

PROCESS FOR PRODUCING CYCLOALKANONE OXIME

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates to a process for producing a cycloalkanone oxime by ammoximation reaction of a cycloalkanone. Cycloalkanone oximes are useful as raw materials for lactams and the like.

2. Description of the Related Art

10 A process for producing a cycloalkanone oxime includes an ammoximation reaction of a cycloalkanone with hydrogen peroxide and ammonia in the presence of a titanasilicate catalyst (see, for example, JP-A-61-59256 (corresponding to USP 4,745,221),
15 JP-A-6-49015 (corresponding to USP 5,312,987), JP-A-6-92922 (corresponding to USP 5,227,525), JP-A-2004-83560 (corresponding to USP 6,828,459) and JP-A-2004-307418 (corresponding to US 2004/204609A)). This ammoximation reaction is advantageously carried out in a
20 continuous method in view of productivity and operationality. For example, JP-A-6-49015, JP-A-6-92922, JP-A-2004-83560 and JP-2004-307418 disclose continuous ammoximation reaction with feeding a cycloalkanone, hydrogen peroxide and ammonia to a reactor and extracting
25 the liquid phase of the reaction mixture in which a

catalyst is dispersed.

In the above-mentioned continuous ammoximation reaction, the activity of the catalyst deteriorates with time lapses, to decrease the conversion of the cycloalkanone, or to decrease the selectivity of the cycloalkanone oxime.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a process which can suppress the deterioration in an activity of a catalyst to produce a cycloalkanone oxime with a high yield for a long time period.

The present invention provides a process for producing a cycloalkanone oxime by a continuous ammoximation reaction in the presence of a titanasilicate catalyst, characterized in that the continuous ammoximation reaction is conducted with feeding a cycloalkanone, hydrogen peroxide, ammonia and a cycloalkanone oxime to the reaction system.

According to the present invention, a cycloalkanone oxime can be produced with a high yield for a long time period in the continuous ammoximation reaction of a cycloalkanone with suppressing deterioration in an activity of a catalyst.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The titanasilicate used as a catalyst in the present invention has titanium, silicon and oxygen as elements which constitute the molecular skeleton. The molecular
5 skeleton of the titanasilicate may be constituted substantially only by titanium, silicon and oxygen, or may further include other elements. The titanasilicate preferably has a molecular ratio of silicon/titanium of from 10 to 1000, and the shape thereof may be in the form
10 of fine powder or pellets. The titanasilicate can be prepared, for example, according to a method disclosed in JP-A-56-96720.

The cycloalkanone used in the present invention usually has 5 to 12 carbon atoms. Examples of the
15 cycloalkanone generally include cyclopentanone, cyclohexanone, cyclooctanone and cyclododecanone. The cycloalkanone may be obtained, for example, by oxidation of a cycloalkane, or by hydration and dehydrogenation of a cycloalkene. In addition, as to cyclohexanone, it may be
20 obtained by hydrogenation reaction of phenol.

Hydrogen peroxide is generally produced by so-called anthraquinone method, and is commercially available as an aqueous solution having a concentration of 10 to 70% by weight, which can be used in the present invention. The
25 amount of hydrogen peroxide to be used is generally from

0.5 to 3 mol, preferably from 0.5 to 1.5 mol relative to 1 mol of a cycloalkanone. To the hydrogen peroxide may be added, for example, a small amount of a stabilizing agent, such as a phosphate (e.g., sodium phosphate, etc.), a
5 polyphosphate (e.g., sodium pyrophosphate, sodium tripolyphosphate, etc.), pyrophosphoric acid, ascorbic acid, ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, and the like, or a derivative thereof.

10 The ammonia may be used in the form of gas or liquid, or a solution in water or an organic solvent. The amount of ammonia to be used is generally not less than 1 mol, preferably not less than 1.5 mol relative to 1 mol of a cycloalkanone.

15 Examples of the solvent which may be used for the reaction include organic solvents such as alcohols (e.g., methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, s-butyl alcohol, t-butyl alcohol, t-amyl alcohol, etc.), aromatic hydrocarbons (e.g., benzene,
20 toluene, xylene, ethylbenzene, etc.) and ethers (e.g., tetrahydrofuran, dioxane, diisopropyl ether, t-butyl methyl ether, etc.); water; and mixed solvents thereof. Among these, alcohols, or mixed solvents of water and alcohols are preferable, because they can keep the liquid phase of
25 the reaction mixture homogeneous.

In the present invention, the continuous ammoximation reaction of a cycloalkanone is conducted by feeding a cycloalkanone, hydrogen peroxide, ammonia and a cycloalkanone oxime to the reaction system, practically is
5 conducted to keep a proper amount of the reaction mixture in a continuous reactor (e.g., a stirrer-type continuous reactor, a loop-type continuous reactor, etc.), by feeding a cycloalkanone, hydrogen peroxide, ammonia, a cycloalkanone oxime and optionally a solvent and the like
10 as raw materials to the reactor while extracting the reaction mixture by the amount substantially same as feeding amount of these raw materials. The method of feeding the raw materials may include a method where each raw material is fed separately or together, some of the raw
15 materials are mixed beforehand and the mixture is fed with other mixture or a raw material, and the like. The extraction of the reaction mixture is preferably carried out by extracting only the liquid phase through a filter or the like so that the catalyst can be kept in the reactor.
20 The concentration of the catalyst, which depends on the activity thereof, the reaction condition and the like, is generally from 1 to 200 g/L based on the weight per the volume of the reaction mixture (the total amount of the catalyst and liquid phase). In addition, in view of
25 further suppressing deactivation of the titanosilicate

catalyst, silicon compounds other than the titanosilicate, such as silica, silicate or the like may be used in combination according to the disclosure in JP-A-2004-307418.

The reaction temperature is generally from 50 to
5 100°C. While the pressure for the reaction may be ordinary pressure, it is preferable to carry out the reaction under pressure in order to increase the amount of ammonia dissolved in the liquid phase of the reaction mixture. In the latter case, the pressure may be adjusted using inert
10 gas such as nitrogen, helium or the like. The reactor is preferably one lining-treated with a fluorine resin or glass, or made of stainless steel, in view of preventing hydrogen peroxide from decomposition.

The place in which an ammoximation reaction is
15 taking place forms a reaction system.

In the present invention, the cycloalkanone oxime, together with the cycloalkanone, hydrogen peroxide and ammonia, is fed to the reaction system during the above-mentioned continuous ammoximation reaction, whereby a
20 cycloalkanone oxime can be produced with a high yield for a long time period while deterioration in the activity of the catalyst can be suppressed. Specifically, in a continuous ammoximation reaction, the activity of the catalyst usually deteriorates more easily when an organic solvent is not
25 used or is used in a small amount, and the present

invention would be advantageously applied for such case. Furthermore, the amount of the organic solvent to be used can be readily decreased by applying the present invention, whereby the costs can be advantageously reduced. JP-A-6-
5 49015 and JP-A-6-92922 describes that it is preferable to use an organic solvent 2.5 to 10 times by weight as much as an amount of a cycloalkanone fed, however, it is preferable in the present invention that, even when an organic solvent is used, the amount of the organic solvent to be used is
10 less than the above-mentioned amount. Specifically, it is preferable to use an amount equal to or less than an amount 2.3 times by weight as much as the amount of the cycloalkanone fed.

The amount of the cycloalkanone oxime to be fed is
15 generally from 0.1 to 5 times, preferably from 0.5 to 3 times, by weight as much as the amount of the cycloalkanone to be fed. The cycloalkanone oxime to be fed is generally a cycloalkanone oxime which corresponds to the cycloalkanone to be fed as a raw material, namely, the same
20 kind of cycloalkanone oxime as the cycloalkanone oxime to be produced. The fed cycloalkanone oxime may be recovered with the produced cycloalkanone oxime from the reaction mixture.

The cycloalkanone oxime to be fed is preferably the
25 cycloalkanone oxime recycled from the reaction mixture. In

this case, the recycled cycloalkanone oxime is not necessarily a purified product having high purity, and it may be obtained by recycling the reaction mixture as it is or by recycling the mixture containing the cycloalkanone oxime obtained during separation and purification of the reaction mixture. For example, when the reaction mixture comprises a cycloalkanone oxime, an organic solvent and water, if the organic solvent has a lower boiling point than those of the cycloalkanone and water, the organic solvent may be removed by distillation so that the mixture of the cycloalkanone oxime and water obtained is to be recycled. The cycloalkanone oxime may be extracted using a cycloalkanone from a mixture of a cycloalkanone oxime and water, and the extract can be fed to the reaction system. In addition, when the reaction mixture includes an organic solvent and unreacted raw materials, these can also be recovered and recycled.

[Examples]

Hereinafter the examples of the present invention are shown in detail, but the present invention is not limited by these examples. The analysis for the cycloalkanone and cycloalkanone oxime was carried out by gas chromatography, and the conversion of the cycloalkanone, the selectivity of the cycloalkanone oxime and the yield of

the cycloalkanone oxime were calculated based on the analytical results.

Example 1

5 To an autoclave made of stainless steel, a reactor,
were fed 12.95 g (0.132 mol) of cyclohexanone, 4.27 g
(0.251 mol) of ammonia, 8.65 g of 60 wt% hydrogen peroxide
(hydrogen peroxide content: 0.153 mol), 31.40 g of t-butyl
alcohol containing water (water content: 15 wt%) and 22.97
10 g of a mixture of cyclohexanone oxime/water = 65/35 (weight
ratio) per hour. Continuous reaction under the condition
at the temperature of 85°C and the pressure of 0.35 MPa
(absolute pressure) was conducted with keeping the liquid
level by extracting the liquid phase of the reaction
15 mixture through a filter so that the dwelling time became
1.2 hours. During this reaction, 1.0 g of titanasilicate
having an MFI structure as a catalyst existed in the
reaction mixture in the reactor [cyclohexanone feeding
ratio = 0.132 mol/h·g-catalyst]. Furthermore, helium gas
20 was flown in the gas phase portion in the reactor at the
rate of 1.2 L/hour, and the oxygen concentration in the
exhaust gas was monitored as an index of deterioration of
the catalyst. When 24 hours and 48 hours elapsed after the
initiation of the reaction, the contents of the
25 cyclohexanone and cyclohexanone oxime in the reaction

mixture were analyzed by gas chromatography, and the amount of the fed cyclohexanone oxime was subtracted from the value to calculate the conversion of cycloalkanone, the selectivity of cycloalkanone oxime and the yield of cycloalkanone oxime. The results are shown in Table 1. The reaction was stopped when 90 hours elapsed after the initiation of the reaction, because the oxygen concentration in the exhaust gas exceeded 10 volume%, which is thought to be caused by a deterioration in the activity of the catalyst.

Comparative Example 1

To an autoclave made of stainless steel, a reactor, were fed 17.41 g (0.177 mol) of cyclohexanone, 5.73 g (0.336 mol) of ammonia, 11.54 g of 60 wt% hydrogen peroxide (hydrogen peroxide content: 0.204 mol) and 41.67 g of t-butyl alcohol containing water (water content: 15 wt%) per hour. Continuous reaction under the condition at the temperature of 85°C and the pressure of 0.35 MPa (absolute pressure) was conducted with keeping the liquid level by extracting the liquid phase of the reaction mixture through a filter so that the dwelling time became 1.2 hours. During this reaction, 1.34 g of titanosilicate having an MFI structure as a catalyst existed in the reaction mixture in the reactor [cyclohexanone feeding ratio = 0.132

mol/h·g-catalyst]. Furthermore, helium gas was flown in the gas phase portion in the reactor at the rate of 1.2 L/hour, and the oxygen concentration in the exhaust gas was monitored as an index of deterioration of the catalyst.

5 When 17 hours and 41 hours elapsed after the initiation of the reaction, the contents of the cyclohexanone and cyclohexanone oxime in the reaction mixture were analyzed by gas chromatography to calculate the conversion of cycloalkanone, the selectivity of cycloalkanone oxime and
10 the yield of cycloalkanone oxime. The results are shown in Table 1. The reaction was stopped when 66 hours elapsed after the initiation of the reaction, because the oxygen concentration in the exhaust gas exceeded 10 volume%, which is thought to be caused by a deterioration in the activity
15 of the catalyst.

[Table 1]

Example	Example 1		Comparative Example 1	
	24 h	48 h	17 h	41 h
Elapsed Time				
Conversion (%)	99.39	99.51	99.12	99.10
Selectivity (%)	99.73	99.74	99.67	99.68
Yield (%)	99.12	99.26	98.79	98.79

WHAT IS CLAIMED IS:

1. A process for producing a cycloalkanone oxime by a continuous ammoximation reaction in the presence of
5 titanasilicate catalyst, characterized in that the continuous ammoximation reaction is conducted with feeding a cycloalkanone, hydrogen peroxide, ammonia and a cycloalkanone oxime to the reaction system, and the amount of the cycloalkanone oxime to be fed is from 0.1 to 5
10 times by weight as much as the amount of the cycloalkanone to be fed.

2. The process according to claim 1, wherein a cycloalkanone oxime in the reaction mixture is recycled as
15 the cycloalkanone oxime to be fed.

3. The process according to claim 1, wherein the continuous ammoximation reaction is conducted in a solvent, and the amount of the solvent is equal to or less
20 than an amount of 2.3 times by weight as much as the amount of the cycloalkanone fed.