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Method for manufacturing cycloalkanol and/or cycloalkanone

Verfahren zur Herstellung von Cycloalkanol und/oder Cycloalkanon

Procédé de préparation de cycloalcanol et/ou de cycloalcanone

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The present invention relates to a method for manufacturing cycloalkanol and/or cycloalkanone by oxidizing cycloalkane with oxygen.

The use of a cobalt catalyst is effective in manufacturing cycloalkanol and/or cycloalkanone by oxidizing cycloalkane with oxygen, and generally it has conventionally been known that the above-mentioned oxidation is performed in a homogeneous system by using a cobalt compound soluble in cycloalkane, such as cobalt carboxylate, as a catalyst. In addition, various heterogeneous catalysts have been proposed, for example, the above-mentioned oxidation by using a molecular sieve compound containing cobalt in a crystal lattice for a catalyst is disclosed in EP 0 519 569 A. Also, the above-mentioned oxidation by using a cobalt-containing compound prepared by a sol-gel method for a catalyst is disclosed in WO99/40055. In JP-A-63 303 936, cyclohexanol and cyclohexanone are produced by the oxidation of cyclohexane with molecular oxygen using a cobalt-containing phyllosilicate catalyst. Further, the above-mentioned oxidation by using a heteropoly acid compound containing cobalt as a skeletal element for a catalyst is disclosed in JP-A-2000-319211.

The above-mentioned conventional methods include unsatisfactory points in view of activity and selectivity of a catalyst, namely, degree of conversion of cycloalkane and selectivity coefficient of cycloalkanol and/or cycloalkanone. The object of the present invention is to provide a method of capably manufacturing cycloalkanol and/or cycloalkanone with a favorable selectivity coefficient by oxidizing cycloalkane with a favorable degree of conversion through oxidation of cycloalkane with the use of a cobalt catalyst, particularly a heterogeneous cobalt catalyst.

It has now surprisingly been found that the adoption of cobalt supported on layer silicate wherein the layer silicate has pillars formed at the interlayer thereof as a catalyst for oxidizing cycloalkane allows the above-mentioned object to be achieved. That is to say, the present invention provides a method for manufacturing cycloalkanol and/or cycloalkanone by oxidizing cycloalkane with oxygen in the presence of a catalyst wherein cobalt is supported on layer silicate wherein the layer silicate has pillars formed at the interlayer thereof.

The present invention allows cycloalkanol and/or cycloalkanone to be manufactured with favorable selectivity coefficient by oxidizing cycloalkane with a favorable degree of conversion.

Fig. 1 is an X-ray diffraction pattern of cobalt-supporting kenyaite prepared according to the Reference Example 1 which had pillars formed at the interlayer thereof.

Fig. 2 is an infrared absorption spectrum of cobalt-supporting kenyaite prepared according to the Reference Example 1 which had pillars formed at the interlayer thereof.

The present invention is hereinafter detailed. In the present invention, corresponding cycloalkanol and/or cycloalkanone are manufactured by using cycloalkane as raw material and oxidizing this with oxygen (molecular oxygen) in the presence of a catalyst.

Examples of cycloalkane for raw materials include, for example, monocyclic cycloalkane having no substituent in a ring such as cyclopropane, cyclobutane, cyclopentane, cyclohexane, cycloheptane, cyclooctane, cycledecane and cyclooctadecane, polycyclic cycloalkane such as decalin and adamantane, and cycloalkane having substituent in a ring such as methylcyclopentane and methylcyclohexane, and also two kinds or more thereof can be used as required.

Oxygen-containing gas is typically used as oxygen source. This oxygen-containing gas may be, for example, air, pure oxygen, or air or pure oxygen diluted with inert gas such as nitrogen, argon and helium. Oxygen enriched air in which pure oxygen is added to air can also be used.

With regard to the present invention, cobalt supported on layer silicate wherein the layer silicate has pillars formed at the interlayer thereof (hereinafter occasionally referred to as 'cobalt-supporting layer silicate having pillars') is used as a catalyst for oxidizing cycloalkane with oxygen. The use of such a catalyst allows cycloalkanol and/or cycloalkanone to be manufactured with a favorable selectivity coefficient by X oxidizing cycloalkane with a favorable degree of conversion.

Examples of layer silicate as a carrier include layer silicates derived from minerals such as makatite, kanemite, magadite and kenyaita, and layer silicates such that a gap at the interlayer is widened by forming a columnar support (pillar) of silicate and silica at its interlayer. Composite layer silicate such that a columnar support of silicate is formed at the interlayer can also be used, for example, MCM-36. In order to form pillars at the interlayer, it is preferable for layer silicate to be contacted with silicon compounds such as silicate ester, and then to be hydrolyzed.

The support percentage of cobalt is typically 0.01 to 20 % in weight percentage with respect to catalyst, namely, the cobalt-supporting layer silicate having pillars, preferably 0.05 to 10 % and more preferably 0.1 to 5 %.

Examples of a method for supporting cobalt on layer silicate include, for example, a method such as to impregnate layer silicate with an aqueous solution of cobalt compounds such as halide of cobalt and carboxylate and oxo acid salt thereof, a method such as to immerse layer silicate in an aqueous solution of cobalt compounds and adsorb cobalt compounds. Cobalt-supporting layer silicate can also be prepared by mixing cobalt compounds with silicon compounds, which can be raw materials for layer silicate, to be subjected to hydrothermal
The oxidation reaction of cycloalkane can be performed by contacting cycloalkane with oxygen in the presence of cobalt-supporting layer silicate as a catalyst. The used quantity of a catalyst is typically 0.01 to 50 parts by weight with respect to 100 parts by weight of cycloalkane, preferably 0.1 to 10 parts by weight.

In order to improve degree of conversion of cycloalkane and selectivity coefficient of cycloalkanol and/or cycloalkanone, the use of a so-called co-catalyst is effective and kinds thereof are properly selected, among which the use of a heteropoly acid compound is advantageous. This heteropoly acid compound may be free heteropoly acid, or an acid salt or a normal salt of heteropoly acid. The structure of a heteropoly acid compound may be, for example, Keggin structure such that an anion exists [CoW₁₁O₃9]⁻ or [CoMo₁₁O₃9]⁻. Such a heteropoly anion is containing cobalt as a central element and a skeletal element (poly element) is 1/12, Anderson structure such that the atomic ratio is 1/6 or Dawson structure such that the atomic ratio is 2/18.

Preferable examples of a heteropoly acid compound include a heteropoly acid compound containing cobalt as a central element and/or a skeletal element, preferably a heteropoly acid compound particularly containing cobalt as a central element and a skeletal element, specifically such that a heteropoly anion is [CoW₁₁O₃9]⁻ or [CoMo₁₁O₃9]⁻. Such a heteropoly acid compound can be prepared in conformance with a method described, for example, on p. 6025 of Vol. 112 in Journal of American Chemical Society, 1990.

A heteropoly acid compound may be molded for use or supported on a carrier, as required. This carrier is properly selected and a so-called hydrotalcite-like compound is preferably used. Here, a hydrotalcite-like compound is a layer compound, similar to hydrotalcite [Mg₆Al₂(OH)₁₆(CO₃)₄·4H₂O], such that an anion exists between positively charged layers composed of bivalent metal and trivalent metal. In the case where a heteropoly acid compound is supported on a carrier, the support percentage thereof is typically 0.01 to 4 % in weight percentage with respect to the total of a heteropoly acid compound and a carrier, preferably 0.1 to 2 %. In the case of using a heteropoly acid compound without being supported on a carrier, the quantity thereof is typically 0.001 to 10 parts by weight with respect to 100 parts by weight of cycloalkane, preferably 0.01 to 5 parts by weight. In the case of using a heteropoly acid compound supported on a carrier, the used quantity thereof is typically 0.01 to 50 parts by weight with respect to 100 parts by weight of cycloalkane in the total of a heteropoly acid compound and a carrier, preferably 0.1 to 10 parts by weight.

The reaction temperature is typically 0 to 200°C, preferably 50 to 170°C and the reaction pressure is typically 0.01 to 10MPa, preferably 0.1 to 2MPa. The reaction solvent can be used as required, for example including nitrile solvents such as acetonitrile and benzonitrile, and carboxylic acid solvents such as acetic acid and pionic acid.

The after-treatment after oxidation reaction is not particularly limited, for example including a process such as to filter the reaction mixture to separate a catalyst therefrom, which mixture is thereafter washed with water and subsequently distilled. In the case where a cycloalkylhydroperoxide corresponding to the cycloalkane raw material is contained in the reaction mixture, the cycloalkylhydroperoxide can be converted into the intended cycloalkanol and cycloalkanone by alkali treatment and reduction treatment.

EXAMPLES

Examples of the present invention are herein-after described and the present invention is not limited thereto. The analysis of cyclohexane, cyclohexanone, cyclohexanol and cyclohexyl hydroperoxide in the reaction liquid was performed by gas chromatography; and the degree of conversion of cyclohexane as well as each selectivity coefficient of cyclohexanone, cyclohexanol and cyclohexyl hydroperoxide were calculated from the results of this analysis.

Reference Example 1 (Preparation of a cobalt-supporting kenyaite having pillars formed at its interlayer)

(A) Preparation of a cobalt-supporting kenyaite

To an aqueous solution of sodium hydroxide (0.13 g) in water (1.9 g) in a beaker, tyramine (1.17 g) and colloidal silica (LUDOX AS-40 manufactured by Aldrich, i.e., an aqueous suspension of 40 wt.% of silica) (2.5 g) were added, and the mixture was stirred. Then, an aqueous solution of cobalt (II) acetate tetrahydrate (0.14 g) in water (1.0 g) was added, and the mixture was stirred for 4 hours. This mixture was set in an autoclave and stirred at 150°C for 10 days. After that, the mixture was filtered, and the resulting solid residue was washed with water and dried in an oven at 100°C for a whole day and night. Thus, a cobalt-supporting kenyaite (1.1 g) was obtained.

(B) Formation of pillars at the interlayer of the cobalt-supporting kenyaite

To an aqueous solution of sodium hydroxide (0.13 g) in water (1.9 g) in a beaker, tyramine (1.17 g) and colloidal silica (LUDOX AS-40 manufactured by Aldrich, i.e., an aqueous suspension of 40 wt.% of silica) (2.5 g) were added, and the mixture was stirred. Then, an aqueous solution of cobalt (II) acetate tetrahydrate (0.14 g) in water (1.0 g) was added, and the mixture was stirred for 4 hours. This mixture was set in an autoclave and stirred at 150°C for 10 days. After that, the mixture was filtered, and the resulting solid residue was washed with water and dried in an oven at 100°C for a whole day and night. Thus, a cobalt-supporting kenyaite (1.1 g) was obtained.

The after-treatment after oxidation reaction is not particularly limited, for example including a process such as to filter the reaction mixture to separate a catalyst therefrom, which mixture is thereafter washed with water and subsequently distilled. In the case where a cycloalkylhydroperoxide corresponding to the cycloalkane raw material is contained in the reaction mixture, the cycloalkylhydroperoxide can be converted into the intended cycloalkanol and cycloalkanone by alkali treatment and reduction treatment.
solid residue was washed with ethanol and then washed with water, and dried in an oven at 100°C for a whole day and night. This solid and water (100 g) were charged in a flask, and the mixture was stirred at room temperature for 7 hours and filtered. The resulting solid residue was washed with water and dried in an oven at 100°C for a whole day and night. Then, the solid was baked at 540°C for 7 hours to obtain a cobalt-supporting kenyaite which had pillars formed at the interlayer thereof. This cobalt-supporting kenyaite was subjected to an X-ray diffraction analysis (copper Kα-ray; see Fig. 1) and an elemental analysis. As a result, it was confirmed that the interlayer height was not lower than 37 Å; the cobalt content, 2.9 wt.%; the silicon content, 44.8 wt.%; and the sodium content, 0.04 wt.%. The cobalt-supporting kenyaite was further subjected to a Fourier transform infrared spectroscopic analysis. The result is shown in Fig. 2.

Reference Example 2 (Preparation of a hydrotalcite-like compound which supports a salt of heteropoly acid)

(a) Preparation of a salt of heteropoly acid

Sodium tungstate dihydrate (19.8 g, 0.06 mol) and water (40 g) were charged in a 500 ml round bottom flask, and stirred at room temperature to form an aqueous solution. To this aqueous solution, acetic acid (4.1 g) was added to adjust the pH thereof to 7. Then, the solution was heated under refluxing. To this solution, an aqueous solution of cobalt (II) acetate tetrahydrate (2.5 g) in water (13 g) was added dropwise over 20 minutes, and the mixture was further heated under refluxing for 15 minutes. The mixture was cooled to a room temperature, and the solid precipitate was filtered off. Then, the resulting filtrate was heated under refluxing. To this filtrate, an aqueous solution of potassium chloride (13 g) in water (25 g) was added, and the mixture was further heated under refluxing for 15 minutes. The resulting mixture was cooled to a room temperature and then was left to stand at 5°C for a whole day and night for crystallization. The resultant crystals (16.5 g) were separated by filtration. The crystals were subjected to an elemental analysis, an X-ray diffraction analysis, an infrared spectroscopic analysis and a UV-visible spectroscopic analysis. As a result, this crystal was found to be a potassium salt of a Keggin type heteropoly acid, i.e., K_2[H(ScO_11W_{11}CoO_{39})(H_2O)_{39}]](14H_2O), which contained cobalt as the core element, and tungsten and cobalt as the skeletal elements. Thus, it was confirmed that the composition and structure of the salt of heteropoly acid obtained in the above preparation (a) were maintained.

(c) Preparation of a hydrotalcite-like compound

Under a nitrogen atmosphere, the crystals (2.0 g) of the salt of heteropoly acid, obtained by repeating the above purification (b) several times, were added to and dissolved in water (74 g) by heating at 60°C. Under a nitrogen atmosphere, to this solution, the hydrotalcite-like compound (3.9 g) obtained in the above preparation (c) was added, and the mixture was stirred at 60°C for 22 hours. The solid was separated from this mixture by filtration, and was washed with water (27.1 g) of 60°C and dried to obtain a solid (3.8 g). The solid obtained was subjected to an elemental analysis, an X-ray diffraction analysis, an infrared spectroscopic analysis and a UV-visible spectroscopic analysis. As a result, it was confirmed that the above salt of heteropoly acid was supported on the above hydrotalcite-like compound in this solid.

Example 1

34 g (0.40 mol) of cyclohexane and 0.2 g of the above-mentioned cobalt-supporting kenyaite were put in a 50-ml autoclave, and the inside of the system was pressurized up to 0.5MPa with oxygen at room temperature and thereafter heated up to a temperature of 130°C and
reacted under the flow of oxygen for 24 hours.

[0029] At a point in time of 5.5 hours after the start of the reaction, degree of conversion of cyclohexane was 3.5 %, selectivity coefficient of cyclohexanone was 44.3 %, selectivity coefficient of cyclohexanol was 52.1 % and selectivity coefficient of cyclohexyl hydroperoxide was 0.1 %. At a point (the end) in time of 24 hours after the start of the reaction, degree of conversion of cyclohexane was 5.4 %, selectivity coefficient of cyclohexanone was 63.7 %, selectivity coefficient of cyclohexanol was 24.3 % and selectivity coefficient of cyclohexyl hydroperoxide was 0.2 %.

Example 2

[0030] 34 g (0.40 mol) of cyclohexane, 0.1 g of the cobalt-supporting kenyaite obtained according to the Reference Example 1 which had pillars formed at the interlayer thereof and 0.1 g of the above-mentioned heteropoly acid salt-supporting hydrotalcite-like compound obtained according to the Reference Example 2 were put in a 50-ml autoclave, and the inside of the system was pressurized up to 0.5MPa with oxygen at room temperature and thereafter heated up to a temperature of 130°C and reacted under the flow of oxygen for 24 hours.

[0031] At a point in time of 6 hours after the start of the reaction, degree of conversion of cyclohexane was 5.5 %, selectivity coefficient of cyclohexanone was 52.0 %, selectivity coefficient of cyclohexanol was 40.7 % and selectivity coefficient of cyclohexyl hydroperoxide was 1.3 %. At a point (the end) in time of 24 hours after the start of the reaction, degree of conversion of cyclohexane was 9.8 %, selectivity coefficient of cyclohexanone was 67.2 %, selectivity coefficient of cyclohexanol was 18.1 % and selectivity coefficient of cyclohexyl hydroperoxide was 0.4 %.

Comparative Example 1

[0032] 34 g (0.40 mol) of cyclohexane and 0.2 g of the above-mentioned heteropoly acid salt-supporting hydrotalcite-like compound obtained according to the Reference Example 2 were put in a 50-ml autoclave, and the inside of the system was pressurized up to 0.5MPa with oxygen at room temperature and thereafter heated up to a temperature of 130°C and reacted under the flow of oxygen for 24 hours.

[0033] At a point in time of 6 hours after the start of the reaction, degree of conversion of cyclohexane was 2.0 %, selectivity coefficient of cyclohexanone was 25.6 %, selectivity coefficient of cyclohexanol was 21.8 % and selectivity coefficient of cyclohexyl hydroperoxide was 52.6 %. At a point (the end) in time of 24 hours after the start of the reaction, degree of conversion of cyclohexane was 5.4 %, selectivity coefficient of cyclohexanone was 58.6 %, selectivity coefficient of cyclohexanol was 32.9 % and selectivity coefficient of cyclohexyl hydroperoxide was 0.2 %.

[0034] The major embodiments and the preferred embodiments of the present invention are listed below.

[1] A method for manufacturing cycloalkanol and/or cycloalkanone wherein cycloalkane is oxidized with oxygen in the presence of a catalyst wherein cobalt is supported on layer silicate wherein the layer silicate has pillars formed at the interlayer thereof.

[2] The method according to [1], wherein the layer silicate is selected from the group consisting of makatite, kanemite, magadilite and kenyaite.

[3] The method according to [2], wherein the layer silicate is kenyaite.

[4] The method according to any one of [1] to [3], wherein said oxidation is performed in the presence of a heteropoly acid compound.

[5] The method according to [4], wherein the heteropoly acid compound contains cobalt as a central element and/or a skeletal element.

[6] The method according to any one of [4] and [5], wherein the heteropoly acid compound is supported on a carrier.

[7] The method according to [6], wherein the carrier is a hydrotalcite-like compound.

[8] The method according to any one of [1] to [7], wherein the cycloalkane is cyclohexane.

[0035] The present application has been filed claiming the Paris Convention priority based on the Japanese patent application No. 2005-101690 (filed on March 31, 2005, entitled “Method for Manufacturing Cycloalkanol and/or Cycloalkanone”).

Claims

1. A method for manufacturing cycloalkanol and/or cycloalkanone wherein cycloalkane is oxidized with oxygen in the presence of a catalyst wherein cobalt is supported on layer silicate wherein the layer silicate has pillars formed at the interlayer thereof.

2. The method according to Claim 1, wherein the layer silicate is selected from the group consisting of makatite, kanemite, magadilite and kenyaite.

3. The method according to Claim 2, wherein the layer silicate is kenyaite.

4. The method according to any one of Claims 1 to 3, wherein said oxidation is performed in the presence of a heteropoly acid compound.

5. The method according to Claim 4, wherein the heteropoly acid compound contains cobalt as a central element and/or a skeletal element.

6. The method according to any one of Claims 4 and 5.
wherein the heteropoly acid compound is supported on a carrier.

7. The method according to Claim 6, wherein the carrier is a hydrotalcite-like compound.

8. The method according to any one of Claims 1 to 7, wherein the cycloalkane is cyclohexane.

Patentansprüche

1. Verfahren zur Herstellung von Cycloalkanol und/oder Cycloalkanon, wobei Cycloalkan mit Sauerstoff in Gegenwart eines Katalysators oxidiert wird, wobei Cobalt auf Phyllosilicat geträgert ist, wobei das Phyllosilicat Säulen, geformt an der Zwischenschicht davon, aufweist.

2. Verfahren gemäß Anspruch 1, wobei das Phyllosilicat aus Makatit, Kanemit, Magadiit und Kenyait ausgewählt ist.

3. Verfahren gemäß Anspruch 2, wobei das Phyllosilicat Kenyait ist.

4. Verfahren gemäß einem der Ansprüche 1 bis 3, wobei die Oxidation in Gegenwart einer Heteropolysäure-Verbindung durchgeführt wird.

5. Verfahren gemäß Anspruch 4, wobei die Heteropolysäure-Verbindung Cobalt als zentrales Element und/oder Gerüstelement enthält.

6. Verfahren gemäß einem der Ansprüche 4 und 5, wobei die Heteropolysäure-Verbindung auf einen Träger geträgert ist.

7. Verfahren gemäß Anspruch 6, wobei der Träger eine hydrotalcit-artige Verbindung ist.

8. Verfahren gemäß einem der Ansprüche 1 bis 7, wobei das Cycloalkan Cyclohexan ist.

Revendications

1. Procédé de fabrication d’un cycloalcanol et/ou d’une cycloalcanone, dans lequel le cycloalcanone est oxydé avec de l’oxygène en présence d’un catalyseur dans lequel du cobalt est supporté sur un silicate en couche, dans lequel le silicate en couche possède des colonnes formées au niveau de sa couche intermédiaire.

2. Procédé selon la revendication 1, dans lequel le silicate en couche est choisi dans le groupe constitué par la makatite, la kanémite, la magadiite et la ke-
REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 9940055 A [0002]
- JP 2005101690 A [0035]

Non-patent literature cited in the description