

Description

A Process for Epoxidising an Olefin

5 **Technical field**

The present invention relates to a process for epoxidising an olefin.

Background

10 Propylene oxide is a common product of organic chemical industries with the third highest outputs just less than polypropylene and acrylonitrile. The propylene oxide is mainly useful for producing polyether, propylene glycol, isopropanolamine, non-polyether polyol and so on, which are in turn used for producing unsaturated polyester resin, polyurethane, surfactant, fire retardant and so on.

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The conventional process of preparing propylene oxide comprises mainly a chlorohydrin process and a co-oxidation process. Using chlorohydrin technology to synthesize propylene oxide results in severe corrosion of the equipment, an abundant consumption of Cl_2 , the
20 generation of abundant waste water and waste residue, and extreme pollution to the environment. As the increased requirement on the environmental protection, the process will be necessarily eliminated ultimately. Meanwhile, the co-oxidation process has a long flow chart needing great invest, and the production is restricted by the potentially
25 useful application of the by-products thereof. Therefore, these conventional processes of preparing propylene oxide restrict the production of propylene oxide.

In order to overcome the defects of the conventional processes of
30 preparing propylene oxide above, a new synthesis process has been developed, which process uses hydrogen peroxide as the oxidizer, and uses a titanium silicate molecular sieve as the catalyst to catalyze the epoxidation of the propylene, so as to obtain propylene oxide. The process has the advantages of mild conditions, environment-friendly procedures,
35 no pollution and so on, which satisfies the requirement of green chemistry and the developing idea of atom economy, such that the process has been

considered as representing the trend of the process for preparing propylene oxide.

5 In the process to synthesize propylene oxide using hydrogen peroxide as the oxidizer and titanium silicate molecular sieve as the catalyst, the pH of the reaction system is one of the crucial technical parameters during the entire process. Generally, the reaction system presents a relatively lower pH without addition of a pH regulator owing to the acidity of H_2O_2 , thereby the reactivity of the reaction system is low, resulting in lower
10 production efficiency; while a too high pH (such as a pH of 9 or more) of the reaction system will result in a side reaction, which decreases the selectivity for propylene oxide, and meanwhile hydrogen peroxide decomposes rapidly, resulting in a decreased availability of hydrogen peroxide.

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Accordingly, those skilled in the art have attempted to add substances adjusting the pH into the reaction system, so as to control the pH of the reaction system within a suitable range.

20 For example, US 5675026 discloses a process of preparing an epoxide by an olefin and hydrogen peroxide in the presence of a titanium atom-containing zeolite as the catalyst, the process comprising the addition of a neutral or acidic reactive salt before or during the reaction. US 6300506 discloses a process of preparing an oxyalkylene by epoxidising
25 directly an olefin with hydrogen peroxide or a compound capable of generating hydrogen peroxide under the reaction conditions, wherein the epoxidation is conducted in the presence of a catalyst system consisting of a titanium-containing zeolite and a buffer system useful for controlling the pH within the range of 5.0-8.0, which buffer system consists of a
30 nitrogenated base and a salt of a nitrogenated base with an organic or inorganic acid. However, the substances adjusting the pH added into the epoxidation systems as stated in the two patents above may possibly result in the generation of a nascent oxygen in the reaction system, which nascent oxygen has very high reactivity and poor selectivity of oxidation,
35 resulting in intensive local reactions within the reaction system, increased side reactions, and decreased selectivity for propylene oxide to be

produced, wherein the by-product generated in turn results in significantly decreased service life of the catalyst.

Summary of the invention

5 In order to overcome the defects above in the conventional processes of epoxidising propylene, the present invention provides a new process of epoxidising an olefin, wherein the conversion of hydrogen peroxide and the selectivity for the epoxidised olefin are both high, and the service life of the catalyst is prolonged.

10 The present invention provides a process of epoxidising an olefin, comprising epoxidising an olefin with hydrogen peroxide in the presence of a catalyst and a basic anion exchange resin under the olefin epoxidation conditions.

15 According to the process of epoxidising an olefin provided by the present invention, the basic anion exchange resin can react with hydrogen ions in the reaction system of the olefin and hydrogen peroxide via an ion-exchange reaction, so as to increase suitably the pH of the reaction
20 system, which can on the other hand prevent the pH of said reaction system from being too high. Therefore, the test results show that using the process provided by the present invention to synthesize the epoxidised olefin will result in less ineffective decomposition of hydrogen peroxide, better selectivity for the epoxidised olefin generated, and less by-products
25 generated from the side reactions, so as to increase significantly the conversion of hydrogen peroxide, the selectivity for the epoxidised olefin and the service life of the catalyst. Without limited to any theory, it is believed that the advantages are attributed to on the one hand the presence of the basic anion exchange resin, which can inhibit the generation of
30 nascent oxygen during decomposition of hydrogen peroxide; and on the other hand the mild ion-exchange reaction of the hydrogen ion in the reaction system with the basic anion exchange resin, which inhibit the side reactions effectively.

Embodiments

The present invention provides a process of epoxidising an olefin,

comprising epoxidising an olefin with hydrogen peroxide in the presence of a catalyst and a basic anion exchange resin under the olefin epoxidation conditions.

5 The process of epoxidising an olefin according to the present invention can be carried out in various conventional reactors, which reactors can for example comprise at least one of a fixed bed reactor, a moving bed reactor, a slurry bed reactor and so on. When the process is carried out in a fixed bed reactor, a moving bed reactor or a continuous
10 slurry bed reactor, the conditions for the olefin epoxidation can further comprise a liquid volume space velocity of $1-15 \text{ h}^{-1}$, preferably $2-10 \text{ h}^{-1}$. When the process is carried out in a batch reactor, the conditions for the olefin epoxidation can further comprise: a total amount of the catalyst and the basic anion exchange resin of 3-10 parts by weight, preferably 4-9
15 parts by weight, and a reaction duration capable of being 0.2-3 hours, based on 100 parts by weight of the total weight of the olefin and hydrogen peroxide.

 In accordance with the present invention, the fixed bed reactor, the
20 moving bed reactor and the slurry bed reactor can be various corresponding reactors conventionally used in the art. In accordance with the present invention, the fixed bed reactor means a reactor widely used in industry, in which a fluid react at the surface of a bed layer formed with immobile solid materials. The slurry bed reactor is a reactor in which the
25 fine solid particles of the catalyst are suspended in a liquid medium. The slurry bed reactor has a large scale of back mixing of the materials, and after a reaction, the next batch of reaction can generally be conducted just after the separation of the catalyst from the materials. The moving bed reactor is a reactor used to achieve the continuous input and output of a
30 gas-solid phase reaction or a liquid-solid phase reaction, which moving bed reactor has a very small scale of back mixing of the materials. Preferably, the process according to the present invention is carried out in a fixed bed reactor.

35 In one embodiment, the process for carrying out the epoxidation comprises: allowing the olefin and hydrogen peroxide to pass through a

fixed bed reactor in a cocurrent flow or in the form of a mixture containing the both, wherein the fixed bed reactor comprises a shell and a catalyst bed packed in the shell, which catalyst bed contains a catalyst and a basic anion exchange resin.

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In the embodiment above, the compounding ratio between the catalyst and the basic anion exchange resin is not specially limited, as long as the amount of the basic anion exchange resin allows adjusting the pH of the reaction system to 3-9, preferably 4-8. However, during the practical
10 production, when the amount of the basic anion exchange resin is relatively too low (for example, the weight ratio of the catalyst to the basic anion exchange resin is greater than 1:0.05), the effect of adjusting the pH brought by the basic anion exchange resin is very weak, such that the conversion of hydrogen peroxide, the selectivity for the epoxidised olefin
15 and the service life of the catalyst cannot be increased significantly. When the amount of the basic anion exchange resin is relatively too high (for example, the weight ratio of the catalyst to the basic anion exchange resin is less than 1:1.5), the relative content of the catalyst in the epoxidation system is too low, resulting in a very low reaction rate in the reaction
20 system. Therefore, in accordance with the present invention, the weight ratio of the catalyst to the basic anion exchange resin is preferably 1:0.05-1.5, further preferably 1:0.1-1, still further preferably 1:0.2-0.8. In such a case, the ion exchange by the basic anion exchange resin with the hydrogen ion in the reaction system can control stably the pH in the
25 epoxidation system within a range of 4-8, which will result in stable epoxidation in the reaction system and will not result in too intensive local reactions. Meanwhile, the decomposition of hydrogen peroxide and side reactions can be inhibited effectively, so as to increase the selectivity for the epoxidised product. Moreover, owing to the less side reactions, the
30 service life of the catalyst is increased too.

According to one preferred embodiment of the present invention, the process of carrying out the epoxidation comprises: allowing the olefin and hydrogen peroxide to pass through a fixed bed reactor in a cocurrent flow
35 or in the form of a mixture containing the both, wherein the fixed bed reactor comprises a shell and a catalyst bed packed in the shell, which

catalyst bed comprises a plurality of catalyst bed layers, at least a part of the catalyst bed layers comprising a basic anion exchange resin in addition to the catalyst; and along the direction of the olefin and hydrogen peroxide flowing in the reactor, the weight percent of the basic anion exchange resin
5 in each catalyst bed layer is less than in a next catalyst bed layer.

In the preferred embodiment above, the basic anion exchange resin can promote hydrogen peroxide to decompose, thus the conversion of hydrogen peroxide can be increased by allowing the olefin and hydrogen
10 peroxide in a cocurrent flow or in the form of a mixture containing the both to pass through the plurality of catalyst bed layers with increasing contents of the basic anion exchange resin. In addition, the basic anion exchange resin can react with the hydrogen ion in the reaction system of the olefin and hydrogen peroxide, so as to increase suitably the pH of the
15 reaction system, which can on the other hand prevent the pH of said reaction system from being too high, resulting in less ineffective decomposition of hydrogen peroxide, better selectivity for the epoxidised olefin generated, and less by-products generated from the side reactions, so as to increase significantly the conversion of hydrogen peroxide, the
20 selectivity for the epoxidised olefin and the service life of the catalyst.

In the preferred embodiment above, the contents of the catalyst and the basic anion exchange resin in each catalyst bed layer can vary in a broad range. More preferably, along the direction of the olefin and
25 hydrogen peroxide flowing in the reactor, the content of the basic anion exchange resin in the first catalyst bed layer is 0-30 wt%, while the content of the basic anion exchange resin in the last catalyst bed layer is 30-100 wt%, preferably 70-100 wt%, based on the total weight of the catalyst and the basic anion exchange resin in each catalyst bed layer.
30 Further preferably, in order to increase the conversion of hydrogen peroxide during the olefin epoxidation, along the direction of the olefin and hydrogen peroxide flowing in the reactor, the difference of the contents of the basic anion exchange resin in adjacent two catalyst bed layers is 5-50 wt%, more preferably 10-30 wt%.

In the preferred embodiment above, the height of each catalyst bed layer is not specially limited. Further preferably, along the direction of the olefin and hydrogen peroxide flowing in the reactor, the height of each catalyst bed layer is 0.5-95%, more preferably 2-60%, further more preferably 2-50%, still further preferably 10-40% of the total height of the catalyst bed.

In the preferred embodiment above, the number of the catalyst bed layers is not specially limited; however, though the increased number of the catalyst bed layers increases the conversion of hydrogen peroxide during the olefin epoxidation, the increased number of the catalyst bed layers also brings increased difficulty of production in the catalyst bed layers and of the regeneration of the catalyst bed layers. Therefore, considering the equilibrium between the cost of the olefin epoxidation process and the conversion of hydrogen peroxide, the catalyst bed has preferably 2-20 catalyst bed layers, more preferably 3-10 catalyst bed layers.

In accordance with the present invention, the basic anion exchange resin can be various basic anion exchange resins known in the art, comprising strong base anion exchange resin and/or weak base anion exchange resin. Further, for example, the basic anion exchange resin can be a styrene-type basic anion exchange resin and/or an acrylic basic anion exchange resin. The basic anion exchange resin can be of a macroporous type or a gel-type, preferably a macroporous type. The basic anion exchange resin can be commercially available, for example, commercially available from Anhui Sanxing Resin Co., Ltd.. The total exchange capacity of the basic anion exchange resin can be 0.5-3mmol/ml, preferably 0.8-2.5mmol/ml, further preferably 1.1-1.6 mmol/ml. In accordance with the present invention, the total exchange capacity means the total amount of all the exchangeable groups in a unit volume of an ion exchange resin.

In accordance with the present invention, the type of the catalyst is not specially limited, which catalyst can be various catalysts conventionally used in an olefin epoxidation process. For example, the

catalyst can be a titanium silicate molecular sieve catalyst, a modified titanium silicate molecular sieve catalyst or a mixture thereof, as well as a heteropolyacid catalyst and so on. Preferably, the catalyst is a titanium silicate molecular sieve catalyst. Specifically, the titanium silicate molecular sieve can be for example at least one of a titanium silicate molecular sieve having a MFI structure, a titanium silicate molecular sieve having a MEL structure, a titanium silicate molecular sieve having a BETA structure and a ZSM-12 type titanium silicate molecular sieve. Generally, the titanium silicate molecular sieve has a structural formula of: $x\text{TiO}_2 \cdot \text{SiO}_2$, wherein x can be 0.0001-0.04, preferably 0.01-0.03. In accordance with the present invention, the titanium silicate molecular sieve can be commercially available or be prepared. The process for preparing the titanium silicate molecular sieve is known to those skilled in the art. For example, the process disclosed by CN 101279959A can be used to prepare the catalyst. In order to further increase the conversion of hydrogen peroxide and the selectivity for the epoxidised olefin during the olefin epoxidation, the catalyst is more preferably a titanium silicate molecular sieve having a crystal grain of a hollow structure, with a radial length of 5-300nm for the cavity portion of the hollow structure, wherein the adsorption capacity of benzene measured for the titanium silicate molecular sieve under the conditions of 25 degrees C, $P/P_0 = 0.10$ and 1 h of adsorption time is at least 70 mg/g, and there is a hysteresis loop between the adsorption isotherm and the desorption isotherm for the nitrogen adsorption by the molecular sieve at a low temperature. In the process of epoxidising the olefin provided by the present invention, when the catalyst is more preferably a titanium silicate molecular sieve having a hollow crystal grain, the reaction raw materials can enter the cavity portion of said catalyst easily to contact and react with the active component of the titanium silicate molecular sieve, so as to enhance the reactivity of the catalyst further. Meanwhile, the epoxidised olefin as the product of epoxidation can also fall off the active sites of the titanium silicate molecular sieve easily, in turn diffuse into the cavity of the titanium silicate molecular sieve, so as to reduce the residence time of the epoxidised olefin at the active sites of the titanium silicate molecular sieve, and further reduce the probability of side reactions of the epoxidised olefin, such that the selectivity of the epoxidation is further increased.

In accordance with the process of epoxidising an olefin provided by the present invention, the epoxidation can be carried out in the presence of an organic solvent. When the epoxidation is carried out in the presence of an organic solvent, the molar ratio among the organic solvent, the olefin and hydrogen peroxide is preferably (4-15): (0.5-5):1, further preferably (5-12): (1-3):1, still further preferably (5-10): (1.5-2.5):1.

In accordance with the present invention, the olefin is not specially limited. For example, the olefin can be an olefin having 3-8 carbon atoms. Specifically, the olefin can be one of propylene, butylene(s) and pentene(s), preferably propylene. In accordance with the present invention, the type of the solvent is not specially limited. For example, the solvent can be at least one of a C1-C6 alcohol and a C2-C6 nitrile, preferably at least one of methanol, ethanol, propanol(s), butanol(s) and acetonitrile, preferably methanol. Said hydrogen peroxide is generally used in the form of an aqueous solution, and the concentration of hydrogen peroxide can be 10-70 wt%, preferably 20-50 wt%.

According to the process provided by the present invention, when the epoxidation is carried out in a fixed bed reactor, the conditions for the olefin epoxidation can be the conventional reaction conditions, without any special limitation by the present invention. Nevertheless, in order to obtain appropriate conversion of hydrogen peroxide and selectivity for the epoxidised olefin, the conditions for the olefin epoxidation comprise preferably: a temperature of 30-90 degrees C, further preferably 40-80 degrees C; a pressure of 0.5-4.5MPa, further preferably 0.6-3MPa; and a liquid volume hourly space velocity of 1-15 h⁻¹, further preferably 2-10 h⁻¹.

The present invention will be further illustrated by the following Examples. In the following Examples, the conversion of hydrogen peroxide and the selectivity for propylene oxide are calculated according to the method below:

The conversion of hydrogen peroxide = the moles of hydrogen peroxide converted/moles of hydrogen peroxide fed * 100%

The selectivity for propylene oxide = the moles of propylene oxide generated/the total moles of epoxide generated * 100%

wherein, the moles of hydrogen peroxide, the moles of propylene oxide and the total moles of the epoxide generated are measured according to methods known to those skilled in the art. For example, the moles of hydrogen peroxide can be measured using an iodimetry, and the moles of propylene oxide and the total moles of the epoxide generated can be measured using a chromatogram internal standard method.

Preparation example 1: preparing a titanium silicate molecular sieve catalyst

100 g of titanium silicate molecular sieve powder (from Hunan Jianchang Co., Ltd., under the trademark of HTS), 1 g of magnesia and 40 g of tetramethoxyl silane were mixed homogeneously; then into which 20 g of silica sol (with 30 wt% of silica), 2 g of polyvinyl alcohol, 1 g of sesbania powder (from Zhuwa (Dongming County) Sesbania Gum Factory) and 20 ml of water were added and mixed homogeneously, which were then extruded and shaped to a strip having a dimension of 2 * 2 mm, which was then dried at 70 degrees C for 4 hours, to obtain a shaped article A.

100g of the shaped article A was placed into a three-necked flask, into which 200ml of 20 wt% sodium hydroxide solution was added, heated to 90 degrees C and kept for 6 hours, and then washed with deionized water till the washed water free of sodium ion. Then, drying at 120 degrees C for 3 hours and calcinating at 550 degrees C for 3 hours provided a roast B.

100g of the roast B was placed into a three-necked flask, into which 200ml of 20 wt% sodium hydroxide solution and 10ml of 27.5 wt% hydrogen peroxide solution were added, heated under reflux at 90 degrees C for 2 hours, and then washed with deionized water till the washed water free of sodium ion. Finally drying at 120 degrees C for 3 hours and calcinating at 550 degrees C for 5 minutes provided the titanium silicate molecular sieve catalysts used by each example and comparative example according to the present invention.

Example 1

The example was provided to illustrate the process of epoxidising an olefin according to the present invention.

5 The titanium silicate molecular sieve catalyst prepared in preparation example 1 and a macroporous styrene-type strong base anion exchange resin (from Anhui Sanxing Resin Co., Ltd., having a total exchange capacity of 1.5mmol/ml) were mixed at a weight ratio of 1:1, and were loaded into a fixed bed reactor (from Penglai Luhao Chemical Machine
10 Co., Ltd., same in the follows) in a loading amount of 15 ml, so as to form a catalyst bed layer in the fixed bed reactor, above and below which catalyst bed layer ceramic ring packing was charged.

Then, a reactant consisting of methanol, propylene and hydrogen peroxide at a molar ratio of 6:2:1 was injected into the fixed bed reactor at
15 a liquid volume space velocity of 7 h^{-1} at 60 degrees C. The pressure in the fixed bed reactor was kept at 2.5MPa, and the fixed bed reactor was operated continuously for 1700 hours. During the operation of the fixed bed reactor, the conversion of hydrogen peroxide and the selectivity for propylene oxide were measured at intervals and calculated to provide
20 results as showed by table 1 below.

Table 1

Reaction duration (hr)	Conversion of hydrogen peroxide (%)	Selectivity for propylene oxide (%)
17.00	89.25	99.55
200.00	93.25	97.56
700.00	92.00	97.50
1206.00	92.10	97.23
1700.00	90.70	97.98

Comparative example 1

25 The process according to example 1 was carried out, except that the catalyst bed layer loaded into the fixed bed reactor did not comprise the macroporous styrene-type strong base anion exchange resin, while a same weight of titanium silicate molecular sieve catalyst prepared in preparation example 1 was used in place of the macroporous styrene-type strong base

anion exchange resin. During the operation of the fixed bed reactor, the conversion of hydrogen peroxide and the selectivity for propylene oxide were measured and calculated to provide results as showed by table 2 below.

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Table 2

Reaction duration (hr)	Conversion of hydrogen peroxide (%)	Selectivity for propylene oxide (%)
17.00	90.85	93.45
200.00	85.25	91.28
300.00	75.69	83.04
406.00	65.56	71.32
521.00	54.18	60.67

Example 2

The example was provided to illustrate the process of epoxidising an olefin according to the present invention.

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The titanium silicate molecular sieve catalyst prepared in preparation example 1 and a macroporous styrene-type strong base anion exchange resin (from Anhui Sanxing Resin Co., Ltd., having a total exchange capacity of 1.3mmol/ml) were mixed at a weight ratio of 1:0.1, and were loaded into a fixed bed reactor in a loading amount of 15 ml, so as to form a catalyst bed layer in the fixed bed reactor, above and below which catalyst bed layer ceramic ring packing was charged.

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Then, a reactant consisting of ethanol, propylene and hydrogen peroxide at a molar ratio of 5:1.5:1 was injected into the fixed bed reactor at a liquid volume space velocity of 10 h^{-1} at 40 degrees C. The pressure in the fixed bed reactor was kept at 1MPa, and the fixed bed reactor was operated continuously for 1700 hours. During the operation of the fixed bed reactor, the conversion of hydrogen peroxide and the selectivity for propylene oxide were measured at intervals and calculated to provide results as showed by table 3 below.

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Table 3

Reaction duration (hr)	Conversion of hydrogen peroxide (%)	Selectivity for propylene oxide (%)
17.00	85.35	99.45
200.00	92.15	97.86
700.00	91.00	97.57
1206.00	90.00	97.58
1700.00	90.10	96.75

Comparative example 2

The process according to example 2 was carried out, except that in the catalyst bed layer loaded into the fixed bed reactor, a same weight of Na_2HPO_4 was used in place of the macroporous styrene-type strong base anion exchange resin. During the operation of the fixed bed reactor, the conversion of hydrogen peroxide and the selectivity for propylene oxide were measured and calculated to provide results as showed by table 4 below.

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Table 4

Reaction duration (hr)	Conversion of hydrogen peroxide (%)	Selectivity for propylene oxide (%)
17.00	85.35	99.35
200.00	90.15	97.74
300.00	89.00	92.53
406.00	81.00	84.36
508.00	75.10	79.65

Example 3

The example was provided to illustrate the process of epoxidising an olefin according to the present invention.

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The titanium silicate molecular sieve catalyst prepared in preparation example 1 and a macroporous acrylic strong base anion exchange resin (from Hangzhou Zhengguang Resin Co., Ltd., having a total exchange capacity of 1.5mmol/ml) were mixed at a weight ratio of 1:0.5, and were loaded into a fixed bed reactor in a loading amount of 15 ml, so as to form

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a catalyst bed layer in the fixed bed reactor, above and below which catalyst bed layer ceramic ring packing was charged.

Then, a reactant consisting of acetonitrile, propylene and hydrogen peroxide at a molar ratio of 10:2.5:1 was injected into the fixed bed reactor at a liquid volume space velocity of 2 h^{-1} at 80 degrees C. The pressure in the fixed bed reactor was kept at 3MPa, and the fixed bed reactor was operated continuously for 1700 hours. During the operation of the fixed bed reactor, the conversion of hydrogen peroxide and the selectivity for propylene oxide were measured at intervals and calculated to provide results as showed by table 5 below.

Table 5

Reaction duration (hr)	Conversion of hydrogen peroxide (%)	Selectivity for propylene oxide (%)
17.00	89.35	99.45
200.00	90.15	98.85
700.00	91.00	97.87
1206.00	90.50	97.85
1700.00	91.10	97.75

Example 4

The example was provided to illustrate the process of epoxidising an olefin according to the present invention.

A titanium silicate molecular sieve powder (from Hunan Jianchang Co., Ltd., under the trademark of HTS) and a styrene-type strong base anion exchange resin in a gel form (from Shandong Dongda Chemicals Co., Ltd., having a total exchange capacity of 1.3mmol/mL) were mixed at a weight ratio of 1:1, and added continuously into the top of a moving bed reactor (from Chengdu Xindu Yongtong Machine Factory). Meanwhile, the titanium silicate molecular sieve catalyst and the styrene-type strong base anion exchange resin in the gel form were discharged continuously from the bottom of the reactor and recycled to the top of the reactor, so as to ensure that the loading amount of the mixture of the titanium silicate molecular sieve catalyst and the styrene-type strong base anion exchange

resin in the gel form in the reactor was 15 ml. Moreover, a reactant of methanol, propylene and hydrogen peroxide at a molar ratio of 6:2:1 was injected continuously at a liquid volume space velocity of 7 h^{-1} into the bottom of the moving bed reactor, which reactor was kept having a temperature of 60 degrees C and a pressure of 2.5MPa. The fixed bed reactor was operated continuously for 1700 hours. During the operation of the fixed bed reactor, the conversion of hydrogen peroxide and the selectivity for propylene oxide were measured at intervals and calculated to provide results as showed by table 6 below.

Table 6

Reaction duration (hr)	Conversion of hydrogen peroxide (%)	Selectivity for propylene oxide (%)
17.00	88.25	99.40
200.00	90.05	98.95
700.00	91.05	97.87
1206.00	90.35	97.84
1700.00	91.05	97.65

It could be seen from the data of tables 1-6 that in examples 1-4, after 1700 hours of continuous operation of the reactor, the conversion of hydrogen peroxide and the selectivity for propylene oxide were still kept at 90% or more, suggesting that the catalyst was still substantially active; while in comparative examples 1 and 2, after a continuous operation of the reactor of no more than 550 hours, the conversion of hydrogen peroxide and the selectivity for propylene oxide were both decreased down to 80% or less, suggesting the significantly decreased activity of the catalyst. Thereby, using the process provided by the present invention to synthesize propylene oxide allowed the catalyst used to keep excellent activity in long term without inactivation. Moreover, very high conversion of hydrogen peroxide and selectivity for propylene oxide were always kept during the propylene oxide synthesis.

Example 5

The example was provided to illustrate the process of epoxidising an olefin according to the present invention.

The titanium silicate molecular sieve catalyst prepared in preparation example 1 and a macroporous styrene-type strong base anion exchange resin (from Anhui Sanxing Resin Co., Ltd., having a total exchange capacity of 1.5mmol/ml) were mixed at weight ratios of 85:15, 70:30 and 55:45, respectively, and were loaded successively into a fixed bed reactor (from Penglai Luhao Chemical Machine Co., Ltd., same in the follows) in a total loading amount of 15 ml, so as to form three catalyst bed layers at a height ratio of 1:1:1, above and below which catalyst bed layers ceramic ring packing was charged.

Then, a reactant consisting of methanol, propylene and hydrogen peroxide at a molar ratio of 6:2:1 was injected into the fixed bed reactor at a liquid volume space velocity of 7 h^{-1} at 60 degrees C. The pressure in the fixed bed reactor was kept at 2.5MPa, and the fixed bed reactor was operated continuously for 1700 hours. During the operation of the fixed bed reactor, the conversion of hydrogen peroxide and the selectivity for propylene oxide were measured at intervals and calculated to provide results as showed by table 7 below.

Table 7

Reaction duration (hr)	Conversion of hydrogen peroxide (%)	Selectivity for propylene oxide (%)
17.00	99.75	99.75
200.00	99.78	99.46
700.00	99.73	98.67
1206.00	98.84	98.23
1700.00	96.31	98.05

Comparative example 3

The process according to example 5 was carried out, except that the catalyst bed layers loaded into the fixed bed reactor did not comprise the macroporous styrene-type strong base anion exchange resin, while a same weight of titanium silicate molecular sieve catalyst prepared in preparation example 1 was used in place of the macroporous styrene-type strong base anion exchange resin. During the operation of the fixed bed reactor, the

conversion of hydrogen peroxide and the selectivity for propylene oxide were measured and calculated to provide results as showed by table 8 below.

5 Table 8

Reaction duration (hr)	Conversion of hydrogen peroxide (%)	Selectivity for propylene oxide (%)
17.00	90.85	93.45
200.00	85.25	91.28
300.00	75.69	83.04
406.00	65.56	71.32
521.00	54.18	60.67

Example 6

10 The titanium silicate molecular sieve catalyst prepared in preparation example 1 and a macroporous styrene-type strong base anion exchange resin (from Anhui Sanxing Resin Co., Ltd., having a total exchange capacity of 1.3mmol/ml) were mixed at weight ratios of 90:10, 80:20, 70:30 and 60:40, respectively, and were loaded successively into a fixed bed reactor (from Penglai Luhao Chemical Machine Co., Ltd., same in the follows) in a total loading amount of 15 ml, so as to form four catalyst bed
15 layers at a height ratio of 4:3:2:1, above and below which catalyst bed layers ceramic ring packing was charged.

20 Then, a reactant consisting of ethanol, propylene and hydrogen peroxide at a molar ratio of 5:1.5:1 was injected into the fixed bed reactor at a liquid volume space velocity of 10 h^{-1} at 40 degrees C. The pressure in the fixed bed reactor was kept at 1MPa, and the fixed bed reactor was operated continuously for 1700 hours. During the operation of the fixed bed reactor, the conversion of hydrogen peroxide and the selectivity for propylene oxide were measured at intervals and calculated to provide
25 results as showed by table 9 below.

Table 9

Reaction duration (hr)	Conversion of hydrogen peroxide (%)	Selectivity for propylene oxide (%)
17.00	99.87	99.85
200.00	99.85	99.63
700.00	99.82	98.96
1206.00	99.04	98.75
1700.00	98.51	98.41

Comparative example 4

The process according to example 6 was carried out, except that in the catalyst bed layers loaded into the fixed bed reactor, a same weight of Na_2HPO_4 was used in place of the macroporous styrene-type strong base anion exchange resin. During the operation of the fixed bed reactor, the conversion of hydrogen peroxide and the selectivity for propylene oxide were measured and calculated to provide results as showed by table 10 below.

Table 10

Reaction duration (hr)	Conversion of hydrogen peroxide (%)	Selectivity for propylene oxide (%)
17.00	85.35	99.35
200.00	90.15	97.74
300.00	89.00	92.53
406.00	81.00	84.36
508.00	75.10	79.65

Example 7

The example was provided to illustrate the process of epoxidising an olefin according to the present invention.

The titanium silicate molecular sieve catalyst prepared in preparation example 1 and a macroporous acrylic strong base anion exchange resin (from Hangzhou Zhengguang Resin Co., Ltd., having a total exchange capacity of 1.5mmol/ml) were mixed at weight ratios of 95:5, 75:25 and

55:45, respectively, and were loaded successively into a fixed bed reactor (from Penglai Luhao Chemical Machine Co., Ltd., same in the follows) in a total loading amount of 15 ml, so as to form three catalyst bed layers at a height ratio of 3:2:1, above and below which catalyst bed layers ceramic ring packing was charged.

Then, a reactant consisting of acetonitrile, propylene and hydrogen peroxide at a molar ratio of 10:2.5:1 was injected into the fixed bed reactor at a liquid volume space velocity of 2 h^{-1} at 80 degrees C. The pressure in the fixed bed reactor was kept at 3MPa, and the fixed bed reactor was operated continuously for 1700 hours. During the operation of the fixed bed reactor, the conversion of hydrogen peroxide and the selectivity for propylene oxide were measured at intervals and calculated to provide results as showed by table 11 below.

Table 11

Reaction duration (hr)	Conversion of hydrogen peroxide (%)	Selectivity for propylene oxide (%)
17.00	99.64	99.65
200.00	99.63	99.21
700.00	99.60	98.57
1206.00	98.75	98.25
1700.00	96.05	98.04

Example 8

The process according to example 7 was carried out, except that the titanium silicate molecular sieve catalyst prepared in preparation example 1 and the macroporous acrylic strong base anion exchange resin (from Hangzhou Zhengguang Resin Co., Ltd., having a total exchange capacity of 1.5mmol/ml) were only mixed at a weight ratio of 95:5 and loaded into a fixed bed reactor. During the operation of the fixed bed reactor, the conversion of hydrogen peroxide and the selectivity for propylene oxide were measured and calculated to provide results as showed by table 12 below.

Table 12

Reaction duration (hr)	Conversion of hydrogen peroxide (%)	Selectivity for propylene oxide (%)
17.00	89.25	99.55
200.00	93.25	97.56
700.00	92.00	97.50
1206.00	92.10	97.23
1700.00	90.70	97.98

Example 9

The example was provided to illustrate the process of epoxidising an olefin according to the present invention.

The titanium silicate molecular sieve catalyst prepared in preparation example 1, a mixture of the titanium silicate molecular sieve catalyst prepared in preparation example 1 and a styrene-type strong base anion exchange resin in a gel form (from Shandong Dongda Chemicals Co., Ltd., having a total exchange capacity of 1.3mmol/ml) mixed at a weight ratio of 70:30, and a styrene-type strong base anion exchange resin in a gel form (from Shandong Dongda Chemicals Co., Ltd., having a total exchange capacity of 1.3mmol/ml) were loaded successively into a fixed bed reactor (from Penglai Luhao Chemical Machine Co., Ltd., same in the follows) in a total loading amount of 15 ml, so as to form three catalyst bed layers at height ratios of 4:2:1, above and below which catalyst bed layers ceramic ring packing was charged.

Then, a reactant consisting of methanol, propylene and hydrogen peroxide at a molar ratio of 6:2:1 was injected into the fixed bed reactor at a liquid volume space velocity of 2 h^{-1} at 40 degrees C. The pressure in the fixed bed reactor was kept at 2.5MPa, and the fixed bed reactor was operated continuously for 1700 hours. During the operation of the fixed bed reactor, the conversion of hydrogen peroxide and the selectivity for propylene oxide were measured at intervals and calculated to provide results as showed by table 13 below.

Table 13

Reaction duration (hr)	Conversion of hydrogen peroxide (%)	Selectivity for propylene oxide (%)
17.00	98.05	99.35
200.00	97.92	99.02
700.00	97.68	97.85
1206.00	97.50	95.28
1700.00	93.58	91.53

It could be seen from the data of tables 7-13 that in examples 5-9, after 1700 hours of continuous operation of the reactor, the conversion of hydrogen peroxide and the selectivity for propylene oxide were still kept at 90% or more, suggesting that the catalyst was still substantially active. Thereby, using the process provided by the present invention to synthesize propylene oxide allowed the catalyst used to keep excellent activity in long term without inactivation. Moreover, very high conversion of hydrogen peroxide and selectivity for propylene oxide were always kept during the propylene oxide synthesis.

Example 10

The titanium silicate molecular sieve catalyst prepared in preparation example 1 and a macroporous styrene-type strong base anion exchange resin (from Anhui Sanxing Resin Co., Ltd., having a total exchange capacity of 1.3mmol/ml) were mixed at weight ratios of 80:20, 50:50 and 20:80, respectively, and were loaded successively into a fixed bed reactor (from Penglai Luhao Chemical Machine Co., Ltd., same in the follows) in a total loading amount of 14 ml, so as to form three catalyst bed layers at a height ratio of 4:2:2, above and below which catalyst bed layers ceramic ring packing was charged.

Then, a reactant consisting of ethanol, propylene and hydrogen peroxide at a molar ratio of 5:1.5:1 was injected into the fixed bed reactor at a liquid volume space velocity of 1.8 h^{-1} at 40 degrees C. The pressure in the fixed bed reactor was kept at 2.0MPa, and the fixed bed reactor was operated continuously for 1108 hours. During the operation of the fixed bed reactor, the conversion of hydrogen peroxide and the selectivity for

propylene oxide were measured at intervals and calculated to provide results as showed by table 14 below.

Table 14

Reaction duration (hr)	Conversion of hydrogen peroxide (%)	Selectivity for propylene oxide (%)
20.00	99.91	99.77
520.00	99.90	99.75
710.00	99.88	99.76
1108.00	99.54	98.88

5

Example 11

The titanium silicate molecular sieve catalyst prepared in preparation example 1 and a macroporous styrene-type strong base anion exchange resin (from Anhui Sanxing Resin Co., Ltd., having a total exchange capacity of 1.3mmol/ml) were mixed at weight ratios of 70:30, 60:40, 50:50, 40:60 and 30:70, respectively, and were loaded successively into a fixed bed reactor (from Penglai Luhao Chemical Machine Co., Ltd., same in the follows) in a total loading amount of 20 ml, so as to form five catalyst bed layers at a height ratio of 4:2:2:2:1, above and below which catalyst bed layers ceramic ring packing was charged.

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Then, a reactant consisting of ethanol, propylene and hydrogen peroxide at a molar ratio of 7:2:1 was injected into the fixed bed reactor at a liquid volume space velocity of 2.0 h^{-1} at 40 degrees C. The pressure in the fixed bed reactor was kept at 2.0MPa, and the fixed bed reactor was operated continuously for 1510 hours. During the operation of the fixed bed reactor, the conversion of hydrogen peroxide and the selectivity for propylene oxide were measured at intervals and calculated to provide results as showed by table 15 below.

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Table 15

Reaction duration (hr)	Conversion of hydrogen peroxide (%)	Selectivity for propylene oxide (%)
16.00	99.97	99.75
400.00	99.94	99.74
1010.00	99.90	99.72
1510.00	99.89	98.90

Claims

1. A process of epoxidising an olefin, characterized in that the process comprises epoxidising the olefin with hydrogen peroxide in the presence of a catalyst and a basic anion exchange resin under the olefin epoxidation conditions.

2. The process according to claim 1, wherein the epoxidation is carried out in a fixed bed reactor.

3. The process according to claim 2, wherein the process for carrying out the epoxidation comprises: allowing the olefin and hydrogen peroxide to pass through a fixed bed reactor in a cocurrent flow or in the form of a mixture containing the both, wherein the fixed bed reactor comprises a shell and a catalyst bed packed in the shell, which catalyst bed contains the catalyst and the basic anion exchange resin.

4. The process according to claim 3, wherein the weight ratio of the catalyst to the basic anion exchange resin is 1:0.05-1.5.

5. The process according to claim 3, wherein the weight ratio of the catalyst to the basic anion exchange resin is 1:0.1-1.

6. The process according to claim 2, wherein the process for carrying out the epoxidation comprises: the catalyst bed comprising a plurality of catalyst bed layers, at least a part of the catalyst bed layers comprising the basic anion exchange resin in addition to the catalyst; and along the direction of the olefin and hydrogen peroxide flowing in the reactor, the content by weight percent of the basic anion exchange resin in each catalyst bed layer is less than that in a following catalyst bed.

7. The process according to claim 6, wherein along the direction of the olefin and hydrogen peroxide flowing in the reactor, the content of the basic anion exchange resin in the first catalyst bed layer is 0-30 wt%, while the content of the basic anion exchange resin in the last catalyst bed

layer is 30-100 wt%, based respectively on the total weight of the catalyst and the basic anion exchange resin in each catalyst bed layer.

8. The process according to claim 7, wherein along the direction of the olefin and hydrogen peroxide flowing in the reactor, the difference of the contents of the basic anion exchange resin in adjacent two catalyst bed layers is 5-50 wt%.

9. The process according to claim 8, wherein along the direction of the olefin and hydrogen peroxide flowing in the reactor, the difference of the contents of the basic anion exchange resin in adjacent two catalyst bed layers is 10-30 wt%.

10. The process according to any one of claims 6-9, wherein along the direction of the olefin and hydrogen peroxide flowing in the reactor, the height of each catalyst bed layer is 0.5-95% of the total height of the catalyst bed.

11. The process according to claim 10, wherein along the direction of the olefin and hydrogen peroxide flowing in the reactor, the height of each catalyst bed layer is 2-60% of the total height of the catalyst bed.

12. The process according to any one of claims 6-9, wherein the catalyst bed has 2-20 catalyst bed layers.

13. The process according to claim 1, 3 or 6, wherein the epoxidation is carried out in the presence of a solvent, which solvent is acetonitrile and/or an alcohol having 1-6 carbon atoms.

14. The process according to claim 13, wherein the molar ratio among the solvent, the olefin and hydrogen peroxide is (4-15): (0.5-5):1.

15. The process according to claim 1, 3 or 6, wherein the total exchange capacity of the basic anion exchange resin is 0.5-3mmol/ml.

16. The process according to claim 1, 3 or 6, wherein the catalyst comprises a titanium silicate molecular sieve as the active component.

5 17. The process according to claim 16, wherein the crystal grain of said titanium silicate molecular sieve has a hollow structure, with a radial length of 5-300nm for the cavity portion of the hollow structure, wherein the adsorption capacity of benzene measured for the titanium silicate molecular sieve under the conditions of 25 degrees C, $P/P_0 = 0.10$ and 1 h
10 of adsorption time is at least 70 mg/g, and there is a hysteresis loop between the adsorption isotherm and the desorption isotherm for the nitrogen adsorption by the molecular sieve at a low temperature.

18. The process according to claim 1, 3 or 6, wherein the olefin has
15 2-8 carbon atoms.

19. The process according to claim 18, wherein said olefin is propylene.

20 20. The process according any one of to claims 1, 2, 3 and 6, wherein the conditions for the olefin epoxidation comprise: a temperature of 30-90 degrees C; a pressure of 0.5-4.5MPa; and a liquid volume space velocity of $1-15 \text{ h}^{-1}$.

25 21. The process according to claim 1, 3 or 6, wherein the basic anion exchange resin is a styrene-type basic anion exchange resin and/or acrylic basic anion exchange resin.