

PROCESS FOR PRODUCING OXIME

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Field of the Invention

5 The present invention relates to a process for producing an oxime by an ammoximation reaction of a ketone. The oxime is useful, for example, as a raw material of an amide or a lactam.

Description of the Related Art

10 As one of the methods for producing an oxime has been known a method of ammoximation reaction of ketones by using a titanosilicate as a catalyst. For example, JP-A-62-59256 discloses an ammoximation reaction by using a titanosilicate having MFI structure (Titanium Silicalite TS-1) as a catalyst.
15 Also, WO 03/074421 discloses an ammoximation reaction by using a titanosilicate having MWW structure as a catalyst.

SUMMARY OF THE INVENTION

20 However, in the method disclosed in the JP-A-62-59256, due to insufficiency of the catalytic performance, a conversion of the ketone or a selectivity of the oxime is sometimes unsatisfactory. Also, the method disclosed in the WO 03/074421 is not sometimes satisfactory in terms of the cost, since the process for producing the catalyst is lengthy and complicated.
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20 due to insufficiency of the catalytic performance, a conversion of the ketone or a selectivity of the oxime is sometimes unsatisfactory. Also, the method disclosed in the WO 03/074421 is not sometimes satisfactory in terms of the cost, since the process for producing the catalyst is lengthy and complicated.
25 An object of the present invention is, therefore, to provide

a process for producing an oxime at a high yield and low cost by carrying out an ammoximation reaction using a catalyst, which has an excellent performance and can be produced advantageously in terms of the cost.

5 The present invention provides a process for producing an oxime by an ammoximation reaction of a ketone with a peroxide and ammonia in the presence of a titanasilicate that shows the x-ray diffraction pattern having peaks at the following points in a chart of lattice spacing:

10 lattice spacing d (Å):

13.2±0.6,

12.3±0.3,

11.0±0.3,

9.0±0.3,

15 6.8±0.3,

3.9±0.2,

3.5±0.1, and

3.4±0.1.

 According to the present invention, an oxime can be
20 produced at a high yield and low cost by an ammoximation reaction of a ketone.

BRIEF DESCRIPTION OF THE DRAWINGS

 Fig. 1 is a chart showing the x-ray diffraction pattern
25 of the titanasilicate (Ti-MWW precursor) produced and used in

Example 1;

Fig. 2 is a chart showing the x-ray diffraction pattern of the titanasilicate (Ti-MWW) produced by calcining the titanasilicate (Ti-MWW precursor) produced in Example 1; and

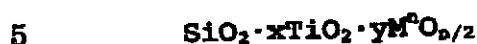
5 Fig. 3 is a chart showing the x-ray diffraction pattern of the titanasilicate (TS-1) used in Comparative Example 1.

DETAILED DESCRIPTION OF THE PREFERRED EXAMPLES

A titanasilicate to be used as a catalyst for the
10 ammoxidation reaction in the present invention is a crystalline titanasilicate containing titanium, silicon and oxygen as elements composing the skeleton, and practically it may include those having a skeleton composed of only titanium, silicon and oxygen and also those having a skeleton composed of titanium,
15 silicon and oxygen as well as other elements such as boron, aluminum, gallium, iron and chromium. The titanasilicate may be used with being formed into granules or pellets with or without a binder, or may be used with being deposited on a support.

In the titanasilicate, the content of titanium is
20 preferably 0.0001 or more, more preferably 0.005 or more, and preferably 0.1 or less, more preferably 0.05 or less by atomic ratio to silicon (Ti/Si). In the case where the titanasilicate comprises other element(s) besides titanium, silicon and oxygen, the content of the element(s) is generally 0.05 or less and
25 preferably 0.02 or less by atomic ratio to silicon. Oxygen may

exist in accordance with the contents and oxidation numbers of the respective elements other than oxygen. The typical composition of such a titanosilicate can be shown by the following formula on the basis of silicon (= 1).



wherein M denotes at least one element other than silicon, titanium and oxygen; n denotes the oxidation number of M; x is from 0.0001 to 0.1; and y is from 0 to 0.05.

The titanosilicate to be used in the present invention
10 has peaks at the following points in a chart of lattice spacing d [Å (angstrom)] in its x-ray diffraction pattern. The titanosilicate that shows such specific x-ray diffraction pattern is excellent in the activity and selectivity as a catalyst in the ammoxidation reaction of a ketone, that is, excellent
15 in a conversion of the ketone and a selectivity of the oxime.

lattice spacing d (Å)

13.2±0.6,

12.3±0.3,

11.0±0.3,

20 9.0±0.3,

6.8±0.3,

3.9±0.2,

3.5±0.1, and

3.4±0.1.

25 The x-ray diffraction pattern can be obtained by a common

x-ray diffraction apparatus using copper K- α radiation beam.

In the case where the copper K- α radiation beam is used,
the peak of $d = 13.2 \pm 0.6$ Å is observed around 2θ (θ is Bragg
angle: hereinafter the same) = 6.7° (6.4 to 7.0°);

5 the peak of $d = 12.3 \pm 0.3$ Å is observed around $2\theta = 7.2^\circ$ (7.0
to 7.4°);

the peak of $d = 11.0 \pm 0.3$ Å is observed around $2\theta = 8.0^\circ$ (7.8
to 8.3°);

the peak of $d = 9.0 \pm 0.3$ Å is observed around $2\theta = 9.8^\circ$ (9.5 to
10 10.2°);

the peak of $d = 6.8 \pm 0.3$ Å is observed around $2\theta = 13.0^\circ$ (12.5
to 13.6°);

the peak of $d = 3.9 \pm 0.2$ Å is observed around $2\theta = 22.8^\circ$ (21.6
to 24.0°);

15 the peak of $d = 3.5 \pm 0.1$ Å is observed around $2\theta = 25.4^\circ$ (24.7
to 26.2°); and

the peak of $d = 3.4 \pm 0.1$ Å is observed around $2\theta = 26.2^\circ$ (25.4
to 27.0°).

In the x-ray diffraction pattern, the existence of peak(s)
20 other than these peaks is optional, and the respective
above-mentioned peaks generally shows the maximum peak in the
lattice spacing however may sometimes be detected as a shoulder
peak while being overlapped with another peak.

The titanosilicate that shows the above-mentioned
25 specific x-diffraction pattern can be obtained as a precursor

when a titanosilicate having MWW structure (hereinafter,
referred to as Ti-MWW in some cases) is supposed to be produced.
That is, for example, Chemistry Letters, p.774-775 (2000) and
JP-A-2002-102709 describe processes for producing Ti-MWW by
5 direct synthetic methods, in which
a structure directing agent (a template), a titanium compound,
a boron compound, a silicon compound and water are mixed,
then treated with an acid if necessary, and
the obtained precursor is calcined to produce Ti-MWW; and the
10 precursor is equivalent to the above-mentioned specific
titanosilicate used in the present invention.
Also, Chemical Communications, p. 1026-1027 (2002),
JP-A-2003-327425 and WO 03/074421 describe processes for
producing Ti-MWW by post-synthesis methods, in which
15 a structure directing agent, a boron compound, a silicon compound
and water are mixed and heated,
then calcined if necessary, and
treated with an acid to obtain a silicate, after that,
the silicate is mixed with a structure directing agent, a titanium
20 compound and water,
heated,
treated with an acid if necessary, and
the obtained precursor is calcined to produce Ti-MWW; and the
precursor is equivalent to the above-mentioned specific
25 titanosilicate used in the present invention.

In such a manner, the titanasilicate (Ti-MWW precursor) used in the present invention is obtained as a precursor, which is obtained before calcination in a process for producing the Ti-MWW, and as compared with Ti-MWW, the facility, energy and time
5 required for calcination can be saved and thus it can be produced at a low cost. Accordingly, the ammoximation reaction using the Ti-MWW precursor of the present invention as a catalyst is advantageous in terms of the production cost of the catalyst as compared with the ammoximation reaction using the Ti-MWW
10 disclosed in WO 03/074421 as a catalyst and is usable for producing the oxime at a lower cost.

Examples of the structure directing agent to be used in the above-mentioned processes may include piperidine and hexamethyleneimine and examples of the titanium compound may
15 include tetraalkyl orthotitanate such as tetra-n-butyl orthotitanate; peroxotitanic acid salt such as tetrapropylammonium peroxotitanate; and titanium halide and examples of the boron compound may include boric acid, and examples of the silicon compound may include tetraalkyl
20 orthosilicate such as tetraethyl orthosilicate and fumed silica.

The heating conditions for the respective mixtures in the above-mentioned processes are generally from 100 to 200°C as the heating temperature, generally from 2 to 240 hours as the heating duration, and generally from 0.01 to 2°C/minute as the
25 heating rate to the heating temperature. A hydrothermal

synthesis under self pressure of the mixture is generally employed at the time of heating and may be a batch type method or a circulation method, and further a zeolite having the MWW structure may be added as a seed crystal or hydrofluoric acid
5 may be added.

In the above-mentioned processes, the treatment with an acid is carried out to remove the structure directing agent, boron, titanium-out-of-the-skeleton and the like, and nitric acid and sulfuric acid are used preferably as the acid.

10 The Ti-MWW precursor obtained in the above-mentioned processes is used, if necessary, after being washed with water and dried. The method for drying includes, for example, a method of heating in a drier, a method of blowing heated gas, and a method of using a spray drier. Among the methods is preferably
15 the method using a spray drier since it can form the precursor into particles with a particle diameter of from about 1 to 1000 μm simultaneously with the drying.

If too high temperature is adopted for drying, the energy costs high and the temperature comes to a range of calcining
20 in which a structural conversion from the Ti-MWW precursor to Ti-MWW takes place. On the other hand, if too low temperature is adopted for drying, it takes a long time for drying to decrease the productivity; therefore the temperature is adjusted properly. According to the descriptions in JP-A-2002-102709 and
25 JP-A-2003-327425 that the calcining temperature for structural

conversion of the Ti-MWW precursor to Ti-MWW is preferably from 200 to 700°C, more preferably from 300 to 650°C, and most preferably from 400 to 600°C, the drying temperature is preferable to be adjusted at lower than 200°C for economical energy cost and generally 20°C or higher in terms of the productivity.

The structural conversion of the Ti-MWW precursor to Ti-MWW by calcining is practically attributed to dehydration condensation of interlayers of the Ti-MWW precursor which is a laminar titanasilicate, and crystallization to the MWW structure; it is confirmed by alteration in the x-ray diffraction pattern. That is, Fig. 1 is a chart of the x-ray diffraction pattern by copper K- α radiation of the Ti-MWW precursor which is prepared and used in Example 1 to be described later, and Fig. 2 is a chart of the x-ray diffraction pattern by copper K- α radiation of the Ti-MWW, which is obtained by calcining the Ti-MWW precursor at 530°C for 6 hours. Due to the structural conversion of the Ti-MWW precursor to the Ti-MWW by calcining, one of the peaks defined in the present invention, that is the peak of the lattice spacing $d = 13.2 \pm 0.6$ Å (around $2\theta = 6.7^\circ$), can be observed to be disappeared. The peak is a peak derived from (002) plane as described in Shokubai, vol. 43, p. 158 (2001) and is characteristic for the laminar structure of the Ti-MWW precursor in comparison with the Ti-MWW.

Using above-mentioned titanasilicate of the Ti-MWW precursor as a catalyst, an oxime can be produced at a high yield

by an ammoximation reaction of a ketone with a peroxide and ammonia in the presence of the catalyst. In the ammoximation reaction, the titanasilicate, the catalyst, is better to exist in solid phase with being suspended in a liquid phase of the reaction mixture, and its proportion may properly be adjusted in consideration of the catalytic activity and dispersibility and is generally 0.1 to 10% by weight to the liquid phase. For the purpose of suppressing deterioration of the catalytic activity of the titanasilicate, a silicon compound such as silica gel, silicic acid and crystalline silica other than titanasilicate may co-exist.

The ketone as a raw material may be aliphatic ketones, alicyclic ketones and aromatic ketones, and based on the necessity, two or more kind of them may be used. Practical examples of the ketone include dialkyl ketones such as acetone, methyl ethyl ketone and isobutyl methyl ketone; alkyl alkenyl ketone such as mesityl oxide; alkyl aryl ketone such as acetophenone; diaryl ketone such as benzophenone, cycloalkanone such as cyclopentanone, cyclohexanone, cyclooctanone and cyclodecanone; and cycloalkenone such as cyclopentenone and cyclohexenone. Among them, cycloalkanone is preferable in the present invention.

The ketone as a raw material may be obtained by oxidation of an alkane or by oxidation (dehydrogenation) of a secondary alcohol or by hydration and oxidation (dehydrogenation) of an

alkene.

Examples of the peroxide include hydrogen peroxide and organic peroxides such as tert-butyl hydroperoxide, di-tert-butyl peroxide and cumene hydroperoxide. Among them, hydrogen peroxide is preferable to be used. Hydrogen peroxide is generally produced by so-called anthraquinone method and generally commercialized in form of an aqueous solution in a concentration of 10 to 70% by weight and it may be used. Hydrogen peroxide can also be produced by reaction of hydrogen and oxygen in an organic solvent in the presence of a solid catalyst on which metal palladium is deposited, and in case of using hydrogen peroxide produced by the method, the organic solvent solution of the hydrogen peroxide obtained by separating the catalyst from the reaction mixture may be used in place of the above-mentioned aqueous hydrogen peroxide solution.

The use amount of peroxide is generally from 0.5 to 3 moles and preferably from 0.5 to 1.5 moles per 1 mole of the ketone. In addition, to the peroxide, phosphoric acid salts such as sodium phosphate; polyphosphoric acid salts such as sodium pyrophosphate and sodium tripolyphosphate; pyrophosphoric acid; ascorbic acid; ethylenediaminetetraacetic acid; nitrotriacetic acid; aminotriacetic acid; diethylenetriaminepentaacetic acid and the like may be added.

Ammonia may be used in gaseous or liquid state and also in form of a solution of water or an organic solvent. The use

amount of ammonia is preferable to be adjusted so as to control the concentration of ammonia in the liquid phase of the reaction mixture at 1% by weight or more. With adjusting the concentration of ammonia in the liquid phase of the reaction mixture to be
5 a prescribed value or more, the conversion of the ketone and the selectivity of the oxime can be improved and accordingly, the yield of the oxime can be improved. The concentration of ammonia is preferably 1.5% by weight or more and generally 10% by weight or less and more preferably 5% by weight or less. The
10 use amount of ammonia is generally 1 mole or higher and more preferably 1.5 moles or higher per 1 mole of the ketone.

The ammoximation reaction may be carried out in a solvent and examples of the solvent include aromatic compounds such as benzene and toluene; alcohols such as methyl alcohol, ethyl
15 alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol and tert-amyl alcohol; and water. Among them, alcohols and water are preferable and a mixed solvent of an alcohol and water is particularly preferable to be used.

20 The ammoximation reaction may be carried out in batch manner or continuously and it is preferable to be carried out continuously by supplying the ketone, peroxide and ammonia to the reaction system and simultaneously discharging the liquid phase of the reaction mixture from the reaction system in terms
25 of the productivity and operationability.

The batch type reaction may be carried out, for example, by putting the ketone, ammonia, catalyst and solvent in a reactor and supplying the peroxide to the mixture under stirring condition, or by putting the ketone, catalyst and solvent in the reactor and supplying the peroxide and ammonia to the mixture under stirring condition, or by putting the catalyst and solvent in the reactor and supplying the ketone, peroxide and ammonia to the mixture under stirring condition.

The continuous reaction can be preferably carried out, for example, by making a reaction mixture in which a catalyst is suspended exist in a reactor, supplying the ketone, peroxide, ammonia and solvent to the reactor and simultaneously discharging the liquid phase of the reaction mixture from the reactor through a filter. The reactor is preferable to be the one lined with glass or made of a stainless steel in terms of prevention of decomposition of the peroxide.

The reaction temperature of the ammoximation reaction is generally from 50 to 120°C and preferably from 70 to 100°C. The reaction pressure may be a normal pressure, however to make dissolution of ammonia in the liquid phase of the reaction mixture easy, the reaction is preferable to be carried out under pressure of generally from 0.2 to 1 MPa and preferably from 0.2 to 0.5 MPa as absolute pressure, and in this case the pressure may be controlled by using an inert gas such as nitrogen and helium.

With respect to post-treatment of the obtained reaction

mixture may properly be selected and for example, after the catalyst is separated from the reaction mixture by filtration or decantation, the liquid phase may be distilled to separate the oxime.

5

EXAMPLES

Hereinafter, Example of the present invention will be described, however it is not intended that the present invention be limited to the illustrated Example.

10

Example 1

(Preparation of catalyst)

9.1 kg of piperidine, 25.6 kg of pure water, 6.2 kg of boric acid, 0.54 kg of tetra-n-butyl orthotitanate and 4.5 kg
15 of fumed silica (CAB-O-SIL M-7D, manufactured by CABOT Inc.) were put in an autoclave and stirred at a room temperature under air atmosphere to produce a gel and aged for 1.5 hours. The autoclave was tightly closed and heated to increase the temperature within 10 hours to 170°C while being stirred, and
20 kept at the temperature for 168 hours for hydrothermal synthesis to obtain a suspension. The suspension was filtered and the residue was washed with water until the pH of washings became around 10 and the residue was dried at 50°C to obtain a white powder still containing water.

25

To 350 g of the water-containing white powder was added

3.5 L of nitric acid of 13 % by weight and the mixture was refluxed for 20 hours. Next, the resulting mixture was filtered and the residue was washed with water until the washings became around neutral and the residue was sufficiently dried at 50°C to obtain
 5 98 g of titanosilicate (Ti-MWW precursor) with Ti/Si (atomic ratio) = 0.0139 in form of a white powder. The x-ray diffraction pattern of the titanosilicate was obtained by an x-ray diffraction apparatus using copper K- α radiation beam to find peaks shown in the following table (see Fig. 1).

10

Table 1

2 θ (°)	Lattice spacing d (Å)
6.82	13.0
7.23	12.2
7.97	11.1
9.78	9.0
12.9	6.8
22.7	3.9
25.2	3.5
26.2	3.4

(Ammoximation reaction)

Ammoximation reaction was carried out using the
 15 above-obtained titanosilicate as a catalyst. That is, using an autoclave of 1 L capacity as a reactor, while supplying cyclohexanone at a rate of 13.4 g/h, water-containing tert-butyl alcohol (water 12% by weight) at a rate of 52 g/h and 60 wt.% hydrogen peroxide at a rate of 8.9 g/h to the reactor and supplying
 20 ammonia to be adjusted to exist at 2 % by weight of ammonia in

the liquid phase of the reaction mixture, the liquid phase of the reaction mixture was simultaneously discharged out of the reactor through a filter to carry out a continuous reaction under conditions of temperature of 85°C, pressure of 0.35 MPa (absolute
5 pressure) and stagnation time of 6 hours. During the reaction, the titanosilicate existed at a ratio of 0.2% by weight to the liquid phase of the reaction mixture in the reactor.

According to analysis of the liquid phase discharged after 1.5 hours from the beginning of the reaction, the conversion
10 of cyclohexanone was 95.7%, the selectivity of cyclohexanoneoxime was 99.0%, and the yield of cyclohexanoneoxime was 94.7%. According to analysis of the liquid phase discharged after 52 hours from the beginning of the reaction, the conversion of cyclohexanone was 99.8%, the
15 selectivity of cyclohexanoneoxime was 99.4%, and the yield of cyclohexanoneoxime was 99.2%. After 106 hours from the beginning of the reaction, the concentration of oxygen in the autoclave sharply increased and therefore, the reaction was stopped.

20

Comparative Example 1

Using TS-1 (commercialized product), which is a titanosilicate having MFI structure, as a catalyst, an ammoximation reaction was carried out in the same manner as
25 Example 1. The x-ray diffraction pattern of the employed TS-1

was as shown in Fig. 3 and the peaks of $d = 13.2 \pm 0.6 \text{ \AA}$ ($2\theta =$ around 6.7°) and $d = 12.3 \pm 0.3 \text{ \AA}$ ($2\theta =$ around 7.2°) specified in the present invention were not observed.

According to analysis of the liquid phase discharged after
5 1.5 hours from the beginning of the reaction, the conversion
of cyclohexanone was 70.9%, the selectivity of
cyclohexanoneoxime was 98.7%, and the yield of
cyclohexanoneoxime was 70.0%. After 3 hours from the beginning
of the reaction, the concentration of oxygen in the autoclave
10 sharply increased and therefore, the reaction was stopped.

WHAT IS CLAIMED IS:

1. A process for producing an oxime by an ammoximation reaction of a ketone with a peroxide and ammonia in the presence
5 of a titanasilicate that shows the x-ray diffraction pattern having peaks at the following points in a chart of lattice spacing:
lattice spacing d (Å):

13.2±0.6,
12.3±0.3,
10 11.0±0.3,
9.0±0.3,
6.8±0.3,
3.9±0.2,
3.5±0.1, and
15 3.4±0.1.

2. The process according to claim 1, wherein the atomic ratio of titanium to silicon in the titanasilicate is in a range of 0.0001 to 0.1.

20

3. The process according to claim 1, wherein the peroxide is hydrogen peroxide.

4. The process according to claim 1, wherein the
25 ammoximation reaction is carried out in a mixed solvent of an

alcohol and water.

5. The process according to claim 1, wherein the ketone is a cycloalkane.

5