually 60°C or higher, preferably 80°C or higher, and more preferably 90°C or higher, and usually 120°C or lower, preferably 110°C or lower and more preferably 100°C or lower. The reaction may be carried out under a normal pressure, under pressure or under reduced pressure. The

reaction is preferably carried out under pressure so that the dissolved amount of ammonia into the reaction mixture is increased. In this case, the pressure may be adjusted using an inert gas such as nitrogen or helium.

5 [0019] The replacement of the titanosilicate is still required in order to maintain the conversion rate of cyclohexanone at a predetermined value or more since it is difficult to completely suppress the deterioration of the catalyst activity of the titanosilicate even if the
10 ammoximation is carried out under coexistence of the titanosilicate and the silicon compound. For this reason, the spent titanosilicate which arises by this replacement is activated and reused in the present invention. This enables the catalyst cost to be further decreased.

15 [0020] The activation of the spent titanosilicate is carried out by calcinating the spent titanosilicate under atmosphere of an oxygen-containing gas (the step (2)). The catalyst activation of the spent titanosilicate that generates during the amnoximation without the silicon
20 compound is not sufficiently recovered by this calcination, but the catalyst activation of the spent titanosilicate that generates during the amnoximation wherein the silicon compound coexists with the titanosilicate is sufficiently recovered by this calcination.

25 [0021] Air is usually employed as the oxygen-containing

gas. Pure oxygen may be used. Further, these gases may be diluted with nitrogen or a carbon dioxide gas. In that case, a concentration of oxygen is preferably 5% by volume or more. The calcination temperature is usually 250°C or higher and preferably 300°C or higher since a longer calcination time is required when the temperature is too low. The calcination temperature is usually 600°C or lower and preferably 550°C or lower. The calcination time is adjusted optimally depending on the calcination temperature and so on and usually from 5 minutes to 10 hours. Any pressure may be employed. The calcination may be usually carried out at a normal pressure.

[0022] The calcination may be carried out in a batch operation or may be carried out in a continuous operation.

In the case of the batch operation, the calcination is preferably carried out by charging a predetermined amount of the spent titanosilicate in a calcination furnace such as an oven and passing the oxygen-containing gas through the furnace. In the case of the continuous operation, the calcination is preferably carried out by passing the oxygen-containing gas through a calcination furnace such as a kiln, introducing the spent titanosilicate at a predetermined speed and retaining it for a predetermined time followed by drawing it.

[0023] In the case where the spent titanosilicate is

mixed with the silicon compound, the calcination may be carried out after separating the titanosilicate from the silicon compound. Alternatively, the titanosilicate and the silicon compound may be calcinated together. Further,
5 the titanosilicate may be optionally washed with water or an organic solvent or may be optionally subjected to pre-drying.

[0024] As described above, the catalyst activity of the spent titanosilicate is recovered by the calcination and
10 the spent titanosilicate after being calcinated can be reused as a regenerated titanosilicate for the ammoximation (the step (1)). Specifically, the regenerated titanosilicate may be used as a supplementary catalyst upon replacement of the titanosilicate for addressing the
15 deterioration of the catalyst activity. For example, when the ammoximation is carried out in the batch operation, at least a part of the collected spent titanosilicate may be drawn every batch or every few batches, while the regenerated titanosilicate may be supplied. When the
20 ammoximation may be carried out in the continuous operation, a part of the spent titanosilicate may be drawn from the reaction system at an appropriate time interval during the operation, and the regenerated titanosilicate may be
25 supplied. Alternatively, the operation may be stopped at an appropriate time interval during the operation to draw

at least a part of the spent titanasilicate from the reaction system and the regenerated titanasilicate may be supplied. The drawn spent titanasilicate is reused as the regenerated titanasilicate after the calcination. When the silicon compound is drawn together with the spent titanasilicate, the silicon compound may be supplied together with the regenerated titanasilicate. In this case, when the regenerated titanasilicate is obtained by calcinating the titanasilicate and the silicon compound together, the regenerated titanasilicate and the silicon compound can be supplied at the same time by supplying the calcinated product. Further, a fresh titanasilicate and/or a fresh silicon compound may be optionally supplied. It is preferable that an amount of the supplemental fresh silicon compound corresponds to an amount of Si which is drawn out of the reaction system during the reaction. In the continuous reaction, the amount of Si drawn out of the reaction system may be calculated based on the amount of the drawn reaction mixture by determining the Si concentration in the drawn reaction mixture. Further, an amount of the supplemental fresh titanasilicate may be optimally determined depending on the decrease in catalyst activity which decrease still appears despite of the above reaction.

[0025] A post-treatment operation of the reaction

mixture after the ammoximation may be carried out by employing known methods. For example, a liquid phase of the reaction mixture may be subjected to distillation, as described in USP 5,227,525 so that the solvent and the remaining unreacted ammonia are separated and collected as a distillate to give a bottom product containing cyclohexanone oxime. Next, cyclohexanone oxime may be extracted with an organic solvent from the bottom product and an extracted liquid may be washed and condensed and optionally subjected to further distillation to give purified cyclohexanone oxime. The cyclohexanone oxime obtained in this manner may be subjected to Beckmann transformation in a liquid phase or a gas phase to give ϵ -caprolactam.

EXAMPLES

[0026] The present invention is described by some examples, but it is not limited to these example.

[0027] Example 1

(a) Ammoximation with fresh titanasilicate
1.5g of a titanasilicate (TS-1), 8g of a silica gel (Wakogel B-0 of Wako Pure Chemical Industries, Ltd.) were charged into an autoclave having a 300mL volume and an inner surface lined with a fluorine resin and they were dispersed in 100mL of a water-containing tert-butyl alcohol

(water content: 15% by weight). Ammoximation was carried out in the continuous operation by feeding, to the dispersion, cyclohexanone at 19.6g/hour, the water-containing tert-butyl alcohol (water content: 15% by weight) at 34.8g/hour, ammonia at 6.45g/hour (1.9 times by mol based on cyclohexanone) and 60wt% hydrogen peroxide aqueous solution at 13.0g/hour (1.15 times by mol based on cyclohexanone) and drawing a liquid phase of the reaction mixture through a filter so that a volume of the reaction mixture in the autoclave was maintained at 100mL. During this operation, the reaction temperature was maintained at 95°C and the reaction pressure was maintained at 0.35MPa by pressurization using a helium gas. The liquid phase of the reaction mixture drawn from the autoclave 5.5 hours after the start of the operation was analyzed by gas chromatography. The analysis showed that the conversion rate of cyclohexanone was 99.1% and the selection rate of cyclohexanone oxime was 99.5%. The gas chromatography analysis was intermittently continued to observe the conversion rate of cyclohexanone oxime. The operation was continued until the conversion rate of cyclohexanone was 90% or less. The operable time was determined as the time between the operation starting and the operation finishing. The operable time was 290 hours.

25 [0028] (a') Ammoximation with fresh titanosilicate

Ammoximation was carried out in the same manner as the above operation (a) except that the amounts of the titanasilicate and the silica gel were doubled, that is, 3.0g of the titanasilicate and 16g of the silica gel were used. The operable time was 628 hours.

[0029] (b) Calcination of spent titanasilicate

The reaction mixture left in the autoclave after the operation according to the above operation (a') was filtrated and the filtrated solid was washed with the water-containing tert-butyl alcohol (water content: 12 wt%) and then washed with water. This washed solid was dried in air at 110°C for 8 hours followed by being calcinated at 350°C for 2 hours. As a result, 15.83g of a regenerated titanasilicate/silica gel mixture was recovered (recovery rate: 83.3%).

[0030] (c) Ammoximation with regenerated titanasilicate

The ammoximation was carried out in the same manner as the above operation (a) except that 9.5 g of the regenerated titanasilicate/silica gel mixture obtained in the above operation (b) was used instead of 1.5g of the titanasilicate and 8g of the silica gel. The operable time was 321 hours which was equal to or more than that of the above operation (a) (290 hours).

[0031] Comparative Example 1

(a) Ammoximation with fresh titanasilicate

The ammoximation was carried out in the same manner as the above operation (a) of Example 1 except that the silica gel was not used. The operable time was 144 hours.

5 **[0032]** (a') Ammoximation with fresh titanosilicate

The ammoximation was carried out in the same manner as the above operation (a) except that the amount of the titanosilicate was doubled, that is, 3.0g of the titanosilicate was used. The operable time was 530 hours.

10 **[0033]** (b) Calcination of spent titanosilicate

The reaction mixture left in the autoclave after the operation according to the above operation (a') was filtrated and the filtrated solid was washed with the water-containing tert-butyl alcohol (water content: 12 wt%) and then washed with water. This washed solid was dried in
15 air at 110°C for 8 hours followed by being calcinated at 350°C for 2 hours. As a result, 1.65g of the regenerated titanosilicate was recovered (recovery rate: 55%).

[0034] (c) Ammoximation with regenerated titanosilicate

20 The ammoximation was carried out in the same manner as the above operation (a) except that 1.5 g of the regenerated titanosilicate obtained in the above operation (b) was used instead of 1.5g of the titanosilicate. The operable time was 86 hours which was significantly below
25 that of the above operation (a) (144 hours).

[0035] Comparative Example 2

The ammoximation was carried out in the same manner as the operation (a) of Example 1 except that 1.5 g of the regenerated titanasilicate obtained in the above operation (b) of Comparative Example 1 was used instead of 1.5g of the titanasilicate. The operable time was 149 hours which was significantly below that of the operation (a) of Example 1 (290 hours).

[0036] Example 2

10 (a) Ammoximation with fresh titanasilicate

The ammoximation was carried out in the same manner as the above operation (a) of Example 1 except that the amount of the titanasilicate was changed to 2g and 3g of a fumed silica (CAB-O-SIL M-7D provided by CABOT CORPORATION) was used instead of 8g of the silica gel. The operable time was 466 hours.

[0037] (b) Calcination of spent titanasilicate

The reaction mixture left in the autoclave after the operation (a) was filtrated and the filtrated solid was washed with the water-containing tert-butyl alcohol (water content: 12 wt%) and then washed with water. This washed solid was dried in air at 110°C for 8 hours followed by being calcinated at 350°C for 2 hours. As a result, 2.75g of a regenerated titanasilicate/fumed silica mixture was recovered (recovery rate: 55%).

[0038] (c) Ammoximation with regenerated titanosilicate

The ammoximation was carried out in the same manner as the above operation (a) except that 2.75 g of the regenerated titanosilicate/fumed silica mixture obtained in the above operation (b) and 2.25g of the fumed silica were used instead of 2g of the titanosilicate and 3g of the fumed silica. The operable time was 459 hours.

[0039] (b-2) Calcination of spent titanosilicate

The reaction mixture left in the autoclave after the above operation (c) was filtrated and the filtrated solid was washed with the water-containing tert-butyl alcohol (water content: 12 wt%) and then washed with water. This washed solid was dried in air at 110°C for 8 hours followed by being calcinated at 350°C for 2 hours. As a result, 3.82g of the regenerated titanosilicate/fumed silica mixture was recovered (recovery rate: 76.4%).

[0040] (c-2) Ammoximation with regenerated titanosilicate

The ammoximation was carried out in the same manner as the above operation (a) except that 3.82 g of the regenerated titanosilicate/fumed silica mixture obtained in the above operation (b-2) and 1.18g of the fumed silica were used instead of 2g of the titanosilicate and 3g of the fumed silica. The operable time was 421 hours.

WHAT IS CLAIMED IS:

1. A process for producing cyclohexanone oxime which includes the steps of:

(1) subjecting cyclohexanone to ammoximation with
5 hydrogen peroxide and ammonia in the presence of a
titanosilicate and a silicon compound other than the
titanosilicate; and

(2) calcinating the titanosilicate which has been
used in the step (1), in the atmosphere of an oxygen-
10 containing gas,

wherein the titanosilicate calcinated in the step (2)
is used in the step (1).

2. The process according to claim 1, wherein the
titanosilicate is calcinated at a temperature of 250°C or
15 higher in the step (2).

3. The process according to claim 1, wherein the
silicon compound other than the titanosilicate is selected
from a group consisting of a silica, a silicic acid, a
silicate salt and a silicate ester and mixtures thereof.