

DESCRIPTION

SPARGER, REACTOR AND PROCESS FOR PRODUCING OXIME
USING THE SAME

5 Technical Field

 The present invention relates to a sparger, and a reactor and a process for producing oxime using the sparger. More specifically, the present invention relates to a sparger which is suitable for use in a reaction conducted
10 with suspended catalyst particles, and to a reactor and a process for producing oxime which use the sparger.

Background Art

 In a tank reactor and so on, a reaction is sometimes
15 conducted while catalyst particles are suspended and a raw material(s) for the reaction is supplied through a sparger or the like. In such case, the catalyst particles may enter the sparger from supplying pores of the sparger. Some of raw materials of the reaction may be decomposed or
20 altered by directly contact with the catalyst, so that the reaction does not proceed as it is aimed.

 For example, a process for producing oxime from ketone by using hydrogen peroxide and ammonia in the presence of a titanasilicate catalyst is known (see, for example,
25 Japanese Patent Kokai Publications No. H6-49015, No. 2000-

72737, and No. 2004-307418). When hydrogen peroxide is supplied to an inside of a reactor through a sparger to conduct this reaction, the catalyst particles may enter the sparger before the supply of hydrogen peroxide, at the
5 change in its flow rate and so on, so that decomposition of hydrogen peroxide is accelerated and the reaction does not proceed as it is aimed.

Disclosure of Invention

10 Problems to be solved by the invention

The purpose of the present invention is to provide a sparger, a reactor and a process for producing oxime which use such sparger, wherein in a use of the sparger for a reaction conducted with suspended catalyst particles, the
15 catalyst particles are hard to enter the sparger, and even if they enter, the catalyst particles can be readily discharged therefrom.

Means for solving the problems

20 As a result of keen examination regarding a sparger to solve such problems, the inventors have found that it becomes possible by reducing a pipe diameter of the sparger step-by-step or substantially continuously in direction of its leading-edge portion to make the catalyst particles
25 hard to enter the sparger and to readily discharge the

catalyst particles from the sparger even if they enter it, and finally accomplished the present invention.

The present invention is as follows:

5 (1) A sparger characterized in that a pipe diameter of the sparger becomes smaller in direction of its leading-edge portion step-by-step or substantially (or generally) continuously.

(2) A reactor for conducting a reaction while catalyst particles are suspended and at least part of a raw material for the reaction is supplied through a sparger, characterized in that a pipe diameter of the sparger becomes smaller in direction of a leading-edge portion of the sparger step-by-step or substantially (or generally) continuously.

15 (3) A reactor for conducting a reaction while catalyst particles are suspended and at least part of a raw material for the reaction is supplied through a sparger, characterized in that the catalyst particles are of titanasilicate catalyst having an average particle size of
20 1 to 50 μm and a density of about 2.0 to 2.5 g/cm^3 , the reaction material supplied through the sparger is hydrogen peroxide solution, and a pipe diameter of the sparger becomes smaller in direction of a leading-edge portion of the sparger step-by-step or substantially (or generally)
25 continuously so that a flow velocity of the hydrogen

peroxide solution in the sparger is 0.12 to 1 m/sec.

(4) A process for producing oxime characterized by using the reactor set forth in the above (2) or (3) and reacting ketone, ammonia, and hydrogen peroxide.

5 (5) A process according to the above (4), wherein the ketone is cyclohexanone and the oxime is cyclohexanone oxime.

Effects of the invention

10 The sparger of the present invention is one to which the catalyst particles hard to enter, and which is possible to discharge the catalyst particles from an inside of the sparger even if they enter it, and therefore it can suppress direct contact between the reaction raw material
15 and the catalyst. Accordingly, when a reactor having the sparger of the present invention is used for conducting a reaction, even if the reaction raw material is decomposable or able to be altered by the catalyst, it becomes possible to suppress the decomposition and alternation of the
20 reaction raw material. Such effect is useful in especially for producing oxime by reacting ketone, ammonia and hydrogen peroxide.

Brief Description of Drawings

25 Fig. 1 is a schematic cross-sectional view showing an

example of a stirred tank reactor.

Fig. 2 is a schematic view showing an example of an annular sparger, in which (A) is its side view, and (B) is a cross-sectional plan view taken along X-X line in the (A).

5 Following numerals denote the following elements:

- 1...reactor;
- 2...stirrer;
- 3...jacket;
- 4, 5, and 6...supplying pipe;
- 10 7...outlet port;
- 8...sparger;
- 9...supplying piping;
- 10...supplying pore.

15 Best Mode for Carrying Out the Invention

The sparger of the present invention is constructed so that a pipe diameter of the sparger becomes smaller in direction of its leading-edge portion step-by-step or substantially continuously, and it is used for, for example,
20 a reactor for conducting a reaction while the catalyst particles are suspended.

As the reactor for conducting a reaction while the catalyst particles are suspended, there are a stirred tank reactor, a fluidized-bed reactor and so on. The catalyst
25 (in the form of particles) is suspended in a reaction

liquid in the reactor by a stirrer or by supplying a raw material gas. The reaction liquid is taken out of the reactor, and obtained after separating the catalyst. The separated catalyst is returned to the reactor.

5 Alternatively, the reaction liquid is obtained by separating the catalyst particles with a filter located in the reactor.

The reaction raw material(s) is, supplied through the sparger(s) or a supplying pipe(s). The sparger is located
10 at a predetermined position in a range from the top to the bottom of the reactor depending on the reaction raw material to be supplied. The sparger of the present invention has, for example, an annular, crucial, or comb-like figure (the last one being composed of plural branched
15 tubes which are laterally connected to a header). The upper or lower portion of the sparger is provided with plural supplying pores for the reaction raw material. Additionally, the supplying pore may be provided with an orifice.

20 Because of, for example, change in the flow rate of the reaction raw material, the catalyst particles may enter the sparger. In certain combination of the reaction raw material and the catalyst, the reaction raw material could be decomposed or altered by directly contacting with the
25 catalyst. Therefore, the sparger should be a sparger which

the catalyst particles hard to enter, and which is possible to readily discharge the catalyst particles therefrom even if they enter it.

For such purpose, a pipe diameter of the sparger is set to become smaller in direction of the leading-edge portion of the sparger, so that it is prevented that the flow velocity of the reaction raw material in the pipe becomes sufficiently smaller in direction of the leading-edge portion to make the catalyst particles sediment in the pipe, and the flow velocity is kept at or above a certain level even at the leading-edge portion. Thus, it is achieved that the catalyst particles hard to enter, and even if they enter, they can be readily discharged.

The minimum flow velocity of the reaction raw material in the piping is determined depending on kinds and properties of the catalyst particles and the reaction raw material.

In order to make the reaction raw material easily flow in direction of the leading-edge portion, the diameter of the sparger's pore for supplying the reaction raw material becomes larger in direction of the leading-edge portion.

When the pipe diameter of the sparger becomes smaller in direction of the leading-edge portion, in order to avoid accumulation of the catalyst, it is preferable to use a reducer for a portion at which the pipe diameter is changed.

When the supplying pores of the sparger are located at the lower portion of the sparger's piping, it is preferable to align the bottom of the piping, including the diameter-changing portion of the sparger. Further, when the reaction raw material comprises gas or has a possibility to generate gas, it is preferable to form a gas venting at, for example, the diameter-changing portion of the sparger.

Fig. 1 is a schematic cross-sectional view showing an example of a stirred tank reactor. A reactor (1) is provided with a stirrer (2) and a jacket (3). Reaction raw materials are supplied from supplying pipes (4), (5) and (6), respectively. The supplying pipes (4) and (5) are composed of a sparger and a supplying piping.

Catalyst is supplied into the reactor from a supplying port (or inlet port, not shown), or from the supplying pipe (6) together with the reaction raw material, stirred by the stirrer, and suspended in a reaction liquid in the reactor. The reaction is conducted usually while a heating medium flows through the jacket.

The reaction liquid is taken out at the outlet port (7) followed by separation of the catalyst, separation of the reaction product and the reaction raw materials and so on. In some cases, the reaction liquid may be taken out through a filter (not shown) and from the outlet port (7).

Fig. 2 is a schematic view showing an example of an

annular sparger, in which (A) is its side view, and (B) is a cross-sectional plan view taken along X-X line in the (A). A reaction raw material is supplied from a supplying piping (9) to a sparger (8) which is provided with supplying pores (10), and the reaction raw material is supplied into the reactor.

The pipe diameter of the sparger becomes smaller in direction from the portion of supplying piping (9) to its leading-edge portion. The pipe diameter made smaller at two stages in this example, but the present invention is not limited to this. The leading-edge of the annular sparger may be communicated therethrough or closed.

Hereinafter, the present invention is described regarding, as an example, a reactor for producing cyclohexanone oxime from cyclohexanone, hydrogen peroxide and ammonia in the presence of a titanosilicate catalyst.

Titanosilicate is a zeolite(s) which contains titanium, silicon, and oxygen as elements composing its framework. The zeolite may have the framework substantially composed of titanium, silicon, and oxygen, or the zeolite may further contain other element(s) as an element(s) composing the framework. As titanosilicate, one having an atomic ratio of silicon/titanium from about 10 to 1000 is preferably used, and it may be in the form of, for example, fine powder or fine granules. Titanosilicate can be

prepared by, for example, a process described in Japanese Patent Kokai Publication No. S56-96720.

As the catalyst, one having an average diameter of about 1 to 50 μm and a density of 2.0 to 2.5 g/cm^3 is preferably used.

Cyclohexanone of the raw material may be, for example, one obtained by an oxidation reaction of cyclohexane, one obtained by hydration and dehydrogenation reactions of cyclohexene, or one obtained by a hydrogenation reaction of phenol.

Hydrogen peroxide is usually produced by a so-called anthraquinone process. It is commercially available in the form of an aqueous solution which usually has a concentration from 10 to 70% by weight, and such aqueous solution of Hydrogen peroxide can be used. Hydrogen peroxide may also be produced by reacting hydrogen and oxygen in an organic solvent in the presence of a metal parradium-supported solid catalyst. When hydrogen peroxide from this process is used, the organic solvent solution of hydrogen peroxide which is obtained by separating the catalyst from the reaction mixture may be used in place of the above-mentioned hydrogen peroxide solution.

The amount of used hydrogen peroxide is usually about 0.5 to 3 moles, and preferably about 0.5 to 1.5 moles per 1 mole of cyclohexanone. It is noted that stabilizers of,

for example, a salt of phosphoric acid such as sodium phosphate, a salt of polyphosphoric acid such as sodium pyrophosphate and sodium tripolyphosphate, pyrophosphoric acid, ascorbic acid, ethylenediaminetetraacetic acid, 5 nitrotriacetic acid, aminotriacetic acid, and diethylenetriaminepentaacetic acid may be added to hydrogen peroxide.

As to ammonia, gaseous ammonia may be used, or liquid ammonia may be used, and it may be in the form of a 10 solution in water or an organic solvent. The amount of used ammonia is not smaller than about 1 mole, and preferably not smaller than about 1.5 moles per 1 mole of cyclohexanone.

The ammoximation reaction may be carried out in a 15 solvent. As this reaction solvent, an alcohol such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol or tert-amyl alcohol, water, or a mixed solvent thereof is preferably used.

20 Regarding a process for conducting the ammoximation reaction, in a case of a batch operation, the reaction may be carried out, for example, by charging cyclohexanone, ammonia, titanasilicate catalyst, and a solvent into the reactor and supplying hydrogen peroxide thereto under 25 stirring, or may be carried out by charging cyclohexanone,

a catalyst, and a solvent into the reactor and supplying hydrogen peroxide and ammonia thereto under stirring, or may be carried out by charging a catalyst and a solvent into the reactor and supplying cyclohexanone, hydrogen peroxide and ammonia thereto under stirring. In a case of continuous operation, the reaction may be carried out, for example, by charging to the reactor a feed liquid (or start-up liquid) in which catalyst particles are suspended, and supplying cyclohexanone, hydrogen peroxide, ammonia, and a solvent thereto while taken out a liquid phase of the reaction mixture through a filter. It is noted that the reactor is preferably glass-lined one or made of stainless steel from the viewpoint of prevention of the decomposition of hydrogen peroxide.

Hydrogen peroxide, ammonia, and/or cyclohexanone is supplied to the reactor from the above-mentioned sparger. Hydrogen peroxide may promote its decomposition by contacting with the catalyst, so that the reaction may not proceed as it is aimed. Therefore, hydrogen peroxide is supplied by using the above-mentioned sparger of the present invention, wherein the pipe diameter becomes smaller in direction of the leading-edge portion so that the catalyst hard to enter the sparger and even if it enter, it can be readily discharged therefrom.

In a case of the used titanosilicate catalyst having

the average particle size of about 1 to 50 μm and the density of about 2.0 to 2.5 g/cm^3 and hydrogen peroxide, the pipe diameter of the sparger is made smaller in direction of the leading-edge portion of the sparger so
5 that the flow velocity of hydrogen peroxide in the sparger is in the range from 0.12 to 1 m/sec. It is noted that the larger flow velocity may be acceptable as long as it is not smaller than 0.12 m/sec, and may not cause any problem even when it exceeds 1 m/sec, however, effects can not be
10 obtained in proportion to so large flow velocity.

The supplying pores of the sparger usually have the same pore diameter, and the flow velocity is calculated on the assumption that hydrogen peroxide flows out of the respective supplying pores at the same flow rate. The
15 minimum flow velocity of hydrogen peroxide in the sparger is a flow velocity at the leading-edge portion for each pipe diameter, and can be calculated based on the amount of hydrogen peroxide supplied to the sparger, the number of supplying pores of the sparger, and the pipe diameter of
20 the sparger.

The concentration of the catalyst in the reaction mixture is usually about 1 to 100 g/L as a weight per unit volume of the reaction mixture, though it depends on the activity of the catalyst, reaction conditions and so on.

25 The reaction temperature of the ammoxidation reaction

is usually about 50°C to 100°C. The reaction pressure may be a normal pressure (or an atmospheric pressure), but the reaction is preferably carried out under an increased pressure to increase the amount of ammonia solved in the liquid phase of the reaction mixture, and in this case, the pressure may be adjusted by using an inactive gas(es) such as nitrogen, helium or the like.

For a post-treatment operation of the reaction mixture thus obtained, known methods can be used if it is suitable. For example, cyclohexanone oxime can be separated by separating the catalyst from the reaction mixture with filtration or so, and thereafter subjecting the obtained liquid phase to distillation.

Examples

Hereinafter, examples are shown to concretely describe the present invention, but the present invention is not limited to these.

Test Example 1

Catalyst was located in a piping of transparent vinyl chloride, and an amount of water was flowed therethrough, then the minimum flow velocity necessary to discharge the catalyst was determined.

As the catalyst, titanosilicate catalyst having the

maximum particle size not larger than 150 μm , the average particle size of 38 μm and the density of 2.2 g/cm^3 was used.

In the piping (length 600 mm) of which one end is closed, the catalyst was located at a point of 400 mm distant from the other end. An amount of water was supplied from the other end via a flowmeter and flowed out through a pore of 2 mm ϕ (in diameter) which was formed in the lower portion at a point of 500 mm distant from the other end (about 100 mm distant from the point of catalyst).

The test was conducted for various piping diameters and flow rates of water. The results are shown in Table 1.

It is shown that the catalyst was readily discharged by selecting the flow velocity not smaller than 0.12 m/sec.

Table 1

No. 1			No. 2		
25A Piping (Inner Diameter: 27.6 mm ϕ) Catalyst Amount: 4.4 g			15A Piping (Inner Diameter: 16.1 mm ϕ) Catalyst Amount: 1.6 g		
Flow Rate (L/min)	Flow Velocity (m/sec)	Discharge Condition	Flow Rate (L/min)	Flow Velocity (m/sec)	Discharge Condition
2	0.056	No	0.83	0.068	No
3	0.084	No	1.0	0.082	No
4	0.111	No	1.2	0.96	No
5	0.139	YES	1.3	0.109	No
6	0.167	YES	1.5	0.123	YES
7	0.195	YES	1.7	0.136	YES

YES: The catalyst was readily discharged.

No: The discharge of the catalyst was insufficient.

Example 1

While using a stirred tank reactor similar to that shown in Fig. 1, the reaction from cyclohexanone, hydrogen peroxide and ammonia to cyclohexanone oxime in the presence of a titanasilicate catalyst was conducted.

Cyclohexanone at the ratio of 3.85 t/hr was supplied from the supplying pipe (6), hydrogen peroxide solution (60% by weight) at the ratio of 2.51 t/hr and ammonia at the ratio of 0.99 t/hr were supplied from the spargers (4) and (5), respectively. Further, tert-butyl alcohol (water 12%) at the ratio of 13.3 t/hr was supplied from the supplying port (not shown).

The titanasilicate catalyst having the maximum particle size not larger than 150 μm , the average particle size of 38 μm and the density of 2.2 g/cm^3 was supplied from the supplying port (not shown) so that its concentration was about 3%.

The used sparger for supplying hydrogen peroxide had an annular figure and a closed end. A portion near the source of hydrogen peroxide 50 was a 25A piping; and a leading-edge portion 51, which is about 1/4 of the annulus of the sparger, was a 15A piping; and supplying pores of 2 mm ϕ diameter were formed therein at generally even intervals. The 25A piping portion was provided with 24

supplying pores at the lower portion of the piping and 4
supplying pores at the upper portion which also serve as
gas venting, and the 15A piping portion was provided with 8
supplying pores at the lower portion of the piping and 2
5 supplying pores at the upper portion which also serve as
gas venting.

Based on the flow rate of hydrogen peroxide supplied
to the sparger, the minimum flow velocities for the 25A
piping portion and the 15A piping portion were determined
10 to be about 0.15 m/sec and about 0.17 m/sec, respectively.

The reaction was conducted during about 6 months at
the temperature of about 85°C and the pressure of about
0.25 MPaG (gage). In that time period, it did not seem
that the decomposition of hydrogen peroxide was accelerated,
15 and therefore the reaction was stably conducted without
increasing the supply amount of hydrogen peroxide. Then,
the reaction was stopped. The sparger from which hydrogen
peroxide had been supplied was observed, and it did not
show any trace that the catalyst had entered the sparger.

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Although the present invention has been explained as
above, it will be understood that the present invention is
not limited to such embodiments or examples and can be
modified in various ways without departing from the scope
25 or spirit of the invention.

The present application claims priority under the Paris Convention to Japanese Patent Application No. 2006-025524 filed on February 2, 2006, entitled "SPARGER,
5 REACTOR AND PROCESS FOR PRODUCING OXIME USING THE SAME."
The contents of that application are incorporated herein by the reference thereto in their entirety.

CLAIMS

1. A sparger characterized in that a pipe diameter of the sparger becomes smaller in direction of its leading-edge portion step-by-step or substantially continuously.

5 2. A reactor for conducting a reaction while catalyst particles are suspended and at least part of a raw material for the reaction is supplied through a sparger, characterized in that a pipe diameter of the sparger becomes smaller in direction of a leading-edge portion of
10 the sparger step-by-step or substantially continuously.

3. A reactor for conducting a reaction while catalyst particles are suspended and at least part of a raw material for the reaction is supplied through a sparger, characterized in that the catalyst particles are of
15 titanasilicate catalyst having an average particle size of 1 to 50 μm and a density of 2.0 to 2.5 g/cm^3 , the reaction material supplied through the sparger is hydrogen peroxide solution, and a pipe diameter of the sparger becomes smaller in direction of a leading-edge portion of the
20 sparger step-by-step or substantially continuously so that a flow velocity of the hydrogen peroxide solution in the sparger is 0.12 to 1 m/sec.

4. A process for producing oxime characterized by using the reactor set forth in Claim 2 or 3 and reacting
25 ketone, ammonia, and hydrogen peroxide.

5. A process according to Claim 4, wherein the ketone is cyclohexanone and the oxime is cyclohexanone oxime.