

Catalyst for addition reaction of alkylene oxide and use thereof

Technical Field

5 The present invention relates to a catalyst for addition reaction of alkylene oxide and use thereof, in particular to a nanocomposite ion-exchange resin catalyst.

Background technology

10 Alkylene carbonates such as ethylene carbonate and propylene carbonate are excellent solvents and fine chemical intermediates with a wide range of uses. As an excellent high boiling solvent and an organic synthesis intermediate, ethylene carbonate is widely used as solvent in textile, printing, polymer synthesis, and electrochemistry. It can also be used as raw materials of cosmetics and drugs and an intermediate of the corresponding diol. In recent years, ethylene carbonate has been used in
15 the production of lithium battery electrolyte and dimethyl carbonate, and the use of aliphatic polycarbonate and its various copolymers as biodegradable materials has attracted much attention to its industrial production.

20 The traditional production method of ethylene carbonate is the phosgene method. Phosgene has high toxicity and serious pollution, and the process has the disadvantages of long process flow, low yield, high cost, and the like. Using carbon dioxide and ethylene oxide as raw materials to directly prepare ethylene carbonate under the action of the corresponding catalyst is a new way of green environmental protection.
25 The process can directly use carbon dioxide, a greenhouse gas, to alleviate the problem of carbon dioxide emissions.

30 Currently known homogeneous catalyst systems that can be used for addition reaction of carbon dioxide and epoxy compounds include catalytic systems such as quaternary ammonium salts, quaternary phosphonium salts, transition metal complexes, main group element complexes and alkali metal salts, ionic liquids, and supercritical carbon dioxide.

35 He Liangnian et al. (Green Chem., 2003, 5, 92-94) developed a class of phosphonium salt catalysts and synthesized ethylene carbonate with the catalyst of Rf_3RPI ($Rf=R=C_4F_9C_2H_4$; $Rf=R=C_6F_{13}C_2H_4$; $Rf=C_6F_{13}C_2H_4$, $R=Me$; $Rf=C_8F_{17}C_2H_4$, $R=Me$; P is phosphorus, I is iodine) in the

supercritical carbon dioxide. The catalyst contains a relatively long fluorine chain and has relatively good solubility in carbon dioxide, while its solubility in the product is relatively small, which is beneficial to the product separation. The in-situ regeneration of the catalyst in the
5 supercritical state and the recycling use of the catalyst were realized. The yield of ethylene carbonate reached more than 90%, but the reaction period was too long (24 hours were needed).

Kim et al. studied the effect of homogeneous catalytic systems such as zinc halides with 1-alkyl-3-methyl-imidazolium halides and
10 phosphine-containing ligands on the reaction (Angew. Chem. Int. Ed. 39 (2000) 4096-4098, Chem. Eur. J. 9 (2003) 678-686, J. Catal. 232 (2005) 80-84). After the reaction, the homogeneous catalyst needed to be separated from the product, and the separation of the product from the homogeneous catalyst by distillation could severely decompose alkylene
15 carbonates.

The characteristics of the homogeneous catalytic system itself determine that the homogeneous process has disadvantages such as the difficulty in product separation, the large amount of catalyst and the difficult recycling, and the environmental pollution. Compared with
20 homogeneous catalysts, heterogeneous catalysts are beneficial to the subsequent separation of products and catalysts, and the catalysts can be easily regenerated and reused many times. As the support of the heterogeneous catalytic system, molecular sieves, silica gels, ion-exchange resins, polyethylene glycol, poly(4-vinylpyridine), chitosan,
25 and the like are commonly used.

Xiao et al. (Appl. Catal. A 279 (2005) 125-129) reported the supported zinc halide catalyst, and the support was poly(4-vinylpyridine) or chitosan. In this system, 1-butyl-3-methylimidazolium bromide must also be homogeneously used as co-catalyst, and the catalytic activity
30 dropped significantly after being recycled. Van Kruchten et al. reported in CN 101511810A a zinc halide catalyst supported on a solid support, where the support was a quaternary-phosphonium or quaternary-ammonium ion-exchange resin, and the activity of the catalytic system decreased rapidly after being recycled.

Lv Xiaobing et al. studied the continuous process of ethylene carbonate fixed bed with Salen (Co) supported on silica gel MCM-41 as
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catalyst. With the addition of n-butylammonium bromide as co-catalyst, the conversion of ethylene oxide could reach 85.6%.

It can be seen that although the heterogeneous catalytic system has many advantages, however the wear resistance, the swelling resistance, and the activity of the catalyst still need to be further improved. It is very important to develop a catalytic system with high activity and easy separation.

Summary of the Invention

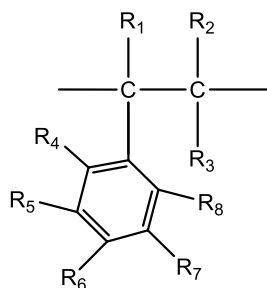
In order to solve the problems existing in the prior art, in the first aspect of the present invention is provided a catalyst for addition reaction of alkylene oxide, the catalyst comprises a nanocomposite ion-exchange resin having a structural formula of $P-Im^+-M^-$, wherein P is a nanocomposite resin matrix, Im^+ is a cation derived from 5-6 membered heterocycle containing at least one nitrogen atom such as imidazolium cation, pyrazolium cation, pyrrolidinium cation, piperidinium cation, piperazinium cation, pyrimidinium cation, pyrazinium cation, pyridazinium cation, triazinium cation (for example a cation derived from 5-6 membered heteroarene containing at least one nitrogen atom, such as imidazolium cation, pyrazolium cation, pyrimidinium cation, pyrazinium cation, pyridazinium cation, triazinium cation), and M^- is an anion. The catalyst of the present invention can be used in the addition reaction of alkylene oxide and carbon dioxide. The catalyst has high wear resistance, high swelling resistance, and high activity. The products after the reaction are easy to separate, and the catalyst can be used continuously many times.

In the second aspect of the present invention is provided a method for an addition reaction of alkylene oxide and carbon dioxide.

According to the first aspect of the present invention, the catalyst comprises a nanocomposite ion-exchange resin having a structural formula of $P-Im^+-M^-$, wherein P is a nanocomposite resin matrix, Im^+ is a cation derived from 5-6 membered heterocycle containing at least one nitrogen atom such as imidazolium cation, pyrazolium cation, pyrrolidinium cation, piperidinium cation, piperazinium cation, pyrimidinium cation, pyrazinium cation, pyridazinium cation, triazinium cation (for example a cation derived from 5-6 membered heteroarene containing at least one nitrogen atom, such as imidazolium cation,

pyrazolium cation, pyrimidinium cation, pyrazinium cation, pyridazinium cation, triazinium cation), M^- is an anion.

According to some embodiments of the present invention, the nanocomposite resin matrix comprises a structure fragment represented by formula I and a structure fragment of $-CH(POSS)-CH_2-$,

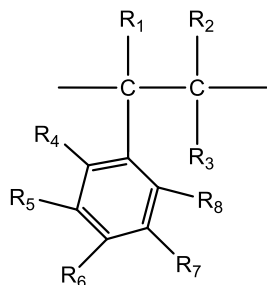


Formula I

In formula I, R_1 - R_8 are identical to or different from each other, and each independently selected from hydrogen and C_1 - C_6 alkyl, preferably selected from hydrogen, methyl, ethyl, propyl, and butyl;

POSS is a polyhedral oligomeric silsesquioxane, which has a general formula of $(-SiO_{1.5})_m$, and m is 6, 8, 10, or 12.

According to some embodiments of the present invention, the catalyst comprises the following structure:



Wherein R_1 - R_3 are identical to or different from each other, and each independently selected from hydrogen and C_1 - C_6 alkyl;

R_4 - R_8 are each independently selected from hydrogen, C_1 - C_6 alkyl, and $CH_2Im^+-M^-$, and at least one of R_4 - R_8 is $CH_2Im^+-M^-$, preferably, R_4 - R_8 are each independently selected from hydrogen and $CH_2Im^+-M^-$, and at least one of R_4 - R_8 is $CH_2Im^+-M^-$.

According to some embodiments of the present invention, the catalyst comprises a structure fragment of $-CH-(Ph-CH_2-Im^+-M^-)-CH_2-$.

According to some embodiments of the present invention, said M^- is one or more of halide ions and organic acid radical ions.

According to some embodiments of the present invention, said M^- is one or more of a fluoride ion, a chloride ion, a bromide ion, an iodide ion,

an acetate group, a formate group, and a bioxalate group.

According to some embodiments of the present invention, the mass content of POSS in the nanocomposite resin matrix P is 0.1-10%, for example 0.1%, 0.2%, 0.5%, 1.0%, 1.2%, 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, 4.0%, 4.3%, 4.5%, 5.0%, 5.5%, 6.0%, 7.0%, 8.0%, 9.1%, 9.5%, 10% and an arbitrary value in between.

According to some embodiments of the present invention, the mass content of POSS in the nanocomposite resin matrix P is 0.2-5%.

According to some embodiments of the present invention, the mass content of POSS in the nanocomposite resin matrix P is 2-5%.

In the present invention, the structural formula $P-Im^+-M^-$ represents a nanocomposite resin matrix P modified with Im^+ and M^- .

According to some embodiments of the present invention, in the infrared spectrum of the nanocomposite resin matrix P, the characteristic absorption peak at 1111 cm^{-1} is attributed to the stretching vibration absorption peak of the Si-O-Si skeleton in the silsesquioxane.

According to some embodiments of the present invention, a process for preparing the catalyst comprises the following steps:

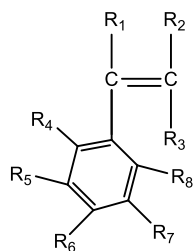
S1: polymerizing a styrene-based monomer, a cross-linking agent, and a polyhedral oligomeric silsesquioxane in the presence of an initiator to obtain a nanocomposite resin matrix P;

S2: subjecting the nanocomposite resin matrix P obtained in step S1 to a chloromethylation reaction, an imidazolation reaction, and an ion-exchange reaction.

According to some embodiments of the present invention, the nanocomposite resin matrix P is a nanocomposite copolymer obtained by in-situ copolymerization of a styrene-based monomer, a cross-linking agent, and a nano-material.

According to some embodiments of the present invention, said nano-material is at least one of a vinyl-containing silsesquioxane, a hydrogen-containing polysilsesquioxane, an alkoxy-containing polysilsesquioxane, and an epoxy-containing polysilsesquioxane.

According to some embodiments of the present invention, said styrene-based monomer is one or more of styrene-based monomers represented by formula II;



Formula II

In formula II, R₁-R₈ are identical to or different from each other, and each independently selected from hydrogen and C₁-C₆ alkyl, preferably selected from hydrogen, methyl, ethyl, propyl, and butyl.

According to some embodiments of the present invention, said styrene-based monomer is at least one of styrene, α-methylstyrene, or 4-butylstyrene, preferably styrene.

According to some embodiments of the present invention, said polyhedral oligomeric silsesquioxane is one or more of a vinyl-containing silsesquioxane, a hydrogen-containing polysilsesquioxane, an alkoxy-containing polysilsesquioxane, and an epoxy-containing polysilsesquioxane.

According to some embodiments of the present invention, said vinyl-containing silsesquioxane is octavinylsilsesquioxane.

According to some embodiments of the present invention, said cross-linking agent is one or more of ethylene glycol bismethacrylate, dipropenylbenzene, divinylphenylmethane, and divinylbenzene.

According to some embodiments of the present invention, said initiator is at least one of benzoyl peroxide, azodiisobutyronitrile, azodiisooheptylonitrile, lauroyl peroxide, and cumene hydroperoxide.

According to some embodiments of the present invention, in step S1, based on the total weight of the raw materials, the mass content of the styrene-based monomer is 85-95%.

According to some embodiments of the present invention, in step S1, based on the total weight of the raw materials, the mass content of said cross-linking agent is 1-6%.

According to some embodiments of the present invention, in step S1, based on the total weight of the raw materials, the mass content of said polyhedral oligomeric silsesquioxane is 0.1-10%, for example 0.1%, 0.2%, 0.5%, 1.0%, 1.2%, 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, 4.0%, 4.3%, 4.5%, 5.0%, 5.5%, 6.0%, 7.0%, 8.0%, 9.1%, 9.5%, 10% and an arbitrary value in between.

According to some embodiments of the present invention, in step S1, based on the total weight of the raw materials, the mass content of said polyhedral oligomeric silsesquioxane is 0.2-5%.

5 According to some embodiments of the present invention, in step S1, based on the total weight of the raw materials, the mass content of said polyhedral oligomeric silsesquioxane is 2-5%.

According to some embodiments of the present invention, in step S1, based on the total weight of the raw materials, the mass content of said initiator is 0.1-5%.

10 According to some embodiments of the present invention, based on the parts by weight, the used amount of the styrene-based monomer is 85-95 parts, the used amount of the cross-linking agent is 2-5 parts, the used amount of the nano-material is 0.1-10 parts, and the used amount of the initiator is 0.1-5 parts.

15 In some preferred embodiments of the present invention, the process for preparing the catalyst comprises the following steps:

a) An auxiliary agent is formulated into an aqueous solution A having a concentration of 0.5-3% by weight, and a styrene-based monomer, a cross-linking agent, a nanomaterial, and an initiator are formulated into a solution B; wherein, said auxiliary agent is at least one of polyvinyl alcohol, gelatin, starch, methylcellulose, bentonite and calcium carbonate; said styrene-based monomer is at least one of styrene, α -methylstyrene and 4-butylstyrene; said cross-linking agent is at least one of ethylene glycol bismethacrylate, dipropenylbenzene, divinylphenylmethane, and divinylbenzene; said nano-material is at least one of a vinyl-containing silsesquioxane, a hydrogen-containing polysilsesquioxane, an alkoxy-containing polysilsesquioxane and an epoxy-containing polysilsesquioxane; said initiator is at least one of benzoyl peroxide, azodiisobutyronitrile, azodiisooheptylonitrile, lauroyl peroxide, and cumene hydroperoxide; based on the parts by weight, the used amount of the styrene-based monomer is 85-95 parts, the used amount of the cross-linking agent is 2-5 parts, the used amount of the nano-material is 0.1-10 parts, the used amount of the initiator is 0.1-5 parts; the used amount of the auxiliary agent is 150-400% of the used amount of the monomer;

b) The solution B and the solution A are combined, stirred at normal

temperature for 1-3 hours, and mixed well; then polymerized at 60-75°C for 0.5-5 hours, gradually warmed up to 70-90°C and reacted for 5-15 hours, then warmed up to 90-100°C and reacted for 5-15 hours; after the completion of the reaction, the reaction mixture is extracted, washed, filtered, dried and sieved to obtain composite microspheres with a particle size ranging from 0.35 to 0.60 mm;

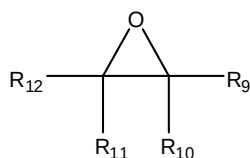
c) To the composite microspheres are added a chloromethylation reagent equivalent to 200-500% of the weight of composite microspheres and a zinc chloride catalyst equivalent to 20-70% of the weight of composite microspheres, reacted at 30-60°C for 8-30 hours, filtered and washed to obtain chloromethylated composite spheres; said chloromethylation reagent is at least one of chloromethyl ether, chloromethyl ethyl ether, and 1,4-dichloromethoxybutane;

d) the chloromethylated composite spheres and an N-alkylimidazole in a mixture are reacted at 60-90°C for 10-48 hours, and after the completion of the reaction, filtered and washed to obtain imidazolated composite microspheres; in the mixture, the chloromethylated composite spheres, the N-alkylimidazole (e.g. N-methylimidazole) and a solvent (e.g. acetonitrile or N,N-dimethylformamide) can be 1:(1-5):(10-50);

f) the imidazolated composite microspheres are washed with a salt solution, after the completion of the washing, washed with deionized water to pH = 7 to obtain the ion-exchange resin, wherein the molar ratio of the imidazolated composite microspheres to the salt solution is (1:1)-(1:10); the concentration of the salt solution is 0.1-1mol/L; the salt solution is a salt solution containing at least one of a fluoride ion, a chloride ion, a bromide ion, an iodide ion, an acetate group, a formate group, and a bioxalate group.

According to the second aspect of the present invention, a method for an addition reaction of alkylene oxide and carbon dioxide comprises reacting alkylene oxide and carbon dioxide in the presence of the above catalyst.

According to some embodiments of the present invention, the alkylene oxide has a general formula of



Wherein, R₉-R₁₂ are identical to or different from each other and each independently selected from hydrogen, C₁-C₆ alkyl, and C₆-C₁₀ aryl, preferably selected from hydrogen, methyl, ethyl, propyl, butyl, and phenyl.

5 According to some embodiments of the present invention, said alkylene oxide is selected from ethylene oxide, propylene oxide, and styrene oxide.

According to some embodiments of the present invention, the mass ratio of the catalyst to the alkylene oxide is (0.001-1):1, preferably
10 (0.1-0.3):1.

According to some embodiments of the present invention, the reaction temperature is 60-180°C, for example, 60°C, 70°C, 80°C, 90°C, 100°C, 110°C, 120°C, 130°C, 140°C, 150°C, 160°C, 170°C, 180°C, and an arbitrary value in between.

15 According to some embodiments of the present invention, the reaction temperature is 100°C-160°C.

According to some embodiments of the present invention, the reaction pressure is 0.1-10.0MPa, for example, 0.1MPa, 0.5MPa, 1MPa, 2MPa, 3MPa, 4MPa, 5MPa, 6MPa, 7MPa, 8MPa, 9MPa, 10MPa, and an
20 arbitrary value in between.

According to some embodiments of the present invention, said reaction pressure is 2-5MPa.

According to some embodiments of the present invention, said reaction time is 1-8 hours, preferably 3-6 hours.

25 The nanocomposite ion-exchange resin catalyst of the present invention can be used in the addition reaction of alkylene oxide and carbon dioxide. The catalyst has high wear resistance, high swelling resistance, and high activity, the products after the reaction are easy to separate, and the catalyst can be used continuously many times.

30 **Brief description of the drawings**

Figure 1: Infrared spectrum of the ion-exchange resin of Example 1.

Detailed description

The present invention will be further described below through examples, but it should be pointed out that the protection scope of the
35 present invention is not limited thereto, but is determined by the appended claims.

It should be particularly noted that two or more aspects (or embodiments) disclosed in the context of this specification can be combined with each other arbitrarily, and the technical solutions formed thereby belong to a part of the original disclosure of this specification, and also falls within the protection scope of the present invention.

Raw materials:

Styrene: analytically pure, purchased from Sinopharm, used after removing a polymerization inhibitor;

Divinylbenzene: analytically pure, purchased from Sinopharm, used after removing a polymerization inhibitor;

Octavinylsilsesquioxane: analytically pure, purchased from Sinopharm, used directly;

Benzoyl peroxide: analytically pure, purchased from Sinopharm, used after recrystallization;

Polyvinyl alcohol\gelatin: analytically pure, purchased from Sinopharm, used directly;

Chloromethyl ether\chloromethyl ethyl ether
1,4-dichloromethoxybutane: analytically pure, purchased from Sinopharm, used directly;

1-methylimidazole\1-butyylimidazole\imidazole: analytically pure, purchased from Sinopharm, used directly;

Acetonitrile: analytically pure, purchased from Sinopharm, used directly;

Other unmentioned reagents used in the examples are commercially available, and were analytically pure, purchased from Sinopharm, and used directly.

[Example 1] Preparation of Ion-exchange Resin

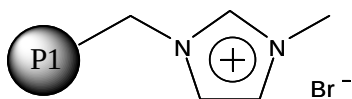
To a 500mL three-necked flask were added 65.0 g of styrene, 1.0 g of divinylbenzene, 3.0 g of octavinylsilsesquioxane, and 1.0 g of benzoyl peroxide, a stirrer was started, and the mixture was stirred for 0.5 hours; a mixed solution of 200 mL of deionized water and 4 g of polyvinyl alcohol was added, the mixture was stirred for 2 hours. Then, the mixture was gradually warmed up to 75°C and reacted for 5 hours, then warmed up to 90°C and reacted for 10 hours, and finally warmed up to 100°C and reacted for 10 hours. After the completion of the reaction, the supernatant liquid was poured out, washed with hot water at 85°C, then washed with

cold water, then filtered, put into an oven and dried at 80°C, sieved to collect composite microspheres A1 with a particle size in the range of 0.35-0.60 mm.

Chloromethylation of composite microspheres: To a 500mL three-necked flask were added 40g of composite microspheres A1 and 250mL of chloromethyl ether; after standing for 3 hours at room temperature, the stirring was started; 10g of zinc chloride was added as the catalyst; the mixture was warmed up to 60°C and reacted for 10 hours, and then cooled to room temperature after the completion of the chloromethylation; the chlorination mother liquor was filtered out, washed with methanol repeatedly, and dried at 100°C for 8 hours to obtain chloromethylated composite spheres A1.

Imidazolation: To a 500mL three-necked flask were added 30 g of chloromethylated composite spheres A1 (having a chlorine content of 3.4mmol Cl/g), 1-methylimidazole (102.0mmol), and 200mL of acetonitrile; the mixture was reacted at 60°C for 24 hours, cooled to room temperature, filtered, washed with ethyl acetate, 0.1 mol/L HCl, deionized water, and methanol successively, and then dried under vacuum at 60°C for 12 hours to obtain imidazolated composite microspheres A1.

Ion-exchange: To a 1000mL three-necked flask were added 30 g of imidazolated composite microspheres A1, and 500mL of a solution of NaBr in deionized water having a concentration of 0.1mol/L; the mixture was stirred at room temperature to perform an ion-exchange reaction for 24 hours, then washed with deionized water until the pH of the washing liquor was 7, and dried under vacuum to obtain an ion-exchange resin catalyst, which was denoted as Cat-A1, and had the following structural formula:



[Example 2] Preparation of Ion-exchange Resin

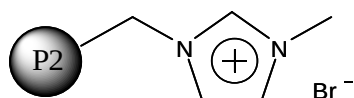
To a 500mL three-necked flask was added a monomer mixture solution containing an initiator (60.0 g of styrene, 1.0 g of divinylbenzene, 1.6 g of octavinylsilsesquioxane, and 1.0 g of benzoyl peroxide, this solution was firstly reacted under stirring at 70°C for 0.5 hours), a stirrer was started, a mixed solution of 200 mL of deionized water and 4 g of polyvinyl alcohol was added, the mixture was warmed up to 85°C and

reacted for 3 hours, then warmed up to 90°C and reacted for 9 hours, and finally warmed up to 100°C and reacted for 10 hours. After the completion of the reaction, the supernatant liquid was poured out, washed with hot water at 85°C, then washed with cold water, then filtered, put into an oven and dried at 80°C, sieved to collect composite microspheres B1 with a particle size in the range of 0.35-0.60 mm.

Chloromethylation of composite microspheres: To a 500mL three-necked flask were added 50g of composite microspheres B1 and 200mL of chloromethyl ethyl ether; after standing for 6 hours at room temperature, 30g of zinc chloride was added as the catalyst and the stirring was started; the mixture was warmed up to 50°C and reacted for 30 hours, and then cooled to room temperature after the completion of the chloromethylation; the chlorination mother liquor was filtered out, washed with methanol repeatedly, and dried at 100°C for 8 hours to obtain chloromethylated composite spheres B1.

Imidazolation: To a 500mL three-necked flask were added 50 g of chloromethylated composite spheres B1 (having a chlorine content of 4.6mmol Cl/g), 1-methylimidazole (230.0mmol), and 300mL of acetonitrile; the mixture was reacted at 80°C for 16 hours, cooled to room temperature, filtered, washed with ethyl acetate, 0.1 mol/L HCl, deionized water, and methanol successively, and then dried under vacuum at 60°C for 12 hours to obtain imidazolated composite microspheres B1.

Ion-exchange: To a 1000mL three-necked flask were added 40 g of imidazolated composite microspheres B1, and 400mL of a solution of NaBr in deionized water having a concentration of 0.1mol/L; the mixture was stirred at room temperature to perform an ion-exchange reaction for 12 hours, then washed with deionized water until the pH of the washing liquor was 7, and dried under vacuum to obtain an ion-exchange resin catalyst, which was denoted as Cat-B1, and had the following structural formula:



[Example 3] Preparation of Ion-exchange Resin

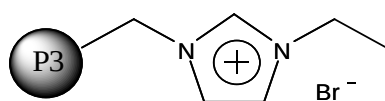
To a 500mL three-necked flask was added a monomer mixture solution containing an initiator (42.5 g of styrene, 2.5 g of divinylbenzene, 0.1 g of octavinylsilsesquioxane, and 2.0 g of benzoyl peroxide, this

solution was firstly reacted under stirring at 70°C for 1.5 hours), a mixed solution of 200 mL of deionized water and 4 g of polyvinyl alcohol was added, the mixture was warmed up to 85°C and reacted for 3 hours, then warmed up to 90°C and reacted for 9 hours, and finally warmed up to 100°C and reacted for 10 hours. After the completion of the reaction, the supernatant liquid was poured out, washed with hot water at 85°C, then washed with cold water, then filtered, put into an oven and dried at 80°C, sieved to collect composite microspheres C1 with a particle size in the range of 0.35-0.60 mm.

Chloromethylation of composite microspheres: To a 250mL three-necked flask were added 20g of composite microspheres C1 and 100mL of 1,4-dichloromethoxybutane; after standing for 6 hours at room temperature, 8g of zinc chloride was added as the catalyst and the stirring was started; the mixture was warmed up to 30°C and reacted for 12 hours, and then cooled to room temperature after the completion of the chloromethylation; the chlorination mother liquor was filtered out, washed with methanol repeatedly, and dried at 100°C for 8 hours to obtain chloromethylated composite spheres C1.

Imidazolization: To a 250mL three-necked flask were added 20 g of chloromethylated composite spheres C1 (having a chlorine content of 1.5mmol Cl/g), 1-ethylimidazole (30.0mmol), and 150mL of acetonitrile; the mixture was reacted at 90°C for 16 hours, cooled to room temperature, filtered, washed with ethyl acetate, 0.1 mol/L HCl, deionized water, and methanol successively, and then dried under vacuum at 60°C for 12 hours to obtain imidazolated composite microspheres C1.

Ion-exchange: To a 500mL three-necked flask were added 20 g of imidazolated composite microspheres C1, and 300mL of a solution of NaBr in deionized water having a concentration of 0.5mol/L; the mixture was stirred at room temperature to perform an ion-exchange reaction for 12 hours, then washed with deionized water until the pH of the washing liquor was 7, and dried under vacuum to obtain an ion-exchange resin catalyst, which was denoted as Cat-C1, and had the following structural formula:



[Example 4] Preparation of Ion-exchange Resin

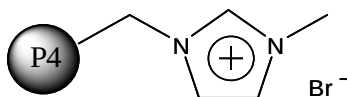
To a 500mL three-necked flask were added 47.0 g of styrene, 2.3 g of divinylbenzene, and 1.6 g of benzoyl peroxide (as an initiator); the mixture was reacted under stirring at 60°C for 2.0 hours; then 0.6 g of octavinylsilsesquioxane was added, the stirring was continued for 1 hour to perform the pre-polymerization. 260 mL of a solution of 2.0 g of gelatin dissolved in deionized water was added. The stirring speed was adjusted, while the mixture was gradually warmed up to 80°C and reacted for 5 hours; then warmed up to 90°C and reacted for 5 hours, and finally warmed up to 98°C and reacted for 6 hours. After the completion of the reaction, the supernatant liquid was poured out, washed with hot water at 85°C, then washed with cold water, then filtered, put into an oven and dried at 80°C, sieved to collect composite microspheres A2 with a particle size in the range of 0.35-0.60 mm.

Chloromethylation of composite microspheres: To a 500mL three-necked flask were added 40g of composite microspheres A2 and 250mL of chloromethyl ether; after standing for 3 hours at room temperature, the stirring was started; 10g of zinc chloride was added as the catalyst; the mixture was warmed up to 60°C and reacted for 10 hours, and then cooled to room temperature after the completion of the chloromethylation; the chlorination mother liquor was filtered out, washed with methanol repeatedly, and dried at 100°C for 8 hours to obtain chloromethylated composite spheres A2.

Imidazolation: To a 500mL three-necked flask were added 30 g of chloromethylated composite spheres A2 (having a chlorine content of 3.6mmol Cl/g), 1-methylimidazole (108.0mmol), and 200mL of acetonitrile; the mixture was reacted at 60°C for 24 hours, cooled to room temperature, filtered, washed with ethyl acetate, 0.1 mol/L HCl, deionized water, and methanol successively, and then dried under vacuum at 60°C for 12 hours to obtain imidazolated composite microspheres A2.

Ion-exchange: To a 1000mL three-necked flask were added 30 g of imidazolated composite microspheres A2, and 500mL of a solution of NaBr in deionized water having a concentration of 0.1mol/L; the mixture was stirred at room temperature to perform an ion-exchange reaction for 24 hours, then washed with deionized water until the pH of the washing liquor was 7, and dried under vacuum to obtain an ion-exchange resin catalyst, which was denoted as Cat-A2, and had the following structural

formula:



[Example 5] Preparation of Ion-exchange Resin

To a 500mL three-necked flask was added a monomer mixture solution containing an initiator (60.0 g of styrene, 1.0 g of divinylbenzene, 1.6 g of octavinylsilsesquioxane, and 1.0 g of benzoyl peroxide, this solution was firstly reacted under stirring at 70°C for 0.5 hours), a stirrer was started, a mixed solution of 200 mL of deionized water and 4 g of polyvinyl alcohol was added, the mixture was warmed up to 85°C and reacted for 3 hours, then warmed up to 90°C and reacted for 9 hours, and finally warmed up to 100°C and reacted for 10 hours. After the completion of the reaction, the supernatant liquid was poured out, washed with hot water at 85°C, then washed with cold water, then filtered, put into an oven and dried at 80°C, sieved to collect composite microspheres B2 with a particle size in the range of 0.35-0.60 mm.

Chloromethylation of composite microspheres: To a 500mL three-necked flask were added 50g of composite microspheres B2 and 200mL of chloromethyl ethyl ether; after standing for 6 hours at room temperature, 30g of zinc chloride was added as the catalyst and the stirring was started; the mixture was warmed up to 50°C and reacted for 30 hours, and then cooled to room temperature after the completion of the chloromethylation; the chlorination mother liquor was filtered out, washed with methanol repeatedly, and dried at 100°C for 8 hours to obtain chloromethylated composite spheres B2.

Imidazolation: To a 500mL three-necked flask were added 50 g of chloromethylated composite spheres B2 (having a chlorine content of 4.7mmol Cl/g), 1-butyylimidazole (235.0mmol), and 300mL of acetonitrile; the mixture was reacted at 80°C for 16 hours, cooled to room temperature, filtered, washed with ethyl acetate, 0.1 mol/L HCl, deionized water, and methanol successively, and then dried under vacuum at 60°C for 12 hours to obtain imidazolated composite microspheres B2.

Ion-exchange: To a 1000mL three-necked flask were added 40 g of imidazolated composite microspheres B2, and 400mL of a solution of NaBr in deionized water having a concentration of 0.1mol/L; the mixture was stirred at room temperature to perform an ion-exchange reaction for

12 hours, then washed with deionized water until the pH of the washing liquor was 7, and dried under vacuum to obtain an ion-exchange resin catalyst, which was denoted as Cat-B2, and had the following structural formula:



[Example 6] Preparation of Ion-exchange Resin

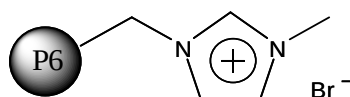
To a 500mL three-necked flask was added a monomer mixture solution containing an initiator (42.5 g of styrene, 2.5 g of divinylbenzene, 0.1 g of octavinylsilsesquioxane and 2.0 g of benzoyl peroxide, this solution was firstly reacted under stirring at 70°C for 1.5 hours), a mixed solution of 200 mL of deionized water and 4 g of polyvinyl alcohol was added, the mixture was warmed up to 85°C and reacted for 3 hours, then warmed up to 90°C and reacted for 9 hours, and finally warmed up to 100°C and reacted for 10 hours. After the completion of the reaction, the supernatant liquid was poured out, washed with hot water at 85°C, then washed with cold water, then filtered, put into an oven and dried at 80°C, sieved to collect composite microspheres C2 with a particle size in the range of 0.35-0.60 mm.

Chloromethylation of composite microspheres: To a 250mL three-necked flask were added 20g of composite microspheres C2 and 100mL of 1,4-dichloromethoxybutane; after standing for 6 hours at room temperature, 8g of zinc chloride was added as the catalyst and the stirring was started; the mixture was warmed up to 30°C and reacted for 12 hours, and then cooled to room temperature after the completion of the chloromethylation; the chlorination mother liquor was filtered out, washed with methanol repeatedly, and dried at 100°C for 8 hours to obtain chloromethylated composite spheres C2.

Imidazolation: To a 250mL three-necked flask were added 20 g of chloromethylated composite spheres C2 (having a chlorine content of 1.6mmol Cl/g), 1-methylimidazole (32.0mmol), and 150mL of acetonitrile; the mixture was reacted at 90°C for 16 hours, cooled to room temperature, filtered, washed with ethyl acetate, 0.1 mol/L HCl, deionized water, and methanol successively, and then dried under vacuum at 60°C for 12 hours to obtain imidazolated composite microspheres C2.

Ion-exchange: To a 500mL three-necked flask were added 20 g of

imidazolated composite microspheres C2, and 300mL of a solution of NaBr in deionized water having a concentration of 0.5mol/L; the mixture was stirred at room temperature to perform an ion-exchange reaction for 12 hours, then washed with deionized water until the pH of the washing liquor was 7, and dried under vacuum to obtain an ion-exchange resin catalyst, which was denoted as Cat-C2, and had the following structural formula:



[Example 7] Preparation of Ion-exchange Resin

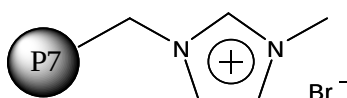
To a 500mL three-necked flask were added 65.0 g of styrene, 1.0 g of divinylbenzene, 0.07 g of octavinylsilsesquioxane and 1.0 g of benzoyl peroxide, a stirrer was started, and the mixture was stirred for 0.5 hours; a mixed solution of 200 mL of deionized water and 4 g of polyvinyl alcohol was added, the mixture was stirred for 2 hours. Then, the mixture was gradually warmed up to 75°C and reacted for 5 hours, then warmed up to 90°C and reacted for 10 hours, and finally warmed up to 100°C and reacted for 10 hours. After the completion of the reaction, the supernatant liquid was poured out, washed with hot water at 85°C, then washed with cold water, then filtered, put into an oven and dried at 80°C, sieved to collect composite microspheres A3 with a particle size in the range of 0.35-0.60 mm.

Chloromethylation of composite microspheres: To a 500mL three-necked flask were added 40g of composite microspheres A3 and 250mL of chloromethyl ether; after standing for 3 hours at room temperature, the stirring was started; 10g of zinc chloride was added as the catalyst; the mixture was warmed up to 60°C and reacted for 10 hours, and then cooled to room temperature after the completion of the chloromethylation; the chlorination mother liquor was filtered out, washed with methanol repeatedly, and dried at 100°C for 8 hours to obtain chloromethylated composite spheres A3.

Imidazolation: To a 500mL three-necked flask were added 30 g of chloromethylated composite spheres A3 (having a chlorine content of 3.4mmol Cl/g), 1-methylimidazole (102.0mmol), and 200mL of acetonitrile; the mixture was reacted at 60°C for 24 hours, cooled to room temperature, filtered, washed with ethyl acetate, 0.1 mol/L HCl, deionized

water, and methanol successively, and then dried under vacuum at 60°C for 12 hours to obtain imidazolated composite microspheres A3.

Ion-exchange: To a 1000mL three-necked flask were added 30 g of imidazolated composite microspheres A3, and 500mL of a solution of NaBr in deionized water having a concentration of 0.1mol/L; the mixture was stirred at room temperature to perform an ion-exchange reaction for 24 hours, then washed with deionized water until the pH of the washing liquor was 7, and dried under vacuum to obtain an ion-exchange resin catalyst, which was denoted as Cat-A3, and had the following structural formula:



[Example 8] Preparation of Ion-exchange Resin

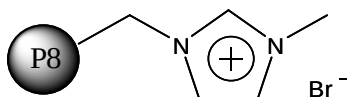
To a 500mL three-necked flask were added 65.0 g of styrene, 1.0 g of divinylbenzene, 7.5 g of octavinylsilsesquioxane and 1.0 g of benzoyl peroxide, a stirrer was started, and the mixture was stirred for 0.5 hours; a mixed solution of 200 mL of deionized water and 4 g of polyvinyl alcohol was added, the mixture was stirred for 2 hours. Then, the mixture was gradually warmed up to 75°C and reacted for 5 hours, then warmed up to 90°C and reacted for 10 hours, and finally warmed up to 100°C and reacted for 10 hours. After the completion of the reaction, the supernatant liquid was poured out, washed with hot water at 85°C, then washed with cold water, then filtered, put into an oven and dried at 80°C, sieved to collect composite microspheres A5 with a particle size in the range of 0.35-0.60 mm.

Chloromethylation of composite microspheres: To a 500mL three-necked flask were added 40g of composite microspheres A4 and 250mL of chloromethyl ether; after standing for 3 hours at room temperature, the stirring was started; 10g of zinc chloride was added as the catalyst; the mixture was warmed up to 60°C and reacted for 10 hours, and then cooled to room temperature after the completion of the chloromethylation; the chlorination mother liquor was filtered out, washed with methanol repeatedly, and dried at 100°C for 8 hours to obtain chloromethylated composite spheres A4.

Imidazolation: To a 500mL three-necked flask were added 30 g of chloromethylated composite spheres A4 (having a chlorine content of

3.4mmol Cl/g), 1-methylimidazole (102.0mmol), and 200mL of acetonitrile; the mixture was reacted at 60°C for 24 hours, cooled to room temperature, filtered, washed with ethyl acetate, 0.1 mol/L HCl, deionized water, and methanol successively, and then dried under vacuum at 60°C for 12 hours to obtain imidazolated composite microspheres A4.

Ion-exchange: To a 1000mL three-necked flask were added 30 g of imidazolated composite microspheres A4, and 500mL of a solution of NaBr in deionized water having a concentration of 0.1mol/L; the mixture was stirred at room temperature to perform an ion-exchange reaction for 24 hours, then washed with deionized water until the pH of the washing liquor was 7, and dried under vacuum to obtain an ion-exchange resin catalyst, which was denoted as Cat-A4, and had the following structural formula:



[Example 9] Preparation of Ion-exchange Resin

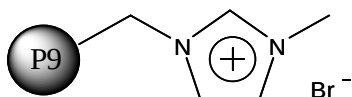
To a 500mL three-necked flask were added 65.0 g of styrene, 1.0 g of divinylbenzene, 11.8 g of octavinylsilsesquioxane, and 1.0 g of benzoyl peroxide, a stirrer was started, and the mixture was stirred for 0.5 hours; a mixed solution of 200 mL of deionized water and 4 g of polyvinyl alcohol was added, the mixture was stirred for 2 hours. Then, the mixture was gradually warmed up to 75°C and reacted for 5 hours, then warmed up to 90°C and reacted for 10 hours, and finally warmed up to 100°C and reacted for 10 hours. After the completion of the reaction, the supernatant liquid was poured out, washed with hot water at 85°C, then washed with cold water, then filtered, put into an oven and dried at 80°C, sieved to collect composite microspheres A5 with a particle size in the range of 0.35-0.60 mm.

Chloromethylation of composite microspheres: To a 500mL three-necked flask were added 40g of composite microspheres A5 and 250mL of chloromethyl ether; after standing for 3 hours at room temperature, the stirring was started; 10g of zinc chloride was added as the catalyst; the mixture was warmed up to 60°C and reacted for 10 hours, and then cooled to room temperature after the completion of the chloromethylation; the chlorination mother liquor was filtered out, washed with methanol repeatedly, and dried at 100°C for 8 hours to obtain

chloromethylated composite spheres A5.

Imidazolation: To a 500mL three-necked flask were added 30 g of chloromethylated composite spheres A5 (having a chlorine content of 3.4mmol Cl/g), 1-methylimidazole (102.0mmol), and 200mL of acetonitrile; the mixture was reacted at 60°C for 24 hours, cooled to room temperature, filtered, washed with ethyl acetate, 0.1 mol/L HCl, deionized water, and methanol successively, and then dried under vacuum at 60°C for 12 hours to obtain imidazolated composite microspheres A5.

Ion-exchange: To a 1000mL three-necked flask were added 30 g of imidazolated composite microspheres A5, and 500mL of a solution of NaBr in deionized water having a concentration of 0.1mol/L; the mixture was stirred at room temperature to perform an ion-exchange reaction for 24 hours, then washed with deionized water until the pH of the washing liquor was 7, and dried under vacuum to obtain an ion-exchange resin catalyst, which was denoted as Cat-A5, and had the following structural formula:



[Comparative Example 10] Preparation of Ion-exchange Resin

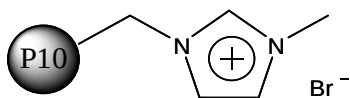
To a 500mL three-necked flask were added 65.0 g of styrene, 1.0 g of divinylbenzene, and 1.0 g of benzoyl peroxide, a stirrer was started, and the mixture was stirred for 0.5 hours; a mixed solution of 200 mL of deionized water and 4 g of polyvinyl alcohol was added, the mixture was stirred for 2 hours. Then, the mixture was gradually warmed up to 75°C and reacted for 5 hours, then warmed up to 90°C and reacted for 10 hours, and finally warmed up to 100°C and reacted for 10 hours. After the completion of the reaction, the supernatant liquid was poured out, washed with hot water at 85°C, then washed with cold water, then filtered, put into an oven and dried at 80°C, sieved to collect microspheres A6 with a particle size in the range of 0.35-0.60 mm.

Chloromethylation of microspheres: To a 500mL three-necked flask were added 40g of microspheres A6 and 250mL of chloromethyl ether; after standing for 3 hours at room temperature, the stirring was started; 10g of zinc chloride was added as the catalyst; the mixture was warmed up to 60° C and reacted for 10 hours, and then cooled to room temperature after the completion of the chloromethylation; the chlorination mother

liquor was filtered out, washed with methanol repeatedly, and dried at 100°C for 8 hours to obtain chloromethylated spheres A6.

Imidazolation: To a 500mL three-necked flask were added 30 g of chloromethylated spheres A6 (having a chlorine content of 3.4mmol Cl/g), 1-methylimidazole (102.0mmol), and 200mL of acetonitrile; the mixture was reacted at 60°C for 24 hours, cooled to room temperature, filtered, washed with ethyl acetate, 0.1 mol/L HCl, deionized water, and methanol successively, and then dried under vacuum at 60°C for 12 hours to obtain imidazolated microspheres A6.

Ion-exchange: To a 1000mL three-necked flask were added 30 g of imidazolated microspheres A6, and 500mL of a solution of NaBr in deionized water having a concentration of 0.1mol/L; the mixture was stirred at room temperature to perform an ion-exchange reaction for 24 hours, then washed with deionized water until the pH of the washing liquor was 7, and dried under vacuum to obtain an ion-exchange resin catalyst, which was denoted as Cat-A6, and had the following structural formula:



[Comparative Example 11] Preparation of Ion-exchange Resin

To a 500mL three-necked flask were added 65.0 g of styrene, 1.0 g of divinylbenzene, and 1.0 g of benzoyl peroxide, a stirrer was started, and the mixture was stirred for 0.5 hours; a mixed solution of 200 mL of deionized water and 4 g of polyvinyl alcohol was added, the mixture was stirred for 2 hours. Then, the mixture was gradually warmed up to 75°C and reacted for 5 hours, then warmed up to 90°C and reacted for 10 hours, and finally warmed up to 100°C and reacted for 10 hours. After the completion of the reaction, the supernatant liquid was poured out, washed with hot water at 85°C, then washed with cold water, then filtered, put into an oven and dried at 80°C, sieved to collect microspheres A7 with a particle size in the range of 0.35-0.60 mm.

Chloromethylation of microspheres: To a 500mL three-necked flask were added 40g of microspheres A7 and 250mL of chloromethyl ether; after standing for 3 hours at room temperature, the stirring was started; 10g of zinc chloride was added as the catalyst; the mixture was warmed up to 60° C and reacted for 10 hours, and then cooled to room temperature

after the completion of the chloromethylation; the chlorination mother liquor was filtered out, washed with methanol repeatedly, and dried at 100°C for 8 hours to obtain chloromethylated spheres A7.

Imidazolization: To a 500mL three-necked flask were added 30 g of chloromethylated spheres A7 (having a chlorine content of 3.4mmol Cl/g), imidazole (102.0mmol), and 200mL of acetonitrile; the mixture was reacted at 80°C for 24 hours, cooled to room temperature, filtered, washed with ethyl acetate, 0.1 mol/L HCl, deionized water, and methanol successively, and then dried under vacuum at 60°C for 12 hours to obtain imidazole microspheres A7.

POSS-incorporated: To a 500mL three-necked flask were added 30 g of imidazole microspheres A7 (having an imidazole group content of 3.1mmol/g), 9.3 g of octachloromethyl silsesquioxane, and 300mL of tetrahydrofuran; the mixture was reacted at 100°C for 24 hours, filtered after the reaction, washed with tetrahydrofuran and deionized water successively to obtain imidazole/POSS microspheres A7.

Ion-exchange: To a 1000mL three-necked flask were added 30 g of imidazole/POSS microspheres A7, and 500mL of a solution of NaBr in deionized water having a concentration of 0.1mol/L; the mixture was stirred at room temperature to perform an ion-exchange reaction for 24 hours, then washed with deionized water until the pH of the washing liquor was 7, and dried under vacuum to obtain an ion-exchange resin catalyst, which was denoted as Cat-A7, and had the following structural formula:



[Example 12]

The ion-exchange resin prepared in [Example 1] was used for the addition reaction of ethylene oxide and carbon dioxide. The experimental conditions were as follows: under the protection of high-purity nitrogen, to a 300 mL autoclave were added 50.0 g of ethylene oxide and 7.5 g of resin catalyst Cat-A1, filled with CO₂ at 1.0 MPa, warmed up to 120°C, refilled with CO₂ to maintain the reaction pressure at 2.0 MPa, reacted for 4 hours and filtered to remove the catalyst. As measured, the ethylene oxide conversion C_{EO} was 96.7 %, and the ethylene carbonate selectivity S_{EC} was 99.3%.

[Examples 13-27]

The type of the resin catalyst and the reaction temperature and pressure were changed, and other reaction conditions were identical to those in [Example 12]. The catalytic reaction of ethylene oxide and carbon dioxide was performed and the analysis results after the reaction were shown in Table 1.

Table 1

Ex.	Catalyst	Catalyst Amount/g	Temp /°C	Time /h	Reaction Pressure /MPa	C _{EO} , %	S _{EC} , %
12	Cat-A2	7.5	120	4	2.0	96.9	99.2
13	Cat-B1	7.5	120	4	2.0	95.5	98.9
14	Cat-B2	7.5	120	4	2.0	95.7	99.1
15	Cat-C1	7.5	120	4	2.0	95.3	99.3
16	Cat-C2	7.5	120	4	2.0	95.6	98.9
17	Cat-A3	7.5	120	4	2.0	92.9	98.9
18	Cat-A4	7.5	120	4	2.0	94.6	98.7
19	Cat-A5	7.5	120	4	2.0	92.8	98.5
20	Cat-A6	7.5	120	4	2.0	89.5	98.6
21	Cat-A7	7.5	120	4	2.0	80.3	95.1
22	Cat-A1	7.5	160	4	2.0	99.4	99.3
23	Cat-A1	7.5	100	4	2.0	94.5	99.2
24	Cat-A1	7.5	180	4	2.0	99.4	99.3
25	Cat-A1	7.5	120	4	0.1	20.2	98.6
26	Cat-A1	7.5	120	4	5	96.8	99.2
27	Cat-A1	7.5	120	4	10.0	95.5	99.1

[Example 28]

The catalyst Cat-A1 used in [Example 12] was filtered, washed, and dried, and then the catalytic reactions of ethylene oxide and carbon dioxide were performed according to the reaction steps and conditions in [Example 12]. The results for which the catalysts were used in two circulations were shown in Table 2. By analogy, the catalytic reactions in which the catalysts were used in 3-5 circulations were performed respectively, and the results were shown in Table 2.

Table 2

Circulation Number	C _{EO} %	S _{EC} %
2	95.6	99.0
3	95.9	99.1

Circulation Number	$C_{EO}\%$	$S_{EC}\%$
4	95.5	99.2
5	95.3	98.9

[Examples 29-32]

The catalyst prepared in [Example 1] was used for the addition reaction of other alkylene oxides and carbon dioxide. The experimental conditions were as follows: under the protection of high-purity nitrogen, to a 300 mL autoclave were added 50.0 g of alkylene oxide and 7.5 g of resin catalyst, filled with CO₂ at 1.0 MPa, warmed up to 120°C, refilled with CO₂ to maintain the reaction pressure at 2.0 MPa, reacted for 4 hours and filtered to remove the catalyst. The alkylene oxide conversion and the obtained carbonate selectivity were measured. The results were shown in Table 3.

Table 3

Examples	Alkylene Oxide	Catalyst	Catalyst Amount/g	Temp /°C	Time /hr	Reaction Pressure/MPa	$C_{on},\%$	$S_{ec},\%$
29	Propylene oxide	Cat-A1	7.5	120	4	2.0	93.5	98.5
30	Styrene oxide	Cat-A1	7.5	120	4	2.0	60.3	98.5
31	Propylene oxide	Cat-B1	7.5	120	4	2.0	90.2	99.0
32	Styrene oxide	Cat-B1	7.5	120	4	2.0	56.5	99.1

[Reference Example 1]

According to the preparation method disclosed in the article of Catal. Sci. Technol., 2014, 4, 1598-1607, the catalyst SiO₂-ethane-Br was prepared. That catalyst was used for the addition reaction of styrene oxide and carbon dioxide. The experimental conditions were as follows: under the protection of high-purity nitrogen, to a 300 mL autoclave were added 50.0 g of styrene oxide and 7.5 g of catalyst, filled with CO₂ at 1.0 MPa, warmed up to 120°C, refilled with CO₂ to maintain the reaction pressure at 2.0 MPa, reacted for 4 hours and filtered to remove the catalyst. The styrene oxide conversion and the obtained cyclic styrene carbonate selectivity were measured. The results were shown in Table 4.

[Reference Example 2]

According to the preparation method disclosed in the article of Catalysis Today 2013, 200, 117-124, the catalyst SBA-15-IL3Br was prepared. That catalyst was used for the addition reaction of propylene oxide and carbon dioxide. The experimental conditions were as follows:

under the protection of high-purity nitrogen, to a 300 mL autoclave were added 50.0 g of propylene oxide and 7.5 g of catalyst, filled with CO₂ at 1.0 MPa, warmed up to 120°C, refilled with CO₂ to maintain the reaction pressure at 2.0 MPa, reacted for 4 hours and filtered to remove the catalyst. The propylene oxide conversion and the obtained propylene carbonate selectivity were measured. The results were shown in Table 4.

[Reference Example 3]

According to the preparation method disclosed in the article of Green Chem., 2013, 15, 1584-1589, the catalyst Poly[bvbim]Cl was prepared. That catalyst was used for the addition reaction of styrene oxide and carbon dioxide. The experimental conditions were as follows: under the protection of high-purity nitrogen, to a 300 mL autoclave were added 50.0 g of styrene oxide and 7.5 g of catalyst, filled with CO₂ at 1.0 MPa, warmed up to 120°C, refilled with CO₂ to maintain the reaction pressure at 2.0 MPa, reacted for 4 hours and filtered to remove the catalyst. The styrene oxide conversion and the obtained cyclic styrene carbonate selectivity were measured. The results were shown in Table 4.

Table 4

Reference Example	Alkylene oxide	Catalyst	Catalyst Amount/g	Temp /°C	Time /hr	Reaction Pressure /MPa	C _{on} , %	S _{ec} , %
1	Styrene oxide	SiO ₂ -ethane-Br	7.5	120	4	2.0	42.1	98.6
2	Propylene oxide	SBA-15-IL3Br	7.5	120	4	2.0	73.5	97.0
3	Styrene oxide	Poly[bvbim]Cl	7.5	120	4	2.0	24.9	98.5

[Example 33: Determination for sphericity after osmotic attrition]

1. 16 mL of a sample was weighed and transferred to an organic glass exchange column, 25 mL of pure water was added; a solution of sodium hydroxide in deionized water (25 mL, 1 mol/L) was quickly poured and drained off within 10-15 seconds, the operation was repeated 5 times; then a solution of sodium hydroxide in deionized water (20 mL, 1 mol/L), no bubble was in the resin layer, 250 mL of pure water was added, and the deionized water was allowed to flow out evenly within 5 minutes;

2. According to the method of (1), the sample was treated with a solution of HCl in deionized water (1 mol/L);

3. To 15mL of the above-treated sample was added a certain amount

of deionized water so that the total volume was 50mL, the mixture was transferred to a rotary drum, 10 ceramic balls were added, and the drum cover was tightened;

4. The rotary drum was placed on a ball mill, and the resin was rotated at a speed of 125r/min for 20 minutes;

5. the treated resin was transferred to a screen cloth with pure water, and dried at 60°C for 2-3 hours until the particles can roll freely;

6. The dried sample was placed in an enamel tray, the tray was slightly inclined to allow the spherical particles to roll down, and the broken particles were brushed to the upper right corner. The sample was divided into two parts, i.e., the spherical particles and the broken particles. For each of two parts, the residual amount of another sample less than 50 particles means that the separation was complete;

7. The masses of spherical particles and broken particles were respectively measured, and denoted as m1 and m2;

8. Sphericity after osmotic attrition $S = m1/(m1+m2) \times 100$.

[Example 34: Determination of sphericity after attrition]

1. 50 mL of an original sample was taken, and 5 mL of pure water was present on the resin layer;

2. The resin was transferred to a rotary drum by using 145 mL of pure water, 10 ceramic balls were added, and the drum cover was tightened;

3. The rotary drum was placed on a ball mill, and the resin was rotated at a speed of 125r/min for 30 minutes;

4. the treated resin was transferred to a screen cloth with pure water, and dried at 60°C for 2-3 hours until the particles can roll freely;

5. The dried sample was placed in an enamel tray, the tray was slightly inclined to allow the spherical particles to roll down, and the broken particles were brushed to the upper right corner. The sample was divided into two parts, i.e., the spherical particles and the broken particles. For each of two parts, the residual amount of another sample less than 50 particles means that the separation was complete;

6. The masses of spherical particles and broken particles were respectively measured, and denoted as m3 and m4;

7. Sphericity after attrition $A = m3/(m3+m4) \times 100$.

The catalyst of the present invention (Cat A1) had sphericity after attrition of 65.3%, and sphericity after osmotic attrition of 37.6%. The

CNT-based catalyst (with reference to CN109569717A) had sphericity after attrition of 54.2% and sphericity after osmotic attrition of 25.5%.

The above experimental data showed that the nanocomposite resin catalyst of the present invention had higher strength.

[Example 35: Determination for swelling ratio]

Determination for swelling ratio:

1. A certain volume of the catalyst was transferred to an organic glass exchange column, and the volume of the catalyst was recorded as V1;

2. A certain amount of deionized water was poured into an organic-glass exchange column, and 5 mL of pure water was present on the resin layer;

3. After standing at room temperature for 24 hours, the volume of the swelled catalyst was recorded, denoted as V2;

4. The swelling ratio of the catalyst was calculated, $S=(V2-V1)/V1 \times 100\%$.

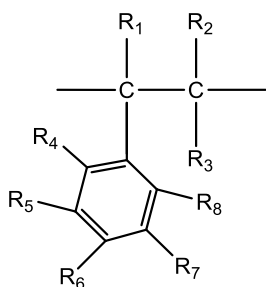
Catalyst	Swelling Ratio (%)
Cat-A6 (Comparative Example)	25.4
Cat-A1	33.2
CNT-based catalyst	27.6

It should be noted that the above-mentioned embodiments are only used to explain the present invention, and do not constitute any limitation to the present invention. The present invention has been described with reference to exemplary embodiments, but it is to be understood that the words used therein are words of description and explanation, rather than words of limitation. The present invention may be modified within the scope of the claims of the present invention as specified and may be modified without departing from the scope and spirit of the present invention. Although the present invention described herein refers to the specific methods, materials, and embodiments, it is not intended to be limited to the specific examples disclosed therein, but rather, the present invention extends to all other methods and applications having the same function.

Claims

1. A catalyst for addition reaction of alkylene oxide, comprising a nanocomposite ion-exchange resin having a structural formula of $P-Im^+-M^-$, wherein P is a nanocomposite resin matrix, Im^+ is a cation derived from 5-6 membered heterocycle containing at least one nitrogen atom such as imidazolium cation, pyrazolium cation, pyrrolidinium cation, piperidinium cation, piperazinium cation, pyrimidinium cation, pyrazinium cation, pyridazinium cation, triazinium cation (for example a cation derived from 5-6 membered heteroarene containing at least one nitrogen atom, such as imidazolium cation, pyrazolium cation, pyrimidinium cation, pyrazinium cation, pyridazinium cation, triazinium cation), M^- is an anion.

2. The catalyst according to claim 1, which is characterized in that the nanocomposite resin matrix comprises a structure fragment represented by formula I and a structure fragment of $-CH(POSS)-CH_2-$,

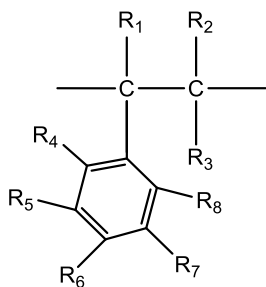


Formula I

In formula I, R_1-R_8 are identical to or different from each other, and each independently selected from hydrogen and C_1-C_6 alkyl, preferably selected from hydrogen, methyl, ethyl, propyl, and butyl;

POSS is a polyhedral oligomeric silsesquioxane, which has a general formula of $(-SiO_{1.5})_m$, and m is 6, 8, 10, or 12.

3. The catalyst according to any of the preceding claims, which is characterized in that the catalyst comprises the following structure:



Wherein R_1-R_3 are identical to or different from each other, and each

independently selected from hydrogen and C₁-C₆ alkyl;
R₄-R₈ are each independently selected from hydrogen, C₁-C₆ alkyl, and
CH₂Im⁺-M⁻, and at least one of R₄-R₈ is CH₂Im⁺-M⁻, preferably, R₄-R₈ are
each independently selected from hydrogen and CH₂Im⁺-M⁻, and at least
one of R₄-R₈ is CH₂Im⁺-M⁻.

4. The catalyst according to any of the preceding claims, which is
characterized in that said M⁻ is one or more of halide ions and organic acid
radical ions, preferably one or more of a fluoride ion, a chloride ion, a
bromide ion, an iodide ion, an acetate group, a formate group, and a
bioxalate group;

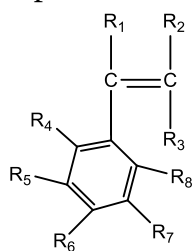
and/or, the mass content of POSS in the nanocomposite resin matrix P is
0.1-10%, preferably 0.2-5%, more preferably 2-5%.

5. A process for preparing a catalyst as claimed in any of claims 1-4,
comprising the following steps:

S1: polymerizing a styrene-based monomer, a cross-linking agent, and a
polyhedral oligomeric silsesquioxane in the presence of an initiator to
obtain a nanocomposite resin matrix P;

S2: subjecting the nanocomposite resin matrix P obtained in step S1 to a
chloromethylation reaction, an imidazolation reaction, and an
ion-exchange reaction.

6. The process according to claim 5, which is characterized in that said
styrene-based monomer is one or more of styrene-based monomers
represented by formula II;



Formula II

In formula II, R₁-R₈ are identical to or different from each other, and each
independently selected from hydrogen and C₁-C₆ alkyl, preferably selected
from hydrogen, methyl, ethyl, propyl, and butyl;

and/or, said polyhedral oligomeric silsesquioxane is one or more of a
vinyl-containing silsesquioxane, a hydrogen-containing
polysilsesquioxane, an alkoxy-containing polysilsesquioxane, and an
epoxy-containing polysilsesquioxane, preferably said vinyl-containing

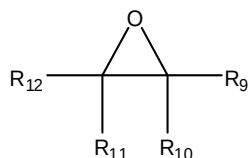
silsesquioxane is an octavinylsilsesquioxane;
and/or, said cross-linking agent is one or more of ethylene glycol
bismethacrylate, dipropenylbenzene, divinylphenylmethane, and
divinylbenzene;

5 and/or, said initiator is at least one of benzoyl peroxide,
azodiisobutyronitrile, azodiisooheptylonitrile, lauroyl peroxide, and cumene
hydroperoxide,

and/or, in step S1, based on the total weight of raw materials, the mass of
said styrene-based monomer is 85-95%, the mass of the cross-linking
10 agent is 1-6%, the mass of said polyhedral oligomeric silsesquioxane is
0.1-10%, preferably 0.2-5%, and more preferably 2-5%, and the mass of
the initiator is 0.1-5%.

7. A method for an addition reaction of alkylene oxide and carbon dioxide,
which comprises reacting alkylene oxide and carbon dioxide in the
15 presence of the catalyst according to any of claims 1-4 or a catalyst
prepared with the process according to claim 5 or 6.

8. The method according to claim 7, which is characterized in that the
alkylene oxide has a general formula of



20 wherein, R₉-R₁₂ are identical to or different from each other and each
independently selected from hydrogen, C₁-C₆ alkyl, and C₆-C₁₀ aryl,
preferably selected from hydrogen, methyl, ethyl, propyl, butyl, and
phenyl; and/or,

The mass ratio of the catalyst to the alkylene oxide is (0.001-1):1,
25 preferably (0.1-0.3):1.

9. The method according to claim 7 or 8, which is characterized in that the
reaction temperature is 60-180°C, preferably 100-160°C; and/or the
reaction pressure is 0.1-10.0MPa, preferably 2-5MPa; and/or, the reaction
time is 1-8 hours, preferably 3-6 hours.

30 10. Use of the catalyst according to any of claims 1-4 or a catalyst
prepared with the process according to claim 5 or 6 in the addition
reaction of alkylene oxide.