

DESCRIPTION

PROCESS FOR PRODUCTION OF POLYETHER AND PROCESS FOR
PRODUCTION OF SOLID ACID CATALYST

Technical Field

[0001]

The present invention relates to a process for production of polyether. The present invention also relates to a solid acid catalyst and a process for production of a solid acid catalyst.

Background Art

[0002]

The polyether is a polymer having a wide range of uses, for example, raw materials for soft segments, e.g., elastic fibers and thermoplastic elastomers, and raw materials for polyurethanes, urethane urea, polyesters, and the like.

[0003]

Typical examples of known polyethers include polyethylene glycol, poly(1,2-propane diol), and polytetramethylene ether glycol. Most of all, polytetramethylene ether glycol synthesized by ring-opening polymerization of tetrahydrofuran (THF) has excellent expansion and contraction properties, excellent elasticity, and the like, and has been noted.

[0004]

[Background of first and second aspects]

The viscosity of the polyether is relatively high. In the case where polyurethane or the like is further produced by using this as a raw material, dilution or heating is required in the reaction process thereof. Therefore, a polyether having a low viscosity (low molecular weight distribution (molecular weight distribution = weight-average molecular weight (Mw)/number-average molecular weight (Mn))) has been desired. In the case where the polyether is produced industrially, it is believed that the molecular weight distribution of the resulting polyether is influenced significantly by a polymerization catalyst to be used. As a matter of course, the performance of the polymerization catalyst also exerts an influence on the degree of conversion in the production of the polyether.

[0005]

Patent Documents 1 and 2 disclose solid acid catalysts, in which metal oxides are supported by oxide carriers, e.g., zeolite or silica, as catalysts to be used in the production of the polyether.

Patent Document 1: Japanese Unexamined Patent Application
Publication No. 9-241374

Patent Document 2: Japanese Unexamined Patent Application
Publication No. 2000-327770

[0006]

According to the studies of the inventors of the present invention, in the case where the polyether was produced industrially, a polyether having quite satisfactory quality was not obtained by the catalysts which were disclosed in Patent Documents 1 and 2 and which had been used previously. That is, regarding the known catalysts, the performance of the catalyst deteriorated significantly as the reaction was continued, and deterioration of the activity and deterioration of the molecular weight distribution of the resulting polyether over time were significant. Consequently, a large amount of catalyst was required for producing the polyether stably, and only polyethers having large molecular weight distributions were able to be produced.

[0007]

[Background of third aspect]

It is known that metal hydroxides and/or metal oxides function as acid-base catalysts on the basis of their respective acid-base strengths. It is also well known that an acid strength stronger than the acid strength exerted by a single metal oxide can be obtained by a plurality of metal oxides being combined into an oxide complex or by at least one type of metal oxide being supported by different types of metal oxide carriers.

[0008]

In general, a method, in which a carrier is allowed to support a metal salt or the like, the metal salt on the carrier is hydrolyzed with an alkali or the like so as to become a metal hydroxide, and the metal hydroxide is converted to a metal oxide by heating and firing, has been used previously as a method for preparing a solid acid catalyst in which a metal oxide is supported by a carrier (Patent Document 3).

[0009]

Examples of uses of the above-described solid acid catalysts include the production of polyethers through a ring-opening polymerization reaction of tetrahydrofuran (THF) and other circular ethers (Patent Document 4). Regarding the production of polyethers by using this solid acid catalyst, it is desired not only that the reaction proceeds at a high degree of conversion, but also that the polyether has a low viscosity from the viewpoint of the handling of the produced polyether. Consequently, it is desired to produce a polyether having a narrow molecular weight distribution, that is, a small ratio (M_w/M_n) of the weight-average molecular weight (M_w) to the number-average molecular weight (M_n).

Patent Document 3: Japanese Unexamined Patent Application Publication No. 2003-113238

Patent Document 4: Japanese Unexamined Patent Application

Publication No. 2004-161893

[0010]

According to the studies of the inventors of the present invention, it was difficult to allow a carrier to support a metal hydroxide and/or a metal oxide in the state of fine dispersion by the method disclosed in Patent Document 3. Even if a solid acid catalyst is prepared by this method, the amount of acid-base thereof may be small and the distribution of acid strength may become wide. The reason therefor is believed as described below. In the case where the carrier is allowed to support the metal salt or the like and hydrolysis is conducted with the alkali, since the alkali is supplied from the outside of the carrier, the amount of supply of alkali is varied depending on the position in the inside of the carrier and, thereby, the rate of hydrolysis is varied. In addition, when the metal hydroxide precipitates, the metal salt or the like is moved due to the concentration gradient. That is, regarding the metal hydroxide in the inside of the carrier, high-concentration portions and low-concentration portions result depending on the positions in the inside of the carrier. Large aggregation of metal hydroxide occurs in the high-concentration portion and small aggregation of metal hydroxide occurs in the low-concentration portion. As a result, the metal hydroxide is supported nonuniformly in the

carrier, and it is believed that the nonuniformity leads to the wide distribution of acid strength and the reduction in the amount of acid-base.

[0011]

For example, in the ring-opening polymerization reaction of tetrahydrofuran, it is also believed that the above-described wide distribution of acid strength of the solid acid catalyst becomes the cause of reduction of the degree of conversion and, furthermore, a wide range of degree of polymerization, that is, the wide molecular weight distribution of the intended polyether.

[0012]

[Background of fourth aspect]

Patent Documents 1 and 2 disclose solid acid catalysts, in which metal oxides are supported by oxide carriers, e.g., zeolite and silica, as the catalyst to be used in the production of polyethers, e.g., polytetramethylene ether glycol, through the ring-opening polymerization of THF and the like.

[0013]

The average molecular weights required of the thus produced polyethers are different depending on uses thereof. Therefore, it is required that polyethers having various average molecular weights are produced from a polyether having a single composition.

[0014]

In the production of polyethers, methods in which the reaction conditions are changed, that is, methods in which the reaction temperature, the degree of conversion, and the like are changed, have been previously adopted as the methods for controlling the average molecular weights of the resulting polyethers.

Patent Document 1: Japanese Unexamined Patent Application
Publication No. 9-241374

Patent Document 2: Japanese Unexamined Patent Application
Publication No. 2000-327770

[0015]

In the case where the average molecular weight of the resulting polyethers are changed by the reaction condition, for example, in the case where an increase of the average molecular weight is intended, a polyether having a large average molecular weight can be obtained by lowering the reaction temperature. However, the reaction activity is reduced by lowering the reaction temperature, and the productivity is reduced. Alternatively, a polyether having a large average molecular weight can be obtained by lowering the degree of conversion. However, the productivity is also reduced in this case.

The average molecular weight of the resulting polyether can also be increased by reducing the concentration of an

initiator-terminator, e.g., acetic anhydride, to be used. However, in this case as well, the productivity is reduced due to a reduction of the initial reaction rate.

[0016]

Conversely, a polyether having a small average molecular weight can be produced by raising the reaction temperature. However, in this case, the molecular weight distribution increases (deteriorates), the viscosity of the polyether increases, and coloring occurs easily.

Alternatively, the average molecular weight of the resulting polyether can be reduced by increasing the concentration of the initiator-terminator, e.g., acetic anhydride, to be used. However, in this case, the amount of acetic anhydride remaining in the reaction solution increases and, thereby, a disadvantage occurs in the following separation step.

[0017]

Under the above-described circumstances, a process for controlling the average molecular weight of the resulting polyether at a desired value without adversely affecting the other performance, e.g., the reaction activity, characteristics of the polyether, and treatment operations, has been required.

Disclosure of Invention

[0018]

[Disclosure of first and second aspects]

It is an object of the first and the second aspects to provide a process capable of reducing the amount of catalyst required and producing a polyether having a narrow molecular weight distribution at a high degree of conversion stably for the long term by using a catalyst, the performance of the catalyst being prevented from deteriorating over time, in the production of a polyether, as well as a solid acid catalyst therefor.

[0019]

A process for production of a polyether according to the first aspect is characterized by including the step of subjecting a raw material compound to a polymerization reaction or a condensation reaction in the presence of a solid acid catalyst so as to produce a polyether, wherein a solid acid catalyst having the amount of surface hydroxyl group of 0.1 to 2.5 $\mu\text{mol}/\text{m}^2$ and the amount of acid exhibiting pKa of -5.6 or less of 20 $\mu\text{mol}/\text{g}$ or more is used as the solid acid catalyst.

According to the first aspect, a solid acid catalyst having the amount of surface hydroxyl group of 0.1 to 2.5 $\mu\text{mol}/\text{m}^2$ and the amount of acid exhibiting pKa of -5.6 or less of 20 $\mu\text{mol}/\text{g}$ or more is also provided as this solid acid catalyst.

[0020]

A process for production of a polyether according to the second aspect is characterized by including the step of subjecting a raw material compound to a polymerization reaction or a condensation reaction in the presence of a solid acid catalyst so as to produce a polyether, wherein a solid acid catalyst having surface hydroxyl groups is allowed to contact with an organic compound and/or an inorganic compound, which can react or interact with the surface hydroxyl groups and which is other than the polyether, and is used in the polymerization reaction or the condensation reaction.

[0021]

[Disclosure of third aspect]

It is an object of the third aspect to provide a process for production of a solid acid catalyst having a large amount of acid-base and a narrow acid strength distribution by allowing a carrier to support a metal hydroxide and a metal oxide in an extremely homogeneous, fine dispersion state.

[0022]

A process for production of a solid acid catalyst, in which a metal hydroxide and/or a metal oxide is supported by a carrier, according to the third aspect is characterized by including the step of allowing the metal hydroxide and/or the metal oxide to be supported in pores of the carrier by

conducting a homogeneous precipitation method in the carrier pores.

[0023]

[Disclosure of fourth aspect]

It is an object of the fourth aspect to provide a process for production of a polyether, the process being capable of easily efficiently controlling the average molecular weight of the resulting polyether at a desired value without adversely affecting the other performance, e.g., the reaction activity, characteristics of the polyether, and treatment operations, in a process for production of a polyether by subjecting a cyclic ether to ring-opening polymerization in the presence of a catalyst.

[0024]

A process for production of a polyether according to the fourth aspect is characterized by including the step of subjecting a cyclic ether to ring-opening polymerization in the presence of a catalyst, wherein a catalyst, in which a solid acid catalyst containing at least one type of element selected from the group consisting of the groups 1, 2, 4, 6, 8, 9, 12, 13, 14, 15, 16, and 17 in the periodic table and being capable of subjecting by itself a cyclic ether to ring-opening polymerization is allowed to contain at least one type of metal element not contained in the solid acid catalyst and selected from the group consisting of the

groups 3, 5, 10, and 11 in the periodic table, is used as the catalyst.

Detailed Description

[0025]

[Description of first and second aspects]

The inventors of the present invention conducted intensive research in order to solve the above-described problems. As a result, it was found that when a solid acid catalyst having surface hydroxyl groups was treated with a specific organic compound and/or inorganic compound, the performance of the catalyst was able to be prevented from deteriorating over time, and when the solid acid catalyst treated with the organic compound and/or the inorganic compound was used, the usage of the catalyst for producing a polyether was reduced and the molecular weight distribution of the polyether was able to be narrowed. Consequently, the present invention has been completed.

[0026]

That is, methods for reducing the amount of surface hydroxyl group of the solid acid catalyst having surface hydroxyl groups include a method in which the solid acid catalyst is fired at high temperatures. In this case, the surface area and the amount of acid of the solid acid catalyst are also reduced and, therefore, the initial performance of the catalyst deteriorates significantly. On

the other hand, in the case where the treatment with the organic compound and/or the inorganic compound is conducted according to the present invention, merely the amount of surface hydroxyl group can be reduced without adversely affecting the surface area and the amount of acid of the solid acid catalyst. As a result, a polyether having a narrow molecular weight distribution can be produced at a high degree of conversion stably for the long term by using a solid acid catalyst having a small amount of surface hydroxyl group and a large amount of acid.

[0027]

That is, the first aspect of the present invention resides in a process for production of a polyether, characterized by including the step of subjecting a raw material compound to a polymerization reaction or a condensation reaction in the presence of a solid acid catalyst so as to produce a polyether, wherein a solid acid catalyst having the amount of surface hydroxyl group of 0.1 to $2.5 \mu\text{mol}/\text{m}^2$ and the amount of acid exhibiting pKa of -5.6 or less of $20 \mu\text{mol}/\text{g}$ or more is used as the solid acid catalyst.

[0028]

The second aspect of the present invention resides in a process for production of a polyether, characterized by including the step of subjecting a raw material compound to

a polymerization reaction or a condensation reaction in the presence of a solid acid catalyst so as to produce a polyether, wherein a solid acid catalyst having surface hydroxyl groups is allowed to contact with an organic compound and/or an inorganic compound, which can react or interact with the surface hydroxyl groups and which is other than the polyether, and is used for the polymerization reaction or the condensation reaction.

[0029]

Regarding the first and the second aspects, the solid acid catalyst may be at least one type selected from the group consisting of composite metal oxide catalysts, metal oxide catalysts, and clay catalysts.

[0030]

Regarding the first and the second aspects, the solid acid catalyst may contain at least one type of metal element selected from the group consisting of the group 2, the group 3, the group 4, the group 5, the group 8, the group 10, the group 11, the group 13, and the group 14 in the periodic table.

[0031]

Regarding the second aspect, the organic compound may be at least one type selected from the group consisting of alcohols, silylating agents, and carbonates.

[0032]

Regarding the first and the second aspects, preferably, a cyclic ether is subjected to a ring-opening polymerization reaction so as to produce a polyether. In particular, it is preferable that a cyclic ether is subjected to a ring-opening polymerization reaction in the presence of a carboxylic anhydride and/or a carboxylic acid so as to produce a polyether.

[0033]

Regarding the first and the second aspects, the solid acid catalyst may be produced by conducting a homogeneous precipitation method in carrier pores.

[0034]

According to the first and the second aspects, a treatment for allowing the solid acid catalyst having surface hydroxyl groups to contact with an organic compound and/or an inorganic compound, which can react or interact with the surface hydroxyl groups and which is other than the resulting polyether, is conducted and, thereafter, the reaction is conducted. Consequently, a polyether having a narrow molecular weight distribution can be produced stably, and the amount of catalyst to be used can be reduced. That is, in the production of the polyether, since deterioration of the performance of the catalyst (catalyst activity) over time is prevented, the usage of catalyst per unit amount of polyether can be reduced. Furthermore, since deterioration

of the molecular weight distribution over time is also prevented, a high-quality polyether having excellent properties, e.g., heat resistance, can be produced.

[0035]

In the case where a polyurethane or the like is further produced by using the polyether, which has been produced according to the first or second aspect and which has a narrow molecular weight distribution, as a raw material, the amount of a diluent required for adjusting the viscosity to make the reaction possible can be reduced, and an advantageous effect can be expected from the viewpoint of the cost and the productivity.

[0036]

The embodiments according to the first and the second aspects will be described below in detail. However, the following description of constituent features is an example (typical example) of execution forms of the first and the second aspects, and the first and the second aspects are not specifically limited to these contents within the bounds of the gist.

[0037]

[Solid acid catalyst]

The solid acid catalyst to be used in the first and the second aspects will be described.

The solid acid catalyst to be used in the first and the

second aspects is a solid acid catalyst having the amount of surface hydroxyl group of 0.1 to 2.5 $\mu\text{mol}/\text{m}^2$ and the amount of acid exhibiting pKa of -5.6 or less of 20 $\mu\text{mol}/\text{g}$ or more. The above-described solid acid catalyst having a small amount of surface hydroxyl group and a large amount of acid can be produced by, for example, allowing a solid acid catalyst having surface hydroxyl groups to contact with a specific organic compound and/or inorganic compound.

[0038]

{Solid acid catalyst having surface hydroxyl groups}

The solid acid catalyst having surface hydroxyl groups in the first and the second aspects refers to a solid acid catalyst in which hydroxyl groups (-OH groups) are present on a surface of a metal and/or a carrier (including inner surfaces of carrier pores).

[0039]

More specific examples of solid acid catalyst having surface hydroxyl groups include zeolite and the like having crystal structures of MFI, X, Y, and the like; metal oxides, e.g., silica, alumina, titania, and zirconia; composite metal oxides, e.g., silica-titania, silica-alumina, silica-zirconia, and alumina-titania, in which a plurality of metal oxides are combined; support type acid catalysts in which compounds, e.g., sulfuric acid, heteropolyacid, and Nafion, having an acidic property or metal oxides different from

carriers are supported by metal oxides or activated carbon serving as carriers; clay and the like, e.g., layered silicate; and clay and the like supporting compounds having an acidic property, metals, or metal oxides.

[0040]

Most of all, in the cases where composite metal oxides and support type acid catalysts are used, silica-zirconia, silica-alumina, zirconia supported by silica, and alumina supported by silica are particularly preferable. In the case where clay and the like, e.g., layered silicate, are used, usually, kaolinite, smectite, and the like are mentioned. Among the smectite, it is preferable that montmorillonite is used. Preferably, clay and the like are used as activated clay washed with an acid. It is particularly preferable that activated clay which is montmorillonite washed with an acid is used.

[0041]

These solid acid catalysts may be used alone or a mixture of at least two types may be used.

[0042]

Known technologies can be used as the process for production of the above-described solid acid catalyst having surface hydroxyl groups, and the process is not specifically limited. Specifically, the production can be conducted by production processes described in Japanese Unexamined Patent

Application Publication No. 9-241374, Japanese Unexamined Patent Application Publication No. 2000-327770, and the like.
[0043]

In particular, it is preferable that the solid acid catalyst to be used according to the first and the second aspects is a solid acid catalyst in which a homogeneous precipitation method is conducted in pores of a carrier and, thereby, a metal hydroxide and/or a metal oxide in a homogeneous, fine dispersion state is supported in pores of the carrier.

An example of process for production of a solid acid catalyst having surface hydroxyl groups on the basis of the homogeneous precipitation method will be described below.
[0044]

The homogeneous precipitation method is conducted by, for example, impregnating a carrier with a metal salt and a precipitant precursor, which generates a precipitant through a chemical reaction, e.g., hydrolysis, in a solution, at the same time, and subjecting the impregnated carrier to a treatment, e.g., a heat treatment, for generating the precipitant from the precipitant precursor. For the homogeneous precipitation method, it is important that the metal salt and the precipitant precursor constitute a liquid phase, that is, a solution. Therefore, the carrier is impregnated with an impregnation solution including the

metal salt and the precipitant precursor and, thereafter, the treatment for generating the precipitant from the precipitant precursor is conducted.

[0045]

(1) Carrier

The carrier is not specifically limited. However, metal oxides, composite metal oxides, zeolite and the like, and clay and the like are preferable. Silica, alumina, zirconia, titania, silica-alumina, silica-zirconia, and silica-titania are more preferable. Silica, alumina, and zirconia are particularly preferable.

[0046]

The particle diameter, the pore diameter, and the pore volume of the carrier are different depending on uses and application forms of the solid acid catalyst, and cannot be univocally specified.

[0047]

These carriers may be used alone or at least two types may be used in combination.

[0048]

(2) Metal hydroxide and/or metal oxide

The metal hydroxide and/or the metal oxide to be supported by the above-described carrier is not specifically limited. It is usually a hydroxide and/or an oxide of a metal element of groups 2 to 14 in the periodic table,

preferably a hydroxide and/or an oxide of at least one type of metal element selected from the group consisting of the group 2, the group 3, the group 4, the group 5, the group 8, the group 10, the group 11, the group 13, and the group 14 in the periodic table, more preferably a hydroxide and/or an oxide of at least one type of metal element selected from the group consisting of Ti, Zr, Hf, Nb, Al, Cu, Ni, Ca, Fe, and Si, and particularly preferably a hydroxide and/or an oxide of at least one type of metal element selected from the group consisting of Ti, Zr, Al, Cu, Ni, and Nb.

[0049]

(3) Metal salt

The metal salt to be used in the homogeneous precipitation method is a metal salt, from which the above-described metal hydroxide and/or the metal oxide to be supported by the resulting solid acid catalyst is generated, and therefore, is usually a salt of the above-described metal element of groups 2 to 14 in the periodic table, preferably a metal element selected from the group consisting of the groups 2, 3, 4, 5, 8, 10, 11, 13, and 14, more preferably Ti, Zr, Hf, Nb, Al, Si, Cu, Ni, Ca, or Fe, and particularly preferably Ti, Zr, Al, Nb, Cu, or Ni.

[0050]

The type of the salt is not specifically limited. However, a nitrate, an acetate, a sulfate, an oxynitrate, a

chloride, or an oxychloride is preferable, and an oxynitrate, an oxychloride, or a sulfate is more preferable.

[0051]

That is, for the metal salt, a nitrate, an acetate, a sulfate, an oxynitrate, a chloride, or an oxychloride of a metal of the groups 2 to 14 in the periodic table is preferable, and zirconium oxynitrate, zirconium oxychloride, zirconium sulfate, titanium chloride, aluminum sulfate, or niobium oxychloride is further preferable.

[0052]

These metal salts may be used alone or at least two types may be used in combination.

[0053]

(4) Precipitant precursor

The precipitant precursor undergoes a chemical reaction, e.g., hydrolysis, by a treatment, e.g., heating, in an impregnation treatment so as to generate a precipitant. The precipitant reacts with a metal salt in the impregnation solution so as to cause precipitation of a metal hydroxide. Among precipitant precursors, a precipitant precursor which generates a base as a precipitant, that is, the precipitant precursor which generates a base through hydrolysis or other chemical reaction in the impregnation solution and increases the pH of the solution so as to precipitate a metal salt as a hydroxide or an oxide, is referred to as a "base

precursor".

[0054]

The precipitant precursor for conducting the homogeneous precipitation method is not specifically limited. However, in general, the base precursor is used.

[0055]

For the base precursor, urea, cyanuric acid, alkyl-substituted urea, thiourea, alkyl-substituted thiourea, amide compounds composed of amines and carboxylic acids, and the like are used. Preferably, urea, cyanuric acid, and alkyl-substituted urea are used. It is particularly preferable to use urea and cyanuric acid from the viewpoint of the ease of availability and the cost. These base precursors may be used alone or at least two types may be used in combination.

[0056]

(5) Basic substance

Not only the above-described base precursor, but also a predetermined amount of basic substance may be added to the impregnation solution in advance in order to increase the pH within the bounds of not causing precipitation. It is also possible to reduce the usage of the base precursor and the time required to generate precipitation by using the basic substance.

[0057]

The basic substance is not specifically limited. Examples thereof include hydroxides, carbonates, bicarbonates, phosphates, and acetates of alkali metals, alkaline earth metals, and ammonium; ammonia; and organic amines. Ammonia; organic amines; and carbonates, bicarbonates, and phosphates of ammonium are preferable, and ammonium carbonates and ammonium bicarbonates are more preferable.

[0058]

These basic substances may be used alone or at least two types may be used in combination.

[0059]

(6) Impregnation solution

Usually, the impregnation solution is prepared by dissolving the above-described metal salt, the precipitant precursor and, if necessary, the basic substance into water.

[0060]

The concentrations of the metal salt and the precipitant precursor in the impregnation solution are not specifically limited, insofar as the dissolution state is maintained and the concentration is suitable for realizing a favorable amount of support by a carrier described later. Usually, the metal salt concentration is 0.01 to 50 percent by weight, preferably 0.1 to 40 percent by weight, and particularly preferably 0.5 to 30 percent by weight. The

precipitant precursor is 0.1 to 10 times the theoretical amount sufficient for precipitating the entire metal salt, preferably 0.2 to 8 times, and particularly preferably 0.3 to 5 times, as described later.

[0061]

The basic substance is used appropriately in such a way that a required pH condition is obtained. That is, since the pH condition required for generating precipitation is different depending on the types and the concentrations of the metal salt and the precipitant precursor to be used, the basic substance is used at an amount required in accordance with these conditions.

[0062]

In order to conduct the homogeneous precipitation method in the carrier, it is necessary that at least one type of metal salt and the precipitant precursor are in a liquid phase, that is, a dissolution state in the impregnation solution, before a treatment, in which the precipitant precursor is converted to a precipitant, is conducted. Substances other than the above-described at least one type of metal salt and the precipitant precursor may be present in any state in the impregnation solution.

[0063]

(7) Homogeneous precipitation method

<Method for impregnating carrier with impregnation solution>

The method for impregnating the carrier with the above-described impregnation solution is not specifically limited. However, it is preferable that a pore-filling method is conducted in order to allow the carrier to uniformly support the metal salt. In this case, it is preferable that the volume of the impregnation solution, with which the carrier is impregnated, is 60% to 120% of the carrier pore volume, further preferably 70% to 110%, and particularly preferably 80% to 105%. If the amount of liquid is too small, the impregnation solution do not uniformly enter carrier pores, and nonuniformity results. Conversely, if the amount is too large, the impregnation solution adheres to the outer surface of the carrier, and nonuniformity also results.

[0064]

Any amount can be selected as the amount of metal salt to be supported by the carrier through impregnation. However, the amount is usually 0.01 to 50 percent by weight relative to the weight of the carrier, preferably 0.05 to 40 percent by weight, and further preferably 0.1 to 30 percent by weight. Usually, the amount of the supported precipitant precursor is specified to be within the range of 0.1 to 10 in terms of mole ratio, where the theoretical amount sufficient for precipitating the entire metal salt supported by the carrier is assumed to be 1, preferably within the range of 0.2 to 8, and further preferably within the range

of 0.3 to 5.

[0065]

<Method for generating and after-treating precipitation>

A treatment, e.g., heating, for converting the precipitant precursor to a precipitant is conducted while the metal salt and the precipitant precursor, which are supported by the carrier through impregnation of the carrier with the impregnation solution, remain in the state of solution in carrier pores, and the metal salt is converted to a corresponding metal hydroxide by the precipitant homogeneously generated in the inside of the carrier.

[0066]

In general, a base precursor is used as the precipitant precursor, and hydrolysis of the base precursor through heating is used as the treatment for converting the base precursor to a base.

[0067]

As described above, in order to conduct the homogeneous precipitation method in the carrier pores, it is required that at least one type of metal salt and the precipitant precursor are in the state of a solution, that is, a liquid phase, before the treatment, in which the precipitant precursor is converted to the precipitant, is conducted. However, substances other than the above-described at least one type of metal salt and the precipitant precursor may be

in any state.

[0068]

In the case where the base precursor is converted to the base through hydrolysis reaction effected by heating, a heating temperature within the range of 50°C to 300°C is usually adopted, and preferably the range of 60°C to 200°C is adopted. The heating temperature can also be changed over time. If the heating temperature is too low, a reaction of generation of the precipitant from the precipitant precursor may not occur or a very long time may be taken. If the heating temperature is too high, in some cases, the entire water required for hydrolysis may be removed before the reaction of generation of the precipitant from the precipitant precursor is finished. In order to conduct a good, stable homogeneous precipitation method, it is preferable that 5% or more of water in the impregnation solution, with which the carrier has been impregnated, remains at the point in time when the precipitation generation reaction is finished, and further preferably 10% or more of water remains.

[0069]

The heating of the carrier impregnated with the impregnation solution may be conducted in the state in which the support carrier does not move as in a fixed-bed heating apparatus. However, particularly in the case where a large

amount of catalyst is prepared, it is more preferable that a fluidized-bed apparatus, a rotary heating apparatus, and the like are used wherein the support carrier is fluidized. In the case where vaporization of water occurs during heating, it is believed that when the support carrier is fluidized, the amount of vaporization of water does not vary on a particle of the support carrier basis and, therefore, the homogeneity is further improved.

[0070]

If vaporization of water during heating is too fast, the entire water may be removed before the hydrolysis of the base precursor is completed and, thereby, the precipitant may not be supplied sufficiently. Therefore, usually, complete removal of water is conducted desirably in such a way that the water is removed completely over 1 hour or more, preferably 3 hours or more, and further preferably 6 hours or more after the heating is started and the precipitation generation reaction is finished.

[0071]

If necessary, the resulting catalyst is washed with water, an alkaline aqueous solution, an acid aqueous solution, an organic solvent, or the like and is dried. Thereafter, firing is conducted in an atmosphere of an inert gas, e.g., nitrogen or argon, or an atmosphere of an oxidizing gas, e.g., air or a diluted oxygen gas, so that a

solid acid catalyst having a desired performance can be obtained. The heating and firing temperature at this time is usually 100°C to 1,200°C, preferably 300°C to 1,100°C, and further preferably 500°C to 1,000°C. The catalyst activity and the stability of the resulting solid acid catalyst can be improved by conducting the above-described heating and firing.

[0072]

However, all the above-described steps are not always necessary insofar as a solid acid catalyst having surface hydroxyl groups are obtained finally. Therefore, the production steps thereof are not specifically limited.

[0073]

Preferably, the amount of the supported metal hydroxide and/or metal oxide of the solid acid catalyst relative to the carrier is 0.05 to 40 percent by weight and, in particular, 0.1 to 30 percent by weight.

[0074]

{Method for treatment with organic compound and/or inorganic compound}

The organic compound and/or the inorganic compound for treating the solid acid catalyst having surface hydroxyl groups, preferably the solid acid catalyst which has been obtained by the above-described homogeneous precipitation method and which has surface hydroxyl groups, is a compound

which reacts with the surface hydroxyl groups of the solid acid catalyst and/or a compound which exerts an interaction. Specific examples thereof include alcohols, e.g., methanol and ethanol; ethers, e.g., diethylether; esters, e.g., methyl acetate and ethyl acetate; acylating agents, e.g., acetic acid, acetyl chloride, and acetic anhydride; carbonates, e.g., dimethyl carbonate and diethyl carbonate; silylating agents, e.g., trimethylsilyl acetate, trimethylsilyl chloride, t-butyldimethylsilyl chloride, hexamethyldisiloxane, trimethylsilane, diethylmethysilane, and triethylsilane; metal hydroxides; metal chlorides; and metal ammine complexes. Here, examples of metal hydroxides, metal chlorides, and metal ammine complexes include copper chloride, nickel chloride, tetraammine copper dichloride, hexaammine nickel dichloride, tetraammine copper dinitrate, and hexaammine nickel dinitrate. Most of all, alcohols, esters, acylating agents, carbonates, and silylating agents are preferable, and alcohols, carbonates, and silylating agents are more preferable. In particular, methanol, ethanol, methyl acetate, ethyl acetate, dimethyl carbonate, diethyl carbonate, trimethylsilyl acetate, trimethylsilane, diethylmethysilane, and triethylsilane are preferable from the viewpoint of the reactivity with the surface hydroxyl groups, ease of removal of unreacted organic compounds, and the like. These organic compounds and/or inorganic

compounds may be used alone or a mixture of at least two types may be used.

[0075]

The method for treating the solid acid catalyst with the organic compound and/or the inorganic compound is not specifically limited, and any one of a liquid phase and a gas phase can be adopted. For the liquid phase, any one of a batch type and a flow type can be adopted.

[0076]

In the case of the liquid phase and the batch type, the treatment of the solid acid catalyst with the organic compound and/or the inorganic compound can be conducted by putting the solid acid catalyst having surface hydroxyl groups directly into the organic compound and/or the inorganic compound for the treatment or into a solution prepared by diluting the organic compound and/or the inorganic compound with an inactive solvent and conducting a heat treatment.

[0077]

In this case, regarding the usage of the organic compound and/or the inorganic compound, usually, the upper limit is 10 times or less, and the lower limit is 0.1 times or more relative to the volume of the catalyst. Preferably, the upper limit is 8 times or less, and the lower limit is 0.2 times or more, and more preferably the upper limit is 5

times or less, and the lower limit is 0.3 times or more. If the usage of the organic compound and/or the inorganic compound is too large, the cost of the organic compound and/or the inorganic compound increases, and the load of removing unreacted organic compounds and/or inorganic compounds increases as well. If the usage is too small, an untreated catalyst remains.

[0078]

The diluent solvent is not specifically limited, and usually, hydrocarbons are used. Preferably, pentane, hexane, heptane, benzene, toluene, and xylene are used. These solvents may be used alone or a mixture of at least two types may be used. The concentration after dilution is determined appropriately on the basis of the type of the organic compound and/or the inorganic compound.

[0079]

The temperature of the heating is different depending on the type of the organic compound and/or the inorganic compound. Usually, the lower limit is 10°C or higher, and the upper limit is 200°C or lower. In particular, 20°C to 150°C is preferable.

The heat treatment time is also different depending on the type of the organic compound and/or the inorganic compound. However, 0.1 to 20 hours is preferable, and 0.5 to 15 hours is particularly preferable.

The treatment with the organic compound and/or the inorganic compound may be conducted a plurality of times in order that the treatment is conducted sufficiently.

[0080]

In the case of the liquid phase and the flow type, the treatment of the solid acid catalyst with the organic compound and/or the inorganic compound can be conducted by passing directly the organic compound and/or the inorganic compound for the treatment or an organic compound and/or an inorganic compound prepared by diluting the organic compound and/or the inorganic compound with a solvent through the solid acid catalyst having surface hydroxyl groups and conducting heating.

[0081]

Any one of a fixed bed and a fluidized bed can be used in a flow apparatus. The fluidized bed is preferable from the viewpoint of ease of uniform treatment of the catalyst.

[0082]

The solvent is not specifically limited, and usually, hydrocarbons are used. Preferably, pentane, hexane, heptane, benzene, toluene, and xylene are used. These solvents may be used alone or a mixture of at least two types may be used. The concentration after dilution is determined appropriately on the basis of the type of the organic compound and/or the inorganic compound for treatment.

[0083]

The flow rate thereof is not specifically limited. However, SV of 0.1 to 100 h⁻¹ is preferable, and SV of 0.5 to 50 h⁻¹ is particularly preferable.

The temperature of the heating is different depending on the type of the organic compound and/or the inorganic compound. Usually, the lower limit is 10°C or higher, and the upper limit is 300°C or lower. In particular, 20°C to 200°C is preferable.

The heat treatment time is different depending on the type of the organic compound and/or the inorganic compound. However, 0.1 to 20 hours are preferable, and 0.5 to 15 hours are particularly preferable.

The treatment with the organic compound and/or the inorganic compound may be conducted a plurality of times in order that the treatment is conducted sufficiently.

[0084]

In the case of the gas phase, the treatment of the solid acid catalyst with the organic compound and/or the inorganic compound can be conducted by heating while the organic compound for the treatment or an organic compound diluted with an inactive gas, each organic compound being in the gasified state, is passed through the solid acid catalyst having surface hydroxyl groups.

[0085]

Any one of a fixed bed and a fluidized bed can be used in a flow apparatus. The fluidized bed is preferable from the viewpoint of ease of uniform treatment of the catalyst.

[0086]

Usually, nitrogen, argon, carbon dioxide gas, helium, and air are used as the inactive diluent gas. Nitrogen, carbon dioxide gas, and argon are preferable. These diluent gases may be used alone or a mixture of at least two types may be used.

[0087]

The concentration of the organic compound gas in the inactive gas is not specifically limited. Usually, the concentration is 0.05 to 100 percent by mole, preferably 0.1 to 80 percent by mole, and particularly preferably 0.1 to 50 percent by mole.

[0088]

The temperature of the heating is different depending on the type of the organic compound. However, 10°C to 400°C is preferable, and 20°C to 300°C is particularly preferable.

The flow rate thereof is not specifically limited. However, SV of 10 to 5,000 h⁻¹ is preferable, and SV of 30 to 4,000 h⁻¹ is particularly preferable.

The heat treatment time is also different depending on the type of the organic compound. However, 0.1 to 20 hours is preferable, and 0.5 to 15 hours is particularly

preferable.

The treatment with the organic compound and/or the inorganic compound may be conducted a plurality of times in order that the treatment is conducted sufficiently.

[0089]

If water is contained in the organic compound and/or the inorganic compound and the solvent to be used in the treatment of the solid acid catalyst, the catalyst performance rather deteriorates. Therefore, it is preferable that the organic compound and/or the inorganic compound and the solvent to be used in the treatment of the solid acid catalyst are subjected to a treatment for removing water to a high degree with a dehydrating agent or the like in such a way that the water content becomes 10 percent by weight or less, preferably 5 percent by weight or less, and particularly preferably 2 percent by weight or less.

[0090]

However, in the case where the organic compound and/or the inorganic compound to be used in the treatment is not decomposed by water, the treated solid acid catalyst can be fired at a temperature of 300°C or higher before being used in a reaction, and the amount of surface hydroxyl group of the solid acid catalyst can be kept at 2.5 $\mu\text{mol/g}$ or less after firing, there is no problem even when water is

contained.

[0091]

<Solid acid catalyst treated with organic compound and/or inorganic compound>

It is believed that the solid acid catalyst produced by the above-described steps has the characteristics described below.

[0092]

That is, it is believed that since hydrophobic groups derived from the organic compound and/or the inorganic compound are bonded to the surface hydroxyl groups, the hydrophobicity of the catalyst surface is improved, an influence of water which may adversely affect the catalyst is reduced, and the performance of the catalyst is prevented from deteriorating over time. Furthermore, it is believed that since the reactive surface hydroxyl groups have been already bonded to the hydrophobic groups, the polyether, which is a reaction product, is prevented from bonding to or interacting with the surface hydroxyl groups, and the performance of the catalyst is prevented from deteriorating over time.

[0093]

The solid acid catalyst treated with the organic compound and/or the inorganic compound may be fired at a temperature of 300°C or higher, for example, 300°C to

1,000°C, for the purpose of removing excess treatment agents and water before being used in a reaction insofar as the amount of surface hydroxyl group can be kept at 2.5 $\mu\text{mol/g}$ or less.

[0094]

Consequently, deterioration of the performance of catalyst over time, that is, deterioration of the catalyst activity over time, and deterioration of the molecular weight distribution of the resulting polyether over time are prevented as compared with a solid acid catalyst which is prepared by a known technology and which is not treated with the organic compound and/or the inorganic compound. Therefore, a polyether having a narrow molecular weight distribution can be produced at a small amount of catalyst stably for the long term.

[0095]

{Solid acid catalyst to be used in reaction}

The solid acid catalyst to be used in the polymerization reaction or condensation reaction of the raw material compound is a solid acid catalyst having an amount of surface hydroxyl group of 0.1 to 2.5 $\mu\text{mol/m}^2$ and an amount of acid exhibiting pKa of -5.6 or less of 20 $\mu\text{mol/g}$ or more.

If the amount of surface hydroxyl group of the solid acid catalyst exceeds 2.5 $\mu\text{mol/m}^2$, the polyether having a

narrow molecular weight distribution, which is the object of the present invention, cannot be obtained.

If the amount of acid exhibiting pKa of -5.6 or less of the solid acid catalyst is less than 20 $\mu\text{mol/g}$, a sufficient polymerization activity cannot be obtained. Consequently, a need for using a large amount of catalyst arises in the production of the polyether.

A preferable amount of surface hydroxyl group of the solid acid catalyst is 0.1 to 2.0 $\mu\text{mol/m}^2$. A preferable amount of acid exhibiting pKa of -5.6 or less is 40 $\mu\text{mol/g}$ or more, and further preferably 60 $\mu\text{mol/g}$ or more.

[0096]

The amount of surface hydroxyl group of the solid acid catalyst and the amount of acid exhibiting pKa of -5.6 or less can be measured as described below, for example.

[Amount of surface hydroxyl group]

After 0.7 g of sample is taken into a U-tube, drying is conducted at 300°C for 1 hour while a high-purity Ar is passed at 40 cc/min. The U-tube is allowed to stand for cooling and is taken off while being kept from the air so as to be transferred to a dry Air grove bag.

The sample is put into an Erlenmeyer flask placed in the glove bag in advance, and 20 cc of dry toluene is added thereto. The Erlenmeyer flask is set in a titration experiment apparatus through which N₂ is passed at 80 cc/min.

In an Ar glove box, 5 cc of ether solution of 1.5-M methyllithium LiBr complex is taken into a plastic syringe, the syringe is taken out while the needlepoint is sealed with rubber, and the ether solution is injected into the Erlenmeyer flask through a septum.

A purge gas is collected into a Tedlar bag for 10 minutes, and the methane concentration is quantified with GC. The purge gas flow rate is measured with a precision film flowmeter. The amount of surface hydroxyl group per weight of catalyst is calculated from the amount of generated methane determined from the methane concentration and the purge gas flow rate.

The surface area per weight of the catalyst is measured with HM Model-1201 produced by Mountech Co., Ltd., by a nitrogen adsorption BET one-point method, and the amount of surface hydroxyl group per catalyst surface area is calculated therefrom.

[0097]

[Amount of acid exhibiting pKa of -5.6 or less]

The catalyst is dried at 200°C for 3 hours in a vacuum, and the catalyst is weighed in the glove box in a nitrogen atmosphere. After 2 ml of toluene is added, setting in a UV measurement apparatus is conducted. As an indicator, 1 ml of 0.2-percent-by-weight benzalacetophenone (for pKa $\leq$ -5.6)/toluene solution is added. The amount of acid

exhibiting pKa of -5.6 or less is calculated from the amount of n-butylamine dropped until a UV peak of benzalacetophenone bonded to acid points is disappeared by using 0.01 mol/L of n-butylamine as a titration reagent.

[0098]

[Process for production of polyether]

The process for production of a polyether according to the second aspect, in which the solid acid catalyst treated with the above-described organic compound and/or the inorganic compound is used, and the process for production of a polyether according to the first aspect, in which the solid acid catalyst having the amount of surface hydroxyl group of 0.1 to 2.5 $\mu\text{mol}/\text{m}^2$ and the amount of acid exhibiting pKa of -5.6 or less of 20 $\mu\text{mol}/\text{g}$ or more is used as the catalyst for polymerization, will be described below.

[0099]

Although not specifically limited, it is preferable that the processes for production of a polyether according to the first and the second aspects are conducted by a ring-opening polymerization reaction of cyclic ethers or a dehydration and condensation reaction of polyols. Processes in which the cyclic ethers are used as raw materials for the reaction, and polyethers are produced by subjecting them to the ring-opening polymerization reaction are more preferable.

[0100]

In the case where polyethers are produced by ring-opening polymerization reaction of cyclic ethers, examples of cyclic ethers to be used as the raw materials for the reaction include cyclic ethers in which the number of carbon constituting the ring is 3 to 10. Furthermore, cyclic ethers including alkyl groups, halogen groups, acyl groups, and the like as substituents can also be used. Specifically, tetrahydrofuran, oxetane, oxepane, 1,4-dioxane, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, and the like are used. Any one of homogeneous polymerization by using merely one type of cyclic ether and copolymerization by using at least two types of cyclic ethers can be conducted.

[0101]

At least one type of the solid acid catalyst treated with the organic compound and/or the inorganic compound or the solid acid catalyst having an amount of surface hydroxyl group of 0.1 to 2.5 $\mu\text{mol}/\text{m}^2$ and an amount of acid exhibiting pK_a of -5.6 or less of 20 $\mu\text{mol}/\text{g}$ or more, as described above, is used as the catalyst.

[0102]

Preferably, the ring-opening polymerization reaction of the cyclic ether is conducted in the presence of a carboxylic anhydride and/or a carboxylic acid from the viewpoint of the molecular weight control. In general, aliphatic or aromatic carboxylic anhydrides and/or

carboxylic acids having 2 to 12 carbon atoms are used, and preferably those having 2 to 8 carbon atoms are used. These carboxylic anhydrides and/or carboxylic acids may be used alone or at least two types may be used in combination. it is favorable that the carboxylic anhydride and/or the carboxylic acid is added usually at within the range of 0.01 to 1.0 (mole ratio) relative to the cyclic ether.

[0103]

In the polymerization reaction, a solvent inactive to the reaction can also be used. In general, at least one type of aliphatic hydrocarbons, aromatic hydrocarbons, and the like inactive to the ring-opening polymerization reaction is used as the solvent.

[0104]

A generally adopted reaction form, e.g., a vessel type or a tower type, is used, and any one of a batch system and a continuous system is adopted. Examples thereof include a method in which the cyclic ether, the catalyst, and the carboxylic anhydride and/or the carboxylic acid are charged and polymerized with agitation (batch system) and a method in which the cyclic ether and the carboxylic anhydride and/or the carboxylic acid are continuously supplied to a reactor including the catalyst and a reaction liquid is continuously taken out (continuous system). The continuous system is preferable from the viewpoint of the productivity.

[0105]

The usage of the solid acid catalyst is determined on the basis of the type thereof, and is not specifically limited. For example, in the batch type reactor, if the amount of catalyst is too small, the polymerization rate is reduced. Conversely, if the amount is too large, removal of a polymerization heat becomes difficult. Furthermore, since the slurry concentration of the reaction system increases, agitation becomes difficult, and a problem tends to occur in separation of the catalyst and the reaction liquid after the completion of the polymerization reaction. Therefore, the usage of the catalyst is usually selected within the range of 0.001 to 50 times on a weight basis relative to the liquid phase, preferably the range of 0.01 to 20 times on a weight basis in consideration of the reaction form being the batch reaction or the flow reaction. For the flow reaction, the usage of the catalyst refers to the amount of the catalyst relative to the amount of supply of the liquid phase per unit time.

[0106]

The reaction temperature is usually 0°C to 200°C, and preferably 10°C to 80°C.

The reaction pressure may be any pressure insofar as the reaction system is allowed to maintain a liquid phase at that pressure. Usually, the pressure is selected within the

range of normal pressure to 10 MPa, and preferably normal pressure to 5 MPa.

The reaction time is not specifically limited. However, in consideration of both the reaction time and the amount of catalyst and in consideration of the yield and the economic efficiency, preferably, the reaction time is within the range of 0.1 to 20 hours, and preferably within the range of 0.5 to 15 hours. In the batch system, the reaction time refers to a period from the point in time when the temperature is raised to the reaction temperature until the reaction is finished and the cooling is started. In the continuous system, the reaction time refers to a residence time of a reaction composition liquid in the reactor.

[0107]

The molecular weight distribution of the resulting polyether is depending on the type of the raw material compound. However, in the case where a ring-opening polymerization reaction of tetrahydrofuran (THF) is conducted by using the solid acid catalyst treated with the organic compound and/or the inorganic compound or the solid acid catalyst having the amount of surface hydroxyl group of 0.1 to 2.5 $\mu\text{mol}/\text{m}^2$ and the amount of acid exhibiting pKa of -5.6 or less of 20 $\mu\text{mol}/\text{g}$ or more according to the present invention, a polyether having a number average molecular weight (M_n) of 200 to 80,000 and, in particular, a low to

middle molecular weight of about 200 to 40,000 can be obtained. Furthermore, it is one of the features that a polyether having a narrow molecular weight distribution can be easily produced. That is, there is a great demand for a polyether exhibiting Mw/Mn of 1.3 to 2.5 industrially. Polytetramethylene ether glycol (PTMG) exhibiting Mw/Mn of less than 3, for example, 1.1 to 3.0, can be obtained by using the solid acid catalyst according to the present invention. In particular, when a preferable condition of the present invention is selected, a polyether having a very narrow molecular weight distribution Mw/Mn of about 1.4 to 1.7 can also be obtained. According to the present invention, the yield of the product is allowed to become 15% or more, preferably 20% or more, and furthermore 25% or more.

[0108]

Moreover, since deterioration of the performance of the catalyst over time is reduced, the state of a high degree of conversion can be maintained even when the reaction is conducted for the long term.

[0109]

The polyethers produced according to the first and the second aspects can be used for applications to elastic fibers, thermoplastic polyester elastomers, thermoplastic polyurethane elastomers, coating materials, and the like.

[Examples and comparative examples]

[0110]

The first and the second aspects will be further specifically described below with reference to synthesis examples, examples, and comparative examples. However the following examples do not limit the scope of the first and the second aspects.

[0111]

In the following description, the degree of conversion, the number average molecular weight (M_n), and the molecular weight distribution (M_w/M_n) of polytetramethylene ether glycol acetic acid ester (PTME) were determined with GPC (gel permeation chromatography) described below.

GPC apparatus: GPC 8220 produced by Tosoh Corporation

Column: TSK-GEL GMHHR-M (30 cm) $\times$ 4 units

Detection method: RI

Column temperature: 40°C

Moving bed: THF

Flow rate: 1 ml/min

Amount of injection of sample: 500 μ l

Sample concentration: adjusted in such a way that the concentration of a polyether becomes about 0.5 percent by weight

[0112]

The amount of surface hydroxyl group and the amount of acid of the solid acid catalyst were measured as described

below.

[Amount of surface hydroxyl group]

After 0.7 g of sample is taken into a U-tube, drying is conducted at 300°C for 1 hour while a high-purity Ar is passed at 40 cc/min. The U-tube is allowed to stand for cooling, and is taken off while being kept from the air so as to be transferred to a dry Air glove bag.

The sample is put into an Erlenmeyer flask placed in the glove bag in advance, and 20 cc of dry toluene is added thereto. The Erlenmeyer flask is set in a titration experiment apparatus in which N₂ is passed at 80 cc/min. In an Ar glove box, 5 cc of ether solution of 1.5-M methyllithium LiBr complex is taken into a plastic syringe, the syringe is taken out while the needlepoint is sealed with rubber, and the ether solution is injected into the Erlenmeyer flask through a septum.

A purge gas is collected into a Tedlar bag for 10 minutes, and the methane concentration is quantified with GC. The purge gas flow rate is measured with a precision film flowmeter. The amount of surface hydroxyl group per weight of catalyst is calculated from the amount of generated methane determined from the methane concentration and the purge gas flow rate.

The surface area per weight of the catalyst is measured with HM Model-1201 produced by Mountech Co., Ltd., by a

nitrogen adsorption BET one-point method, and the amount of surface hydroxyl group per catalyst surface area is calculated therefrom.

[Amount of acid exhibiting pKa of -5.6 or less]

The catalyst is dried at 200°C for 3 hours in a vacuum, and the catalyst is weighed in the glove box in a nitrogen atmosphere. After 2 ml of toluene is added, setting in a UV measurement apparatus is conducted. As an indicator, 1 ml of 0.2-percent-by-weight benzalacetophenone (for pKa $\leq$ -5.6)/toluene solution is added. The amount of acid exhibiting pKa of -5.6 or less is calculated from the amount of n-butylamine dropped until a UV peak of benzalacetophenone bonded to acid points is disappeared by using 0.01 mol/L of n-butylamine as a titration reagent.

[0113]

<Preparation of solid acid catalyst having surface hydroxyl groups>

Catalyst synthesis example 1-1:

After 89.66 g of zirconium oxynitrate aqueous solution (produced by Shin Nippon Metal & Chemical Co., Ltd., concentration 18.12 percent by weight in terms of ZrO_2) was blended with 18.72 g of desalted water, mixing was conducted homogeneously. The resulting mixture was blended with 11.84 g of urea and mixing was conducted homogeneously so as to prepare an impregnation solution. The resulting solution

was blended with 80 g of SiO₂ (produced by Fuji Silysia Chemical Ltd., CARIACT Q15, particle diameter 75 to 500 μ m, average particle diameter 200 μ m, pore volume 1.16 ml/g, average pore diameter 15 nm), and impregnation was conducted by pore-filling (the amount of impregnation solution was 100% of the carrier pore volume) while mixing was conducted by shaking for about 1 hour.

[0114]

This was put into a 500-ml pear-shaped flask, a joint and a curved tube filled with glass wool were connected to the upper portion of the flask, and a thermometer was connected to a measurement portion. Thereafter, the flask was fixed with a clamp to a rotating shaft of a rotary drier. The rotating shaft was rotated at a speed of 10 rpm, the temperature of the drier was set at 105°C, and heating was conducted for 6 hours. At this time, it was ascertained by the weight change that 90% of water in the impregnation solution remained. After the curved tube filled with glass wool at the upper portion was removed, the temperature of the drier was set at 120°C, and heating was conducted for 16 hours.

After the joint at the upper portion was removed, the temperature of the drier was set at 140°C, and heating was conducted for 4 hours so as to remove the water almost completely. The heating and rotation were terminated after

a lapse of 4 hours, and the catalyst was taken out.

[0115]

The catalyst was transferred to a 500-ml beaker and stood for cooling to room temperature. After about 300 ml of desalted water was added, suspension washing was conducted for about 10 minutes. The catalyst was filtrated and was transferred to the 500-ml beaker again. A solution, in which 30 g of ammonium bicarbonate was dissolved into 300 ml of desalted water, was added and suspension washing was conducted for about 10 minutes. The catalyst was filtrated and was transferred to the 500-ml beaker again. After about 300 ml of desalted water was added, suspension washing was conducted for about 10 minutes. This washing with the desalted water was repeated two times. The catalyst was air-dried and dried with a drier at 120°C for a night. Subsequently, firing was conducted at 900°C for 2 hours while the air was passed.

The resulting solid acid catalyst was assumed to be "Catalyst 1". The amount of supported zirconium oxide of Catalyst 1 determined by calculation on the basis of the impregnation solution composition was 16.9 percent by weight relative to the entire amount of the catalyst.

The amount of surface hydroxyl group of Catalyst 1 was $2.6 \mu\text{mol}/\text{m}^2$, and the amount of acid exhibiting pKa of -5.6 or less was 110 $\mu\text{mol}/\text{g}$.

[0116]

Catalyst synthesis example 1-2

A homogeneous solution was prepared by adding 0.44 g of desalted water to 89.66 g of zirconium oxynitrate aqueous solution (produced by Shin Nippon Metal & Chemical Co., Ltd., concentration 18.12 percent by weight in terms of ZrO_2). A homogeneous solution was prepared by gradually adding 26.94 g of 25-percent-by-weight ammonium carbonate aqueous solution thereto with agitation. Thereafter, 7.94 g of urea was gradually added so as to prepare an impregnation solution. The resulting solution was blended with 80 g of SiO_2 (produced by Fuji Silysia Chemical Ltd., CARIAMIT Q30, particle diameter 75 to 500 μm , average particle diameter 200 μm , pore volume 1.21 ml/g, average pore diameter 30 nm), and impregnation was conducted by pore-filling (the amount of impregnation solution was 100% of the carrier pore volume) while mixing was conducted by shaking for about 1 hour.

[0117]

This was put into a 500-ml pear-shaped flask, a joint and a curved tube filled with glass wool were connected to the upper portion of the flask, and a thermometer was connected to a measurement portion. Thereafter, the flask was fixed with a clamp to a rotating shaft of a rotary drier. The rotating shaft was rotated at a speed of 10 rpm, the

temperature of the drier was set at 105°C, and heating was conducted for 2 hours. After the curved tube filled with glass wool at the upper portion was removed, the temperature of the drier was set at 120°C, and heating was conducted for 16 hours.

After the joint at the upper portion was removed, the temperature of the drier was set at 140°C, and heating was conducted for 4 hours, so as to remove the water completely. The heating and rotation were terminated after a lapse of 4 hours, and the catalyst was taken out.

[0118]

The catalyst was transferred to a 500-ml beaker and stood for cooling to room temperature. After about 300 ml of desalted water was added, suspension washing was conducted for about 10 minutes. The catalyst was filtrated and was transferred to the 500-ml beaker again. A solution, in which 30 g of ammonium bicarbonate was dissolved into 300 ml of desalted water, was added and suspension washing was conducted for about 10 minutes. The catalyst was filtrated and was transferred to the 500-ml beaker again. After about 300 ml of desalted water was added, suspension washing was conducted for about 10 minutes. This washing with the desalted water was repeated two times. The catalyst was air-dried and dried with a drier at 120°C for a night. Subsequently, firing was conducted at 900°C for 2 hours

while the air was passed.

The resulting solid acid catalyst was assumed to be "Catalyst 2". The amount of supported zirconium oxide of Catalyst 2 determined by calculation on the basis of the impregnation solution composition was 16.9 percent by weight relative to the entire amount of the catalyst.

The amount of surface hydroxyl group of Catalyst 2 was $3.4 \mu\text{mol}/\text{m}^2$, and the amount of acid exhibiting pKa of -5.6 or less was $100 \mu\text{mol}/\text{g}$.

[0119]

Catalyst synthesis example 1-3

After 88.01 g of zirconium oxynitrate aqueous solution (produced by Shin Nippon Metal & Chemical Co., Ltd., concentration 18.12 percent by weight in terms of ZrO_2) was blended with 26.13 g of desalted water, mixing was conducted homogeneously. The resulting mixture was blended with 11.84 g of urea and mixing was conducted homogeneously so as to prepare an impregnation solution. The resulting solution was blended with 80 g of SiO_2 (produced by Fuji Silysia Chemical Ltd., CARIACT Q30), and impregnation was conducted by pore-filling (the amount of impregnation solution was 100% of the carrier pore volume) while mixing was conducted by shaking for about 1 hour.

[0120]

This was put into a 500-ml pear-shaped flask, a joint

and a curved tube filled with glass wool were connected to the upper portion of the flask, and a thermometer was connected to a measurement portion. Thereafter, the flask was fixed with a clamp to a rotating shaft of a rotary drier. The rotating shaft was rotated at a speed of 10 rpm, the temperature of the drier was set at 105°C, and heating was conducted for 2 hours. After the curved tube filled with glass wool at the upper portion was removed, the temperature of the drier was set at 120°C, and heating was conducted for 16 hours.

After the joint at the upper portion was removed, the temperature of the drier was set at 140°C, and heating was conducted for 4 hours, so as to remove the water completely. The heating and rotation were terminated after a lapse of 4 hours, and the catalyst was taken out.

[0121]

The catalyst was transferred to a 500-ml beaker and stood for cooling to room temperature. After about 300 ml of desalted water was added, suspension washing was conducted for about 10 minutes. The catalyst was filtrated and was transferred to the 500-ml beaker again. A solution, in which 30 g of ammonium bicarbonate was dissolved into 300 ml of desalted water, was added and suspension washing was conducted for about 10 minutes. The catalyst was filtrated and was transferred to the 500-ml beaker again. After about

300 ml of desalted water was added, suspension washing was conducted for about 10 minutes. This washing with the desalted water was repeated two times. The catalyst was air-dried and dried with a drier at 120°C for a night. Subsequently, firing was conducted at 900°C for 2 hours while the air was passed.

The resulting solid acid catalyst was assumed to be "Catalyst 3". The amount of supported zirconium oxide of Catalyst 3 determined by calculation on the basis of the impregnation solution composition was 16.9 percent by weight relative to the entire amount of the catalyst.

The amount of surface hydroxyl group of Catalyst 3 was $3.3 \mu\text{mol}/\text{m}^2$, and the amount of acid exhibiting pKa of -5.6 or less was 100 $\mu\text{mol}/\text{g}$.

[0122]

Catalyst synthesis example 1-4

A solid acid catalyst obtained by firing Tonsil OptimumFF, which was a clay (activated clay) catalyst and which was produced by Sued Chemie, at 400°C for 1 hour while the air was passed was assumed to be "Catalyst 4".

The amount of surface hydroxyl group of Catalyst 4 was $3.5 \mu\text{mol}/\text{m}^2$, and the amount of acid exhibiting pKa of -5.6 or less was 190 $\mu\text{mol}/\text{g}$.

[0123]

<Treatment of solid acid catalyst with organic compound

and/or inorganic compound and production of polyether>

Example 1-1

[Treatment of solid acid catalyst with organic compound and/or inorganic compound]

In a nitrogen atmosphere, 100 ml of ethanol (water content 50 ppm) dehydrated with molecular sieve 3A in advance and 98.3 g (832.2 mmol) of diethyl carbonate (water content 50 ppm) were mixed in a 500-ml flask provided with a reflux cooling pipe. Here, after 50 g of (Catalyst 1) was added to the above-described mixed solution while agitation was conducted, and heating was conducted in an oil bath for 1 hour with reflux. After standing for cooling, the reflux cooling pipe was replaced with a distillation head, the temperature was gradually raised by heating in the oil bath, ethanol and diethyl carbonate were removed by distillation at 90°C to 140°C, and a treatment was conducted for 4 hours in the oil bath at 140°C while nitrogen was passed. After standing for cooling, the resulting catalyst was preserved in an enclosed container in a nitrogen atmosphere so as to serve as a catalyst for evaluation.

The amount of surface hydroxyl group of this catalyst for evaluation was $1.5 \mu\text{mol}/\text{m}^2$, and the amount of acid exhibiting pKa of -5.6 or less was 110 $\mu\text{mol}/\text{g}$.

[0124]

[Evaluation of polyether production reaction]

A flow reaction apparatus having a volume of 520 ml was charged with 22 g of this catalyst for evaluation. A mixed solution of THF, acetic anhydride, and acetic acid (weight ratio, THF 258.6, acetic anhydride 29.3, acetic acid 1) was passed at a flow rate of 87.4 ml/h, and heating was conducted up to 35°C. A reaction solution was taken at evenly spaced time intervals, and the yield, the number average molecular weight (M_n), and the molecular weight distribution (M_w/M_n) were measured with GPC.

[0125]

The initial degree of conversion was 34.2%, the initial M_n was 2,257, and the initial M_w/M_n was 1.81. When the reaction time was 162.5 h, the degree of conversion was 28.3% (the degree of conversion relative to the initial value was 83%), M_n was 2,232, and M_w/M_n was 1.80 (deterioration relative to the initial value was -0.01).

[0126]

Comparative example 1-1

Evaluation of polyether production reaction was conducted as in Example 1-1 except that 22g of the above-described Catalyst 1 was used without being treated.

The initial degree of conversion was 39.7%, the initial M_n was 1,851, and the initial M_w/M_n was 1.82. When the reaction time was 161.5 h, the degree of conversion was 28.2% (the degree of conversion relative to the initial

value was 71%), Mn was 1,813, and Mw/Mn was 1.85 (deterioration relative to the initial value was +0.03).

[0127]

Example 1-2

A fixed-bed flow treatment apparatus was filled with 40 g of the above-described Catalyst 2, and nitrogen was passed at a flow rate of 0.8 L/min. Thereafter, in addition to the nitrogen, passing of methanol (water content 50 ppm) in a gaseous state at a flow rate of 32 mg /min was started, heating was conducted up to 100°C, and that state was kept for 5 hours. The passing of methanol was terminated after a lapse of 5 hours, merely nitrogen was passed, and that state was kept for 4 hours. After standing for cooling, the resulting catalyst was preserved in an enclosed container in a nitrogen atmosphere so as to serve as a catalyst for evaluation.

The amount of surface hydroxyl group of this catalyst for evaluation was $2.0 \mu\text{mol}/\text{m}^2$, and the amount of acid exhibiting pKa of -5.6 or less was $90 \mu\text{mol}/\text{g}$.

[0128]

Evaluation of polyether production reaction was conducted as in Example 1-1 except that 22g of this catalyst for evaluation was used.

The initial degree of conversion was 34.4%, the initial Mn was 2,399, and the initial Mw/Mn was 1.76. When the

reaction time was 162.0 h, the degree of conversion was 25.3% (the degree of conversion relative to the initial value was 74%), Mn was 2,322, and Mw/Mn was 1.77 (deterioration relative to the initial value was +0.01).
[0129]

Example 1-3

A fluidized-bed flow treatment apparatus was filled with 80 g of the above-described Catalyst 2, and nitrogen was passed at a flow rate of 1.6 L/min. Thereafter, in addition to the nitrogen, passing of trimethylsilyl acetate in a gaseous state at a flow rate of 88 mg /min was started, heating was conducted up to 100°C, and that state was kept for 5 hours. The passing of trimethylsilyl acetate was terminated after a lapse of 5 hours, heating was conducted up to 200°C, merely nitrogen was passed, and that state was kept for 4 hours. After standing for cooling, the resulting catalyst was preserved in an enclosed container in a nitrogen atmosphere so as to serve as a catalyst for evaluation.

The amount of surface hydroxyl group of this catalyst for evaluation was $1.4 \mu\text{mol}/\text{m}^2$, and the amount of acid exhibiting pKa of -5.6 or less was $100 \mu\text{mol}/\text{g}$.

[0130]

Evaluation of polyether production reaction was conducted as in Example 1-1 except that 22g of this catalyst

for evaluation was used.

The initial degree of conversion was 33.0%, the initial Mn was 3,090, and the initial Mw/Mn was 1.80. When the reaction time was 162.0 h, the degree of conversion was 27.0% (the degree of conversion relative to the initial value was 82%), Mn was 2,967, and Mw/Mn was 1.78 (deterioration relative to the initial value was -0.02).
[0131]

Comparative example 1-2

Evaluation of polyether production reaction was conducted as in Example 1-1 except that 22g of the above-described Catalyst 2 was used without being treated.

The initial degree of conversion was 32.0%, the initial Mn was 2,287, and the initial Mw/Mn was 1.76. When the reaction time was 163.7 h, the degree of conversion was 23.5% (the degree of conversion relative to the initial value was 73%), Mn was 2,282, and Mw/Mn was 1.81 (deterioration relative to the initial value was +0.05).
[0132]

Example 1-4

A fluidized-bed flow treatment apparatus was filled with 80 g of the above-described Catalyst 3, and nitrogen was passed at a flow rate of 1.6 L/min. Heating was conducted up to 100°C. Thereafter, in addition to the nitrogen, passing of trimethylsilyl acetate (water content

10 ppm or less) in a gaseous state at a flow rate of 88 mg/min was started, and that state was kept for 5 hours. The passing of trimethylsilyl acetate was terminated after a lapse of 5 hours, heating was conducted up to 200°C, merely nitrogen was passed, and that state was kept for 4 hours. After standing for cooling, the resulting catalyst was preserved in an enclosed container in a nitrogen atmosphere so as to serve as a catalyst for evaluation.

The amount of surface hydroxyl group of this catalyst for evaluation was $1.6 \mu\text{mol}/\text{m}^2$, and the amount of acid exhibiting pKa of -5.6 or less was $100 \mu\text{mol}/\text{g}$.

[0133]

Evaluation of polyether production reaction was conducted as in Example 1-1 except that 22g of this catalyst for evaluation was used.

The initial degree of conversion was 28.8%, the initial Mn was 2,022, and the initial Mw/Mn was 1.64. When the reaction time was 142.5 h, the degree of conversion was 23.5% (the degree of conversion relative to the initial value was 82%), Mn was 1,890, and Mw/Mn was 1.66 (deterioration relative to the initial value was +0.02).

[0134]

Example 1-5

A fluidized-bed flow treatment apparatus was filled with 80 g of the above-described Catalyst 3, and nitrogen

was passed at a flow rate of 1.6 L/min. Heating was conducted up to 100°C. Thereafter, in addition to the nitrogen, passing of diethylmethyilsilane (water content 10 ppm or less) in a gaseous state at a flow rate of 68 mg /min was started, and that state was kept for 5 hours. The passing of diethylmethyilsilane was terminated after a lapse of 5 hours, heating was conducted up to 200°C, merely nitrogen was passed, and that state was kept for 4 hours. After standing for cooling, the resulting catalyst was preserved in an enclosed container in a nitrogen atmosphere so as to serve as a catalyst for evaluation.

The amount of surface hydroxyl group of this catalyst for evaluation was $2.0 \mu\text{mol}/\text{m}^2$, and the amount of acid exhibiting pKa of -5.6 or less was $100 \mu\text{mol}/\text{g}$.

[0135]

Evaluation of polyether production reaction was conducted as in Example 1-1 except that 22g of this catalyst for evaluation was used.

The initial degree of conversion was 31.4%, the initial Mn was 1,746, and the initial Mw/Mn was 1.64. When the reaction time was 139.7 h, the degree of conversion was 25.3% (the degree of conversion relative to the initial value was 81%), Mn was 1,797, and Mw/Mn was 1.66 (deterioration relative to the initial value was +0.02).

[0136]

Example 1-6

A fluidized-bed flow treatment apparatus was filled with 80 g of the above-described Catalyst 3, and nitrogen was passed at a flow rate of 1.6 L/min. Heating was conducted up to 140°C. Thereafter, in addition to the nitrogen, passing of diethylmethylsilane (water content 10 ppm or less) in a gaseous state at a flow rate of 23 mg /min was started, and that state was kept for 5 hours. The passing of diethylmethylsilane was terminated after a lapse of 5 hours, heating was conducted up to 200°C, merely nitrogen was passed, and that state was kept for 4 hours. After standing for cooling, the resulting catalyst was preserved in an enclosed container in a nitrogen atmosphere so as to serve as a catalyst for evaluation.

The amount of surface hydroxyl group of this catalyst for evaluation was $2.0 \mu\text{mol}/\text{m}^2$, and the amount of acid exhibiting pKa of -5.6 or less was $100 \mu\text{mol}/\text{g}$.

[0137]

Evaluation of polyether production reaction was conducted as in Example 1-1 except that 22g of this catalyst for evaluation was used.

[0138]

The initial degree of conversion was 33.1%, the initial Mn was 2,090, and the initial Mw/Mn was 1.66. When the reaction time was 161.7 h, the degree of conversion was

27.4% (the degree of conversion relative to the initial value was 83%), Mn was 2,108, and Mw/Mn was 1.68 (deterioration relative to the initial value was +0.02).
[0138]

Comparative example 1-3

Evaluation of polyether production reaction was conducted as in Example 1-1 except that 22g of the above-described Catalyst 3 was used without being treated.

The initial degree of conversion was 29.6%, the initial Mn was 1,582, and the initial Mw/Mn was 1.68. When the reaction time was 139.5 h, the degree of conversion was 23.0% (the degree of conversion relative to the initial value was 78%), Mn was 1,567, and Mw/Mn was 1.74 (deterioration relative to the initial value was +0.06).
[0140]

Example 1-7

A fluidized-bed flow treatment apparatus was filled with 80 g of the above-described Catalyst 4, and nitrogen was passed at a flow rate of 1.6 L/min. Thereafter, in addition to the nitrogen, passing of trimethylsilyl acetate in a gaseous state at a flow rate of 88 mg /min was started, heating was conducted up to 100°C, and that state was kept for 5 hours. The passing of trimethylsilyl acetate was terminated after a lapse of 5 hours, heating was conducted up to 200°C, merely nitrogen was passed, and that state was

kept for 4 hours. After standing for cooling, the resulting catalyst was preserved in an enclosed container in a nitrogen atmosphere so as to serve as a catalyst for evaluation.

The amount of surface hydroxyl group of this catalyst for evaluation was $2.4 \mu\text{mol}/\text{m}^2$, and the amount of acid exhibiting pKa of -5.6 or less was $190 \mu\text{mol}/\text{g}$.

[0141]

Evaluation of polyether production reaction was conducted as in Example 1-1 except that 22g of this catalyst for evaluation was used.

[0142]

The initial degree of conversion was 29.0%, the initial Mn was 3,500, and the initial Mw/Mn was 1.84. When the reaction time was 165.4 h, the degree of conversion was 12.2% (the degree of conversion relative to the initial value was 42%), Mn was 3,470, and Mw/Mn was 1.85 (deterioration relative to the initial value was +0.01).

[0143]

Comparative example 1-4

Evaluation of polyether production reaction was conducted as in Example 1-1 except that 22g of the above-described Catalyst 4 was used without being treated.

The initial degree of conversion was 28.1%, the initial Mn was 2,668, and the initial Mw/Mn was 1.85. When the

reaction time was 165.4 h, the degree of conversion was 10.1% (the degree of conversion relative to the initial value was 36%), Mn was 2,794, and Mw/Mn was 2.00 (deterioration relative to the initial value was +0.15).
[0144]

The above-described evaluation results are shown in Table 1-1 and Table 1-2 collectively.

[0145]

[Table 1-1]

	Catalyst	Organic compound used for treatment	Catalyst used for reaction	
			Amount of surface hydroxyl group ($\mu\text{mol}/\text{m}^2$)	Amount of acid ($\mu\text{mol}/\text{g}$)
Comparative example 1-1	Catalyst 1	—	2.6	110
Example 1-1	Catalyst 1	ethanol/ diethyl carbonate	1.5	110
Comparative example 1-2	Catalyst 2	—	3.4	100
Example 1-2	Catalyst 2	methanol	2.0	90
Example 1-3	Catalyst 2	trimethylsilyl acetate	1.4	100
Comparative example 1-3	Catalyst 3	—	3.3	100
Example 1-4	Catalyst 3	trimethylsilyl acetate	1.6	100
Example 1-5	Catalyst 3	diethylmethysilane	2.0	100
Example 1-6	Catalyst 3	diethylmethysilane	2.0	100
Comparative example 1-4	Catalyst 4	—	3.5	190
Example 1-7	Catalyst 4	trimethylsilyl acetate	2.4	190

[0146]

[Table 1-2]

	Initial degree of conversion (%)	Initial Mn	Initial Mw/Mn	Elapsed time of reaction (h)	Degree of conversion after a lapse of time (%)	Mn after a lapse of time	Mw/Mn after a lapse of time	Relative degree of conversion (%)	Deterioration in Mw/Mn
Comparative example1-1	39.7	1851	1.82	161.5	28.2	1813	1.85	71	+0.03
Example1-1	34.2	2257	1.81	162.5	28.3	2232	1.80	83	-0.01
Comparative example1-2	32.0	2287	1.76	142.5	23.5	2282	1.81	73	+0.05
Example1-2	34.4	2399	1.76	162.0	25.3	2322	1.77	74	+0.01
Example1-3	33.0	3090	1.80	163.7	27.0	2967	1.78	82	-0.02
Comparative example1-3	29.6	1582	1.68	139.5	23.0	1567	1.74	78	+0.06
Example1-4	28.8	2022	1.64	142.5	23.5	1890	1.66	82	+0.02
Example1-5	31.4	1746	1.64	139.7	25.3	1797	1.66	81	+0.02
Example1-6	33.1	2090	1.66	161.7	27.4	2108	1.68	83	+0.02
Comparative example1-4	28.1	2668	1.85	165.4	10.1	2794	2.00	36	+0.15
Example1-7	29.0	3500	1.84	165.4	12.2	3470	1.85	42	+0.01

[0147]

As is clear from Table 1-1 and Table 1-2, the solid acid catalyst having a small amount of surface hydroxyl group and a large amount of acid can be obtained by treating the solid acid catalyst with an organic compound and/or an inorganic compound in advance, and deterioration in the degree of conversion over time can be prevented by using this solid acid catalyst. Furthermore, deterioration in the molecular weight distribution (M_w/M_n) of the resulting polyether over time can be prevented and a polyether having a narrow molecular weight distribution can be obtained.

[0148]

[Description of the third aspect]

The inventors of the present invention found that a metal hydroxide and/or a metal oxide was able to be supported in a carrier while being in a homogeneous, fine dispersion state by conducting a homogeneous precipitation method, which was a precipitation generation reaction from a homogeneous solution, in pores of a carrier. Consequently, the third aspect has been completed.

[0149]

In the homogeneous precipitation method, a precipitant (for example, a base) for converting metal salts to metal hydroxides is generated in the insides of carrier pores homogeneously. Therefore, it is believed that differences

in concentration of the metal hydroxide depending on the positions in the inside of the carrier become extremely small, and thereby, fine, homogeneous aggregations of metal hydroxide can be generated in the carrier without generating large aggregations so as to obtain a solid acid catalyst having a large amount of acid-base and a narrow acid strength distribution.

[0150]

The gist of the third aspect resides in a process for production of a solid acid catalyst, in which a metal hydroxide and/or a metal oxide is supported by a carrier, characterized by including the step of allowing the metal hydroxide and/or the metal oxide to be supported in pores of the carrier by conducting a homogeneous precipitation method in the carrier pores.

[0151]

According to the third aspect, the homogeneous precipitation method may be a homogeneous precipitation method by using a precipitant precursor.

[0152]

The above-described precipitant precursor may be a base precursor.

[0153]

The metal hydroxide and/or the metal oxide may be a hydroxide and/or an oxide of at least one type of metal

element selected from the group consisting of the group 3, the group 4, the group 5, the group 13, and the group 14 in the periodic table.

[0154]

The base precursor may be urea.

[0155]

According to the third aspect, a metal hydroxide and/or a metal oxide can be supported in a carrier while being in a homogeneous, fine dispersion state by conducting a homogeneous precipitation method, which is a precipitation generation reaction from a homogeneous solution, in pores of the carrier. As a result, a solid acid catalyst having a large amount of acid-base and a narrow acid strength distribution can be obtained.

[0156]

For example, in the ring-opening polymerization reaction of tetrahydrofuran, a polyether having a narrow molecular weight distribution can be produced at a high degree of conversion by using the above-described solid acid catalyst.

[0157]

The embodiment according to the third aspect will be described below in detail. However, the following description of constituent features is an example (typical example) of execution forms of the third aspect, and the

third aspect is not specifically limited to these contents within the bounds of the gist.

[0158]

The solid acid catalyst produced according to the third aspect is a solid acid catalyst, in which a metal hydroxide and/or a metal oxide is supported in carrier pores while being in a homogeneous, fine dispersion state by conducting a homogeneous precipitation method in the carrier pores.

[0159]

This homogeneous precipitation method is conducted by, for example, impregnating a carrier with a metal salt and a precipitant precursor, which generates a precipitant through a chemical reaction, e.g., hydrolysis, in a solution, at the same time, and subjecting the impregnated carrier to a treatment, e.g., a heat treatment, for generating the precipitant from the precipitant precursor. For the homogeneous precipitation method, it is important that the metal salt and the precipitant precursor constitute a liquid phase, that is, a solution. In the present invention, the carrier is impregnated with an impregnation solution including the metal salt and the precipitant precursor and, thereafter, the treatment for generating the precipitant from the precipitant precursor is conducted.

[0160]

[Process for production of solid acid catalyst]

A process for production of a solid acid catalyst according to the third aspect by the homogeneous precipitation method, in which the carrier is impregnated with the impregnation solution including the metal salt and the precipitant precursor and, thereafter, the treatment for generating the precipitant from the precipitant precursor is conducted, as described above, will be described.

[0161]

(1) Carrier

The carrier to be used in the third aspect is not specifically limited. However, metal oxides, composite metal oxides, zeolite and the like, and clay and the like are preferable. Silica, alumina, zirconia, titania, silica-alumina, silica-zirconia, and silica-titania are more preferable. Silica, alumina, and zirconia are particularly preferable.

[0162]

The particle diameter, the pore diameter, and the pore volume of the carrier are different depending on uses and application forms of the solid acid catalyst, and cannot be univocally specified.

[0163]

These carriers may be used alone or at least two types may be used in combination.

[0164]

(2) Metal hydroxide and/or metal oxide

The metal hydroxide and/or the metal oxide to be supported by the above-described carrier is not specifically limited. It is usually a hydroxide and/or an oxide of a metal element of groups 2 to 14 in the periodic table, preferably a hydroxide and/or an oxide of at least one type of metal element selected from the group consisting of the group 3, the group 4, the group 5, the group 13, and the group 14 in the periodic table, more preferably a hydroxide and/or an oxide of at least one type of metal element selected from the group consisting of Ti, Zr, Hf, Nb, Al, and Si, and particularly preferably a hydroxide and/or an oxide of at least one type of metal element selected from the group consisting of Ti, Zr, Al, and Nb.

[0165]

(3) Metal salt

The metal salt to be used in the homogeneous precipitation method is a metal salt, from which the above-described metal hydroxide and/or the metal oxide to be supported by the resulting solid acid catalyst is generated, and therefore, is usually a salt of the above-described metal element of groups 2 to 14 in the periodic table, preferably a metal element selected from the group consisting of the groups 3, 4, 5, 13, and 14, more preferably Ti, Zr, Hf, Nb, Al, or Si, and particularly

preferably Ti, Zr, Al, or Nb.

[0166]

The type of the salt is not specifically limited. However, a nitrate, an acetate, a sulfate, an oxynitrate, a chloride, or an oxychloride is preferable, and an oxynitrate, an oxychloride, and a sulfate is more preferable.

[0167]

That is, for the metal salt, a nitrate, an acetate, a sulfate, an oxynitrate, a chloride, or an oxychloride of a metal of the groups 2 to 14 in the periodic table is preferable, and zirconium oxynitrate, zirconium oxychloride, zirconium sulfate, titanium chloride, aluminum sulfate, or niobium oxychloride is further preferable.

[0168]

These metal salts may be used alone or at least two types may be used in combination.

[0169]

(4) Precipitant precursor

The precipitant precursor according to the present invention undergoes a chemical reaction, e.g., hydrolysis, by a treatment, e.g., heating, in an impregnation solution so as to generate a precipitant. The precipitant reacts with a metal salt in the impregnation solution so as to cause precipitation of a metal hydroxide and/or a metal oxide. Among precipitant precursors, a precipitant

precursor which generates a base as a precipitant, that is, the precipitant precursor which generates a base through hydrolysis or other chemical reaction in an impregnation solution and increases the pH of the solution so as to precipitate a metal salt as a hydroxide or an oxide, is referred to as a "base precursor".

[0170]

The precipitant precursor for conducting the homogeneous precipitation method is not specifically limited. However, in general, the base precursor is used.

[0171]

For the base precursor, urea, cyanuric acid, alkyl-substituted urea, thiourea, alkyl-substituted thiourea, amide compounds composed of amines and carboxylic acids, and the like are used. Preferably, urea, cyanuric acid, and alkyl-substituted urea are used. It is particularly preferable to use urea and cyanuric acid from the viewpoint of the ease of availability and the cost. These base precursors may be used alone or at least two types may be used in combination.

[0172]

(5) Basic substance

Not only the above-described base precursor, but also a predetermined amount of basic substance may be added to the impregnation solution in advance in order to increase the pH

within the bounds of not causing precipitation. It is also possible to reduce the usage of the base precursor and the time required to generate precipitation by using the basic substance.

[0173]

The basic substance is not specifically limited. Examples thereof include hydroxides, carbonates, bicarbonates, phosphates, and acetates of alkali metals, alkaline earth metals, and ammonium; ammonia; and organic amines. Ammonia; organic amines; and carbonates, bicarbonates, and phosphates of ammonia are preferable, and ammonium carbonates and ammonium bicarbonates are more preferable.

[0174]

These basic substances may be used alone or at least two types may be used in combination.

[0175]

(6) Impregnation solution

Usually, the impregnation solution is prepared by dissolving the above-described metal salt, the precipitant precursor and, if necessary, the basic substance into water.

[0176]

The concentrations of the metal salt and the precipitant precursor in the impregnation solution are not specifically limited, insofar as the dissolution state is

maintained and the concentration is suitable for realizing a favorable amount of support by a carrier described later. Usually, the metal salt concentration is 0.01 to 50 percent by weight, preferably 0.1 to 40 percent by weight, and particularly preferably 0.5 to 30 percent by weight. The precipitant precursor is 0.1 to 10 times the theoretical amount sufficient for precipitating the entire metal salt, preferably 0.2 to 8 times, and particularly preferably 0.3 to 5 times, as described later.

[0177]

The basic substance is used appropriately in such a way that a required pH condition is obtained. That is, since the pH condition required for generating precipitation is different depending on the types and the concentrations of the metal salt and the precipitant precursor to be used, the basic substance is used at an amount required in accordance with these conditions.

[0178]

In the present invention, in order to conduct the homogeneous precipitation method in the carrier, it is necessary that at least one type of metal salt and the precipitant precursor are in a liquid phase, that is, dissolution state, in the impregnation solution before a treatment, in which the precipitant precursor is converted to a precipitant, is conducted. Substances other than the

above-described at least one type of metal salt and the precipitant precursor may be present in any state in the impregnation solution.

[0179]

(7) Homogeneous precipitation method

<Method for impregnating carrier with impregnation solution>

The method for impregnating the carrier with the above-described impregnation solution is not specifically limited. However, it is preferable that a pore-filling method is conducted in order to allow the carrier to uniformly support the metal salt. In this case, it is preferable that the volume of the impregnation solution, with which the carrier is impregnated, is 60% to 120% of the carrier pore volume, further preferably 70% to 110%, and particularly preferably 80% to 105%. If the amount of liquid is too small, the impregnation solution do not uniformly enter carrier pores, and nonuniformity results. Conversely, if the amount is too large, the impregnation solution adheres to the outer surface of the carrier, and nonuniformity also results.

[0180]

Any amount can be selected as the amount of metal salt to be supported by the carrier through impregnation. However, the amount is usually 0.01 to 50 percent by weight relative to the weight of the carrier, preferably 0.05 to 40 percent by weight, and further preferably 0.1 to 30 percent

by weight. Usually, the amount of the supported precipitant precursor is specified to be within the range of 0.1 to 10 in terms of mole ratio, where the theoretical amount sufficient for precipitating the entire metal salt supported by the carrier is assumed to be 1, preferably within the range of 0.2 to 8, and further preferably within the range of 0.3 to 5.

[0181]

<Method for generating and after-treating precipitation>

According to the third aspect, a treatment, e.g., heating, for converting the precipitant precursor to a precipitant is conducted while the metal salt and the precipitant precursor, which are supported by the carrier through impregnation of the carrier with the impregnation solution, remain in the state of solution in carrier pores, and the metal salt is converted to a corresponding metal hydroxide by the precipitant homogeneously generated in the inside of the carrier.

[0182]

In general, a base precursor is used as the precipitant precursor, and hydrolysis of the base precursor through heating is used as the treatment for converting the base precursor to a base.

[0183]

As described above, according to the third aspect, in

order to conduct the homogeneous precipitation method in the carrier pores, it is required that at least one type of metal salt and the precipitant precursor are in the state of a solution, that is, a liquid phase, before the treatment, in which the precipitant precursor is converted to the precipitant, is conducted. However, substances other than the above-described at least one type of metal salt and the precipitant precursor may be in any state.

[0184]

In the case where the base precursor is converted to the base through hydrolysis reaction effected by heating, a heating temperature within the range of 50°C to 300°C is usually adopted, and preferably the range of 60°C to 200°C is adopted. The heating temperature can also be changed over time. If the heating temperature is too low, a reaction of generation of the precipitant from the precipitant precursor may not occur or a very long time may be taken. If the heating temperature is too high, in some cases, the entire water required for hydrolysis may be removed before the reaction of generation of the precipitant from the precipitant precursor is finished. In order to conduct a good, stable homogeneous precipitation method, it is preferable that 5% or more of water in the impregnation solution, with which the carrier has been impregnated, remains at the point in time when the precipitation

generation reaction is finished, and further preferably 10% or more of water remains.

[0185]

The heating of the carrier impregnated with the impregnation solution may be conducted in the state in which the support carrier does not move as in a fixed-bed heating apparatus. However, particularly in the case where a large amount of catalyst is prepared, it is more preferable that a fluidized-bed apparatus, a rotary heating apparatus, and the like are used wherein the support carrier is fluidized. In the case where vaporization of water occurs during heating, it is believed that when the support carrier is fluidized, the amount of vaporization of water does not vary on a particle of the support carrier basis and, therefore, the uniformity is further improved.

[0186]

If vaporization of water during heating is too fast, the entire water may be removed before the hydrolysis of the base precursor is completed and, thereby, the precipitant may not be supplied sufficiently. Therefore, usually, complete removal of water is conducted desirably in such a way that the water is removed completely over 1 hour or more, preferably 3 hours or more, and further preferably 6 hours or more after the heating is started and the precipitation generation reaction is finished.

[0187]

If necessary, the resulting catalyst is washed with water, an alkaline aqueous solution, an acid aqueous solution, an organic solvent, or the like and is dried. Thereafter, firing is conducted in an atmosphere of an inert gas, e.g., nitrogen or argon, or an atmosphere of an oxidizing gas, e.g., air or a diluted oxygen gas, so that a solid acid catalyst having a desired performance can be obtained. The heating and firing temperature at this time is usually 100°C to 1,200°C, preferably 300°C to 1,100°C, and further preferably 500°C to 1,000°C. The catalyst activity and the stability of the resulting solid acid catalyst can be improved by conducting the above-described heating and firing.

[0188]

(8) Solid acid catalyst

The crystallite size of the metal oxides and/or the metal hydroxide supported by the solid acid catalyst obtained by the above-described steps is different depending on the type of the metal element, the amount of support, the type of the carrier, the firing condition, and the like. However, in the case where the same metal salt is used and preparation is conducted with the same amount of support, the same carrier, and the same firing condition, the crystallite size becomes 90% or less of the crystallite size

in the case where preparation is conducted on the basis of a known technology, preferably 80% or less, and further preferably 75% or less. This crystallite size is calculated from the half-width of an XRD measurement peak.

[0189]

In the solid acid catalyst obtained by the method according to the third aspect, preferably, the amount of the supported metal hydroxide and/or metal oxide relative to the carrier is 0.05 to 40 percent by weight and, in particular, 0.1 to 30 percent by weight.

[0190]

[Process for production of polyether]

The solid acid catalyst produced by the process according to the third aspect is favorably used as a polymerization catalyst in the production of polyethers, in particular, the production of polyethers through ring-opening polymerization reaction of cyclic ethers.

[0191]

The process for production of a polyether by using the solid acid catalyst according to the present invention as a polymerization catalyst will be described below.

[0192]

In the case where polyethers are produced by ring-opening polymerization reaction of cyclic ethers, examples of cyclic ethers to be used as the raw materials for the

reaction include cyclic ethers in which the number of carbon constituting the ring is 3 to 10. Furthermore, cyclic ethers including alkyl groups, halogen groups, acyl groups, and the like as substituents can also be used. Specifically, tetrahydrofuran, oxetane, oxepane, 1,4-dioxane, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, and the like are used. Any one of homogeneous polymerization by using merely one type of cyclic ether and copolymerization by using at least two types of cyclic ethers can be conducted.

[0193]

Preferably, the ring-opening polymerization reaction of the cyclic ether is conducted in the presence of a carboxylic anhydride and/or a carboxylic acid from the viewpoint of the molecular weight control. In general, aliphatic or aromatic carboxylic anhydrides and/or carboxylic acids having 2 to 12 carbon atoms are used, and preferably those having 2 to 8 carbon atoms are used. These carboxylic anhydrides and/or carboxylic acids may be used alone or at least two types may be used in combination. it is favorable that the carboxylic anhydride and/or the carboxylic acid is added usually at within the range of 0.01 to 1.0 (mole ratio) relative to the cyclic ether.

[0194]

In the polymerization reaction, a solvent inactive to the reaction can also be used. In general, at least one

type of aliphatic hydrocarbon, aromatic hydrocarbon, and the like inactive to the ring-opening polymerization reaction is used as the solvent.

[0195]

A generally adopted reaction form, e.g., a vessel type or a tower type, is used, and any one of a batch system and a continuous system is adopted. Examples thereof include a method in which the cyclic ether, the catalyst, and the carboxylic anhydride and/or the carboxylic acid are charged and polymerized with agitation (batch system) and a method in which the cyclic ether and the carboxylic anhydride and/or the carboxylic acid are continuously supplied to a reactor including the catalyst and a reaction liquid is continuously taken out (continuous system). The continuous system is preferable from the viewpoint of the productivity.

[0196]

The usage of the solid acid catalyst is determined on the basis of the type thereof, and is not specifically limited. For example, in the batch type reactor, if the amount of catalyst is too small, the polymerization rate is reduced. Conversely, if the amount is too large, removal of a polymerization heat becomes difficult. Furthermore, since the slurry concentration of the reaction system increases, agitation becomes difficult, and a problem tends to occur in separation of the catalyst and the reaction liquid after the

completion of the polymerization reaction. Therefore, the usage of the catalyst is usually selected within the range of 0.001 to 50 times on a weight basis relative to the liquid phase, preferably the range of 0.01 to 20 times on a weight basis in consideration of the reaction form being the batch reaction or the flow reaction. For the flow reaction, the usage of the catalyst refers to the amount of the catalyst relative to the amount of supply of the liquid phase per unit time.

[0197]

The reaction temperature is usually 0°C to 200°C, and preferably 10°C to 80°C.

The reaction pressure may be any pressure insofar as the reaction system is allowed to maintain a liquid phase at that pressure. Usually, the pressure is selected within the range of normal pressure to 10 MPa, and preferably normal pressure to 5 MPa.

The reaction time is not specifically limited. However, in consideration of both the reaction time and the amount of catalyst and in consideration of the yield and the economic efficiency, preferably, the reaction time is within the range of 0.1 to 20 hours, and preferably within the range of 0.5 to 15 hours. In the batch system, the reaction time refers to a period from the point in time when the temperature is raised to the reaction temperature until the

reaction is finished and the cooling is started. In the continuous system, the reaction time refers to a residence time of a reaction composition liquid in the reactor.

[0198]

In the case where a ring-opening polymerization reaction of tetrahydrofuran (THF) is conducted by using the solid acid catalyst produced according to the third aspect, a polyether having a number average molecular weight (M_n) of 200 to 80,000 and, in particular, a low to middle molecular weight of about 200 to 40,000 can be obtained. Furthermore, it is one of the features that a polyether having a narrow molecular weight distribution can be easily produced. That is, there is a great demand for a polyether exhibiting M_w/M_n of 1.3 to 2.5 industrially. Polytetramethylene ether glycol (PTMG) exhibiting M_w/M_n of less than 3, for example, 1.1 to 3.0, can be obtained by using the solid acid catalyst according to the present invention. In particular, when a preferable condition of the present invention is selected, a polyether having a very narrow molecular weight distribution M_w/M_n of about 1.5 to 1.8 can also be obtained. Moreover, the yield of the product is allowed to become 25% or more, preferably 30% or more, and furthermore 35% or more.

[Examples and comparative examples]

[0199]

The third aspect will be further specifically described

below with reference to examples and comparative examples. However the following examples do not limit the scope of the present invention.

[0200]

In the following description, the yield, the number average molecular weight (Mn), and the molecular weight distribution (Mw/Mn) of polytetramethylene ether glycol acetic acid ester (PTME) were determined with GPC (gel permeation chromatography) described below.

GPC apparatus: GPC 8220 produced by Tosoh Corporation

Column: TSK-GEL H 30 cm x 2 units

Detection method: RI

Column temperature: 40°C

Moving bed: THF

Flow rate: 1 ml/min

Amount of injection of sample: 500 µl

Sample concentration: adjusted in such a way that the concentration of a polyether becomes about 0.1 percent by weight

[0201]

Example 2-1

<Preparation of solid acid catalyst>

[Impregnation of impregnation solution]

After 89.66 g of zirconium oxynitrate aqueous solution (produced by Shin Nippon Metal & Chemical Co., Ltd.,

concentration 18.12 percent by weight in terms of ZrO_2) was blended with 18.72 g of desalted water, mixing was conducted homogeneously. The resulting mixture was blended with 11.84 g of urea and mixing was conducted homogeneously so as to prepare an impregnation solution. The resulting solution was blended with 80 g of SiO_2 (produced by Fuji Silysia Chemical Ltd., CARIACT Q15, particle diameter 75 to 500 μm , average particle diameter 200 μm , pore volume 1.16 ml/g, average pore diameter 15 nm), and impregnation was conducted by pore-filling (the amount of impregnation solution was 100% of the carrier pore volume) while mixing was conducted by shaking for about 1 hour.

[0202]

[Heat treatment]

The carrier impregnated with the above-described impregnation solution was put into a 500-ml pear-shaped flask, a joint and a curved tube filled with glass wool were connected to the upper portion of the flask, and a thermometer was connected to a measurement portion. Thereafter, the flask was fixed with a clamp to a rotating shaft of a rotary drier. The rotating shaft was rotated at a speed of 10 rpm, the temperature of the drier was set at 105°C, and heating was conducted for 6 hours. At this time, it was ascertained by the weight change that 90% of water in the impregnation solution remained. After the curved tube

filled with glass wool at the upper portion was removed, the temperature of the drier was set at 120°C, and heating was conducted for 16 hours.

[0203]

After the joint at the upper portion was removed, the temperature of the drier was set at 140°C, and heating was conducted for 4 hours so as to remove the water almost completely. The heating and rotation were terminated after a lapse of 4 hours, and the catalyst was taken out.

[0204]

The catalyst was transferred to a 500-ml beaker and stood for cooling to room temperature. After about 300 ml of desalted water was added, suspension washing was conducted for about 10 minutes. The catalyst was filtrated and was transferred to the 500-ml beaker again. The suspension washing was conducted three times in total. The catalyst was air-dried and dried with a drier at 120°C for a night. Subsequently, firing was conducted at 900°C for 2 hours while the air was passed so as to obtain a solid acid catalyst. The average crystallite diameter of zirconium oxide supported by the solid acid catalyst was determined on the basis of an XRD measurement and was 22 Å. The amount of supported zirconium oxide determined by calculation on the basis of the impregnation solution composition was 16.9 percent by weight relative to the entire amount of the

catalyst.

[0205]

<Production of polyether>

In a nitrogen atmosphere, 133.5 g of THF and 6.85 g of acetic anhydride were put in a 500-ml four-neck flask and were mixed with agitation. In a nitrogen atmosphere, 4.68 g of solid acid catalyst obtained in the above-described preparation of solid acid catalyst was weighed and added to the resulting mixed solution with agitation. Thereafter, a reaction was conducted at 40°C for 5 hours. The reaction liquid was analyzed with GPC so as to measure the degree of conversion of THF, the number average molecular weight (M_n) of PTME, and the molecular weight distribution (M_w/M_n). As a result, the degree of conversion was 56.3%, M_n was 2,563, and M_w/M_n was 1.88.

[0206]

Example 2-2

A catalyst was prepared as in Example 2-1 except that an impregnation solution was prepared by dissolving 42.46 g of zirconium oxychloride octahydrate into 59.48 g of desalted water, adding 11.84 g of urea thereto, and mixing homogeneously. A polyether was produced by using the resulting catalyst. The average crystallite diameter of zirconium oxide determined on the basis of the XRD measurement was less than or equal to the lower limit (10 Å)

of the detection, and the amount of supported zirconium oxide was 16.9 percent by weight relative to the entire amount of the catalyst. The degree of conversion was 55.1%, Mn was 2,520, and Mw/Mn was 1.87.

[0207]

Example 2-3

A catalyst was prepared as in Example 2-1 except that an impregnation solution was prepared by dissolving 46.95 g of zirconium sulfate aqueous solution (produced by Shin Nippon Metal & Chemical Co., Ltd., concentration 15.1 percent by weight in terms of ZrO_2) into 56.95 g of desalted water, adding 23.78 g of urea thereto, and mixing homogeneously. A polyether was produced by using the resulting catalyst. The average crystallite diameter of zirconium oxide determined on the basis of the XRD measurement was 22 Å, and the amount of supported zirconium oxide was 16.9 percent by weight relative to the entire amount of the catalyst. The degree of conversion was 51.2%, Mn was 2,252, and Mw/Mn was 1.87.

[0208]

Example 2-4

After 86.80 g of zirconium oxynitrate aqueous solution (produced by Shin Nippon Metal & Chemical Co., Ltd., concentration 18.72 percent by weight in terms of ZrO_2) was blended with 17.84 g of desalted water, mixing was conducted

homogeneously. The resulting mixture was blended with 10.84 g of ammonium bicarbonate gradually, mixing was conducted homogeneously, 7.92 g of urea was added thereto, and mixing was conducted homogeneously so as to prepare an impregnation solution. The resulting solution was blended with 80 g of SiO₂ (produced by Fuji Silysia Chemical Ltd., CARIACT Q15), and impregnation was conducted by pore-filling (the amount of impregnation solution was 100% of the carrier pore volume) while mixing was conducted by shaking for about 1 hour.

[0209]

This was put into a 500-ml pear-shaped flask, and a solid acid catalyst was obtained by conducting a series of heating, washing, and firing treatments as in Example 2-1 except that the heating at a drier temperature of 105°C was changed from 6 hours to 1.5 hours. The average crystallite diameter of zirconium oxide determined on the basis of the XRD measurement was 22 Å, and the amount of supported zirconium oxide was 16.9 percent by weight relative to the entire amount of the catalyst.

[0210]

A polyether was produced as in Example 2-1 except that the resulting catalyst was used. The degree of conversion was 55.4%, Mn was 2,626, and Mw/Mn was 1.87.

[0211]

Comparative example 2-1

After 89.66 g of zirconium oxynitrate aqueous solution (produced by Shin Nippon Metal & Chemical Co., Ltd., concentration 18.12 percent by weight in terms of ZrO_2) was blended with 18.72 g of desalted water, mixing was conducted homogeneously. The resulting mixture was blended with 11.84 g of urea, and mixing was conducted homogeneously so as to prepare an impregnation solution. The resulting solution was blended with 80 g of SiO_2 (produced by Fuji Silysia Chemical Ltd., CARIACT Q15), and impregnation was conducted by pore-filling (the amount of impregnation solution was 100% of the carrier pore volume) while mixing was conducted by shaking for about 1 hour. This was subjected to drying at a reduced pressure and, thereby, 97% or more of the water in the impregnation solution was removed so as to obtain a support carrier in which a dried metal salt and precipitant precursor in a solid phase state were supported.

[0212]

This was put into a 500-ml pear-shaped flask, and a solid acid catalyst was obtained by conducting a series of heating, washing, and firing treatments as in Example 2-1. The average crystallite diameter of zirconium oxide determined on the basis of the XRD measurement was 47 Å, and the amount of supported zirconium oxide was 16.9 percent by weight relative to the entire amount of the catalyst.

[0213]

A polyether was produced as in Example 2-1 except that the resulting catalyst was used. The degree of conversion was 29.8%, Mn was 3,019, and Mw/Mn was 2.01.

[0214]

Comparative example 2-2

After 89.66 g of zirconium oxynitrate aqueous solution (produced by Shin Nippon Metal & Chemical Co., Ltd., concentration 18.12 percent by weight in terms of ZrO_2) was blended with 27.72 g of desalted water, mixing was conducted homogeneously. The resulting solution was blended with 80 g of SiO_2 (produced by Fuji Silysia Chemical Ltd., CARIACT Q15), and impregnation was conducted by pore-filling (the amount of impregnation solution was 100% of the carrier pore volume) while mixing was conducted by shaking for about 1 hour.

[0215]

This was put into a 500-ml pear-shaped flask, a joint and a curved tube filled with glass wool were connected to the upper portion of the flask, and a thermometer was connected to a measurement portion. Thereafter, the flask was fixed with a clamp to a rotating shaft of a rotary drier. The rotating shaft was rotated at a speed of 10 rpm, the temperature of the drier was set at 105°C, and heating was conducted for 6 hours. After the curved tube filled with

glass wool at the upper portion was removed, the temperature of the drier was set at 120°C, and heating was conducted for 16 hours.

[0216]

After the joint at the upper portion was removed, the temperature of the drier was set at 140°C, and heating was conducted for 4 hours. The heating and rotation were terminated after a lapse of 4 hours, and the catalyst was taken out.

[0217]

The catalyst was transferred to a 500-ml beaker and stood for cooling to room temperature. A solution, in which 35 g of ammonium bicarbonate was dissolved into 350 ml of desalted water, was added, and agitation was conducted for about 10 minutes. The catalyst was filtrated, about 300 ml of desalted water was added thereto, and suspension washing was conducted for about 10 minutes. The catalyst was filtrated and transferred to the 500-ml beaker again. The suspension washing was conducted three times in total. The catalyst was air-dried and dried with a drier at 120°C for a night. Subsequently, firing was conducted at 900°C for 2 hours while the air was passed so as to obtain a solid acid catalyst. The average crystallite diameter of zirconium oxide determined on the basis of an XRD measurement was 30 Å. The amount of supported zirconium oxide was 16.9 percent by

weight relative to the entire amount of the catalyst.

[0218]

A polyether was produced as in Example 2-1 except that the resulting catalyst was used. The degree of conversion was 45.7%, Mn was 2,947, and Mw/Mn was 2.03.

[0219]

Example 2-5

After 89.66 g of zirconium oxynitrate aqueous solution (produced by Shin Nippon Metal & Chemical Co., Ltd., concentration 18.12 percent by weight in terms of ZrO_2) was blended with 20.65 g of desalted water, mixing was conducted homogeneously. The resulting mixture was blended with 6.74 g of ammonium carbonate gradually and mixing was conducted homogeneously. After 11.84 g of urea was added thereto, mixing was conducted homogeneously so as to prepare an impregnation solution. The resulting solution was blended with 80 g of SiO_2 (produced by Fuji Silysia Chemical Ltd., CARIACT Q30, particle diameter 75 to 500 μm , average particle diameter 200 μm , pore volume 1.21 ml/g, average pore diameter 30 nm), and impregnation was conducted by pore-filling (the amount of impregnation solution was 100% of the carrier pore volume) while mixing was conducted by shaking for about 1 hour.

[0220]

This was put into a 500-ml pear-shaped flask, and a

solid acid catalyst was obtained by conducting a series of heating, washing, and firing treatments as in Example 2-2. The average crystallite diameter of zirconium oxide determined on the basis of the XRD measurement was 28 Å, and the amount of supported zirconium oxide was 16.9 percent by weight relative to the entire amount of the catalyst.

[0221]

A polyether was produced as in Example 2-1 except that the resulting catalyst was used. The degree of conversion was 52.7%, Mn was 2,875, and Mw/Mn was 1.85.

[0222]

Example 2-6

After 88.01 g of zirconium oxynitrate aqueous solution (produced by Shin Nippon Metal & Chemical Co., Ltd., concentration 18.46 percent by weight in terms of ZrO_2) was blended with 26.83 g of desalted water, mixing was conducted homogeneously. The resulting mixture was blended with 11.84 g of urea and mixing was conducted homogeneously so as to prepare an impregnation solution. The resulting solution was blended with 80 g of SiO_2 (produced by Fuji Silysia Chemical Ltd., CARIACT Q30), and impregnation was conducted by pore-filling (the amount of impregnation solution was 100% of the carrier pore volume) while mixing was conducted by shaking for about 1 hour.

[0223]

This was put into a 500-ml pear-shaped flask, and a solid acid catalyst was obtained by conducting a series of heating, washing, and firing treatments as in Example 2-1 except that the heating at a drier temperature of 105°C was changed from 6 hours to 2 hours. The average crystallite diameter of zirconium oxide determined on the basis of the XRD measurement was 28 Å, and the amount of supported zirconium oxide was 16.9 percent by weight relative to the entire amount of the catalyst.

[0224]

A polyether was produced as in Example 2-1 except that the resulting catalyst was used. The degree of conversion was 41.9%, Mn was 2,436, and Mw/Mn was 1.73.

[0225]

Comparative example 2-3

After 89.66 g of zirconium oxynitrate aqueous solution (produced by Shin Nippon Metal & Chemical Co., Ltd., concentration 18.12 percent by weight in terms of ZrO_2) was blended with 22.72 g of desalted water, mixing was conducted homogeneously. The resulting mixture was blended with 11.84 g of urea, and mixing was conducted homogeneously so as to prepare an impregnation solution. The resulting solution was blended with 80 g of SiO_2 (produced by Fuji Silysia Chemical Ltd., CARIACT Q30), and impregnation was conducted by pore-filling (the amount of impregnation solution was

100% of the carrier pore volume) while mixing was conducted by shaking for about 1 hour. This was subjected to drying at a reduced pressure and, thereby, 97% or more of the water in the impregnation solution was removed so as to obtain a support carrier in which a dried metal salt and precipitant precursor in a solid phase state were supported.

[0226]

This was put into a 500-ml pear-shaped flask, and a solid acid catalyst was obtained by conducting a series of heating, washing, and firing treatments as in Example 2-1. The average crystallite diameter of zirconium oxide determined on the basis of the XRD measurement was 71 Å, and the amount of supported zirconium oxide was 16.9 percent by weight relative to the entire amount of the catalyst.

[0227]

A polyether was produced as in Example 2-1 except that the resulting catalyst was used. The degree of conversion was 13.0%, Mn was 3,167, and Mw/Mn was 2.13.

[0228]

Comparative example 2-4

After 89.66 g of zirconium oxynitrate aqueous solution (produced by Shin Nippon Metal & Chemical Co., Ltd., concentration 18.12 percent by weight in terms of ZrO_2) was blended with 31.72 g of desalted water, mixing was conducted homogeneously. The resulting solution was blended with 80 g

of SiO₂ (produced by Fuji Silysia Chemical Ltd., CARIACT Q30), and impregnation was conducted by pore-filling (the amount of impregnation solution was 100% of the carrier pore volume) while mixing was conducted by shaking for about 1 hour. This was put into a 500-ml pear-shaped flask, and a solid acid catalyst was obtained by heating as in Comparative example 2-2, and by conducting a treatment with ammonium bicarbonate, separation of a catalyst through filtration, washing, drying, and firing as in Comparative example 2-2. The average crystallite diameter of zirconium oxide determined on the basis of the XRD measurement was 53 Å, and the amount of supported zirconium oxide was 16.9 percent by weight relative to the entire amount of the catalyst.

[0229]

A polyether was produced as in Example 2-1 except that the resulting catalyst was used. The degree of conversion was 35.9%, Mn was 3,943, and Mw/Mn was 1.97.

[0230]

The results of Examples 2-1 to 2-6 and Comparative examples 2-1 to 2-4 described above are shown in Table 2-1 collectively.

[0231]

[Table 2-1]

	Type of carrier	Crystallite size (Å)	Production of polyether		
			Degree of conversion (%)	Mn	Mw/Mn
Example2-1	Q15	22	56.3	2563	1.88
Example2-2	Q15	lower limit (10) or less	55.1	2520	1.87
Example2-3	Q15	22	51.2	2252	1.87
Example2-4	Q15	22	55.4	2626	1.87
Comparative example2-1	Q15	47	29.8	3019	2.01
Comparative example2-2	Q15	30	45.7	2947	2.03
Example2-5	Q30	28	52.7	2875	1.85
Example2-6	Q30	28	41.9	2436	1.73
Comparative example2-3	Q30	71	13.0	3167	2.13
Comparative example2-4	Q30	53	35.9	3943	1.97

[0232]

The following is clear from Table 2-1.

[0233]

As is clear from comparisons between Examples 2-1 to 2-3 and Comparative example 2-1, the performance of the catalyst obtained not by the homogeneous precipitation method in carrier pores, but by drying the impregnated carrier so as to allow the metal salt and the precipitant precursor in the impregnant to become in the solid state and, thereafter, starting the heat treatment is poor.

[0234]

Likewise, as is clear from comparisons between Examples 2-1 to 2-3 and Comparative example 2-2, the performance of the catalyst obtained not by the homogeneous precipitation method in carrier pores, but by putting the carrier impregnated with the metal salt into the alkali solution and supplying the alkali from the outside is poor.

[0235]

Furthermore, as is clear from comparisons between Examples 2-5 and 2-6 and Comparative examples 2-3 and 2-4, similar results are obtained in the case where different carriers are used. Therefore, it is clear that the process according to the third aspect, in which the homogeneous precipitation method is conducted in carrier pores, can produce a high-performance solid acid catalyst.

[0236]

[Description of the fourth aspect]

The inventors of the present invention found that regarding a process for production of a polyether including the step of subjecting a cyclic ether to a ring-opening polymerization in the presence of a catalyst, when a polyether was produced by using a solid acid catalyst, which contained at least one type of element selected from the group consisting of the groups 1, 2, 4, 6, 8, 9, 12, 13, 14, 15, 16, and 17 in the periodic table and which was capable of subjecting by itself a cyclic ether to ring-opening

polymerization, as the catalyst, the average molecular weight of the resulting polyether was able to be easily efficiently controlled at a desired value without adversely affecting the other performance. Consequently, the fourth aspect has been completed.

[0237]

That is, the gist of the fourth aspect resides in a process for production of a polyether characterized by including the step of subjecting a cyclic ether to a ring-opening polymerization in the presence of a catalyst, wherein a catalyst, in which a solid acid catalyst containing at least one type of element selected from the group consisting of the groups 1, 2, 4, 6, 8, 9, 12, 13, 14, 15, 16, and 17 in the periodic table and being capable of subjecting by itself a cyclic ether to ring-opening polymerization is allowed to contain at least one type of metal element not contained in the solid acid catalyst and selected from the group consisting of the groups 3, 5, 10, and 11 in the periodic table, is used as the catalyst.

[0238]

In the fourth aspect, preferably, at least one type of solid acid catalyst selected from the group consisting of metal oxide catalysts, composite metal oxide catalysts, clay catalysts, and zeolite catalysts is used as the solid acid catalyst capable of subjecting by itself a cyclic ether to

ring-opening polymerization.

[0239]

Preferably, copper and/or nickel is used as the metal element not contained in the solid acid catalyst and selected from the group consisting of the groups 3, 5, 10, and 11 in the periodic table.

[0240]

Preferably, at least one type of solid acid catalyst selected from the group consisting of clay catalysts, silica-alumina, silica-titania, and silica-zirconia is used as the solid acid catalyst capable of subjecting a cyclic ether to ring-opening polymerization.

[0241]

Preferably, the catalyst is produced by allowing the metal hydroxide and/or the metal oxide to be supported in pores of a carrier by conducting a homogeneous precipitation method in the carrier pores.

[0242]

According to the process for production of a polyether of the forth aspect, the average molecular weight of the resulting polyether can be changed merely by changing the components and the composition of a catalyst to be used without changing the reaction condition nor adversely affecting the performance other than the average molecular weight.

Therefore, according to the fourth aspect, a polyether having a desired average molecular weight in accordance with the uses of the polyether can be easily efficiently produced.

[0243]

The embodiments according to the fourth aspect will be described below in detail. However, the following description of constituent features is an example (typical example) of execution forms of the fourth aspect, and the fourth aspect is not specifically limited to these contents within the bounds of the gist.

[0244]

[Catalyst]

The catalyst to be used in the fourth aspect will be described. The catalyst to be used in the present invention is a solid acid catalyst allowed to contain a specific metal element (the group 3, 5, 10, or 11 in the periodic table).

[0245]

<Solid acid catalyst>

In the present invention, examples of solid acid catalysts include zeolite and the like having crystal structures of MFI, X, Y, and the like; metal oxides, e.g., silica, alumina, titania, and zirconia; composite metal oxides, e.g., silica-titania, silica-alumina, silica-zirconia, and alumina-titania, in which a plurality of metal oxides are combined; support type acid catalysts in which

metal oxides, clay, or zeolite serving as carriers support metal oxides different from carriers or compounds having an acidic property; and clay and the like, e.g., activated clay.

Most of all, composite metal oxides, support type acid catalysts, and clay and the like are preferable, and silica-zirconia, silica-alumina, silica-titania, and clay and the like are particularly preferable.

[0246]

<Process for production of solid acid catalyst>

Known technologies can be used as the process for production of the solid acid catalyst and the process is not specifically limited. Specifically, the production processes described in the above-described Patent Document 1, Patent Document 2, and the like can be adopted.

[0247]

It is preferable that the solid acid catalyst to be used in the fourth aspect is a catalyst in which a metal hydroxide and/or metal oxide is supported in pores of the carrier by conducting a homogeneous precipitation method in the carrier pores.

[0248]

<Method for allowing solid acid catalyst to contain specific metal element>

Any one of the following methods can be adopted as the method for allowing a solid acid catalyst to contain at

least one metal element which is not contained in the solid acid catalyst and which is selected from the group consisting of the groups 3, 5, 10, and 11 in the periodic table (hereafter may be referred to as additive element):

(1) a method in which the additive element is contained in advance in a carrier to be used in the preparation of a solid acid catalyst,

(2) a method in which the additive element is contained at the same time with the preparation of a solid acid catalyst, and

(3) a method in which the additive element is added after a solid acid catalyst is prepared,

and the method of item (2), that is, the method in which the additive element is contained at the same time with the preparation of a solid acid catalyst, is preferable.

[0249]

<Production of catalyst by homogeneous precipitation method>

The process for production of a catalyst to be used in the fourth aspect will be described below, wherein the additive element is contained at the same time with the preparation of a solid acid catalyst in the production of the catalyst by a homogeneous precipitation method in carrier pores.

In the case where the catalyst to be used in the fourth aspect is a support type acid catalyst, preferably, the

total amount of supported metals relative to the carrier, the amount of supported metal serving as the solid acid catalyst, and the amount of the supported additive element are the amounts determined by conversion of the amount of supported metal salt or metal oxide described later.

[0250]

The homogeneous precipitation method is conducted by, for example, impregnating a carrier with a metal salt and a precipitant precursor, which generates a precipitant through a chemical reaction, e.g., hydrolysis, in a solution, at the same time, and subjecting the impregnated carrier to a treatment, e.g., a heat treatment, for generating the precipitant from the precipitant precursor. For the homogeneous precipitation method, it is important that the metal salt and the precipitant precursor constitute a liquid phase, that is, a solution. Therefore, the carrier is impregnated with an impregnation solution including the metal salt and the precipitant precursor and, thereafter, the treatment for generating the precipitant from the precipitant precursor is conducted.

[0251]

For the metal salt to be dissolved into the impregnation solution, a metal salt for generating a solid acid catalyst (hereafter may be referred to as an "acid-generating metal salt") and a metal salt for generating the

additive element (hereafter may be referred to as an "additive element salt") are used in combination.

[0252]

(1) Carrier

The carrier of the catalyst is not specifically limited. However, metal oxides, composite metal oxides, zeolite and the like, and clay and the like are preferable. Silica, alumina, zirconia, titania, silica-alumina, silica-zirconia, silica-titania, and clay and the like are more preferable. Silica, alumina, zirconia, and clay and the like are particularly preferable.

[0253]

These carriers may be used alone or at least two types may be used in combination.

[0254]

(2) Metal salt to be dissolved into impregnation solution

(2-1) Acid-generating metal salt

For the metal element of the metal salt which is supported by the carrier and which manifests a solid acid, at least one type of metal element of the groups 1, 2, 4, 6, 8, 9, 12, 13, 14, 15, 16, and 17 in the periodic table is used. Preferably, metal elements of the group 4, the group 13, and the group 14 in the periodic table are used. Metal elements of Ti, Zr, Hf, Al, and Si are more preferable, and Ti, Zr, and Al are particularly preferable.

[0255]

The type of the salt is not specifically limited. However, a nitrate, an acetate, a sulfate, an oxynitrate, a chloride, or an oxychloride is preferable, and an oxynitrate, an oxychloride, or a sulfate is more preferable.

[0256]

That is, for the acid-generating metal salt, a nitrate, an acetate, a sulfate, an oxynitrate, a chloride, or an oxychloride of an element of the group 1, 2, 4, 6, 8, 9, 12, 13, 14, 15, 16, or 17 in the periodic table is preferable, and zirconium oxynitrate, zirconium oxychloride, zirconium sulfate, titanium chloride, or aluminum sulfate is further preferable.

[0257]

These acid-generating metal salts may be used alone or at least two types may be used in combination.

[0258]

(2-2) Additive element salt

On the other hand, metal elements of the group 3, the group 5, the group 10, and the group 11 in the periodic table are used as at least one type of metal element (additive element) which is to be added to the solid acid catalyst, which is not contained in the solid acid catalyst, and which is selected from the group consisting of the groups 3, 5, 10, and 11 in the periodic table. Metal

elements of Ni, Cu, and Ce are preferable, and Ni and Cu are particularly preferable.

[0259]

Salts of these additive elements are not specifically limited. However, a nitrate, an acetate, a sulfate, an oxynitrate, a chloride, or an oxychloride is preferable, and an oxynitrate, an oxychloride, or a sulfate is more preferable.

[0260]

That is, for the additive element salt, a nitrate, an acetate, a sulfate, an oxynitrate, a chloride, or an oxychloride of a metal of the group 3, the group 5, the group 10, or the group 11 in the periodic table is preferable, and nickel nitrate, nickel chloride, copper nitrate, or copper chloride is further preferable.

[0261]

These additive element salts may be used alone or at least two types may be used in combination.

[0262]

(3) Precipitant precursor

The precipitant precursor undergoes a chemical reaction, e.g., hydrolysis, by a treatment, e.g., heating, in an impregnation solution so as to generate a precipitant. The precipitant reacts with a metal salt in the impregnation solution so as to cause precipitation of a metal hydroxide.

Among precipitant precursors, a precipitant precursor which generates a base as a precipitant, that is, the precipitant precursor which generates a base through hydrolysis or other chemical reaction in an impregnation solution and increases the pH of the solution so as to precipitate a metal salt as a hydroxide or an oxide, is referred to as a "base precursor".

[0263]

The precipitant precursor for conducting the homogeneous precipitation method is not specifically limited. However, in general, the base precursor is used.

[0264]

For the base precursor, urea, cyanuric acid, alkyl-substituted urea, thiourea, alkyl-substituted thiourea, amide compounds composed of amines and carboxylic acids, and the like are used. Preferably, urea, cyanuric acid, and alkyl-substituted urea are used. It is particularly preferable to use urea and cyanuric acid from the viewpoint of the ease of availability and the cost. These base precursors may be used alone or at least two types may be used in combination.

[0265]

(4) Basic substance

Not only the above-described base precursor, but also a predetermined amount of basic substance may be added to the

impregnation solution in advance in order to increase the pH within the bounds of not causing precipitation. It is also possible to reduce the usage of the base precursor and the time required to generate precipitation by using the basic substance.

[0266]

The basic substance is not specifically limited. Examples thereof include hydroxides, carbonates, bicarbonates, phosphates, and acetates of alkali metals, alkaline earth metals, and ammonium; ammonia; and organic amines. Ammonia; organic amines; and carbonates, bicarbonates, and phosphates of ammonium are preferable, and ammonium carbonates and ammonium bicarbonates are more preferable.

[0267]

These basic substances may be used alone or at least two types may be used in combination.

[0268]

(5) Impregnation solution

Usually, the impregnation solution is prepared by dissolving the above-described acid-generating metal salt, the additive element salt, the precipitant precursor and, if necessary, the basic substance into water.

[0269]

The concentrations of the metal salt and the

precipitant precursor in the impregnation solution are not specifically limited, insofar as the dissolution state is maintained and the concentration is suitable for realizing a favorable amount of support by a carrier described later. Usually, the metal salt concentration is 0.01 to 50 percent by weight, preferably 0.1 to 40 percent by weight, and particularly preferably 0.5 to 30 percent by weight in total concentration of the acid-generating metal salt and the additive element salt. The precipitant precursor is 0.1 to 10 times the theoretical amount sufficient for precipitating the entire metal salt, preferably 0.2 to 8 times, and particularly preferably 0.3 to 5 times, as described later.

[0270]

The basic substance is used appropriately in such a way that a required pH condition is obtained. That is, since the pH condition required for generating precipitation is different depending on the types and the concentrations of the metal salt and the precipitant precursor to be used, the basic substance is used at an amount required in accordance with these conditions.

[0271]

In order to conduct the homogeneous precipitation method in the carrier, it is necessary that at least two types of metal salts of the acid-generating metal salt and the additive element salt and the precipitant precursor are

in a liquid phase, that is, a dissolution state, in the impregnation solution before a treatment, in which the precipitant precursor is converted to a precipitant, is conducted. Substances other than the above-described at least two types of metal salts and the precipitant precursor may be present in any state in the impregnation solution.

[0272]

(6) Homogeneous precipitation method

(6-1) Method for impregnating carrier with impregnation solution

The method for impregnating the carrier with the above-described impregnation solution is not specifically limited. However, it is preferable that a pore-filling method is conducted in order to allow the carrier to uniformly support the acid-generating metal salt and the additive element salt. In this case, it is preferable that the volume of the impregnation solution, with which the carrier is impregnated, is 60% to 120% of the carrier pore volume, further preferably 70% to 110%, and particularly preferably 80% to 105%. If the amount of liquid is too small, the impregnation solution do not uniformly enter carrier pores, and nonuniformity results. Conversely, if the amount is too large, the impregnation solution adheres to the outer surface of the carrier, and nonuniformity also results.

[0273]

Any amount can be selected as the amount of metal salt to be supported by the carrier through impregnation. However, the amount is usually 0.01 to 50 percent by weight in total of the acid-generating metal salt and the additive element salt relative to the weight of the carrier, preferably 0.05 to 40 percent by weight, and further preferably 0.1 to 30 percent by weight. Usually, the amount of the supported precipitant precursor is specified to be within the range of 0.1 to 10 in terms of mole ratio, where the theoretical amount sufficient for precipitating the entire metal salt supported by the carrier is assumed to be 1, preferably within the range of 0.2 to 8, and further preferably within the range of 0.3 to 5.

[0274]

(6-2) Method for generating and after-treating precipitation

A treatment, e.g., heating, for converting the precipitant precursor to a precipitant is conducted while the metal salt and the precipitant precursor, which are supported by the carrier through impregnation of the carrier with the impregnation solution, remain in the state of solution in carrier pores, and the metal salt is converted to a corresponding metal hydroxide by the precipitant homogeneously generated in the inside of the carrier.

[0275]

In general, a base precursor is used as the precipitant

precursor, and hydrolysis of the base precursor through heating is used as the treatment for converting the base precursor to the base.

[0276]

As described above, in order to conduct the homogeneous precipitation method in the carrier pores, it is required that at least two types of metal salts and the precipitant precursor are in the state of a solution, that is, a liquid phase, before the treatment, in which the precipitant precursor is converted to the precipitant, is conducted. However, substances other than the at least two types of metal salts and the precipitant precursor may be in any state.

[0277]

In the case where the base precursor is converted to the base through hydrolysis reaction effected by heating, a heating temperature within the range of 50°C to 300°C is usually adopted, and preferably the range of 60°C to 200°C is adopted. The heating temperature can also be changed over time. If the heating temperature is too low, a reaction of generation of the precipitant from the precipitant precursor may not occur or a very long time may be taken. If the heating temperature is too high, in some cases, the entire water required for hydrolysis may be removed before the reaction of generation of the precipitant

from the precipitant precursor is finished. In order to conduct a good, stable homogeneous precipitation method, it is preferable that 5% or more of water in the impregnation solution, with which the carrier has been impregnated, remains at the point in time when the precipitation generation reaction is finished, and further preferably 10% or more of water remains.

[0278]

The heating of the carrier impregnated with the impregnation solution may be conducted in the state in which the support carrier does not move as in a fixed-bed heating apparatus. However, particularly in the case where a large amount of catalyst is prepared, it is more preferable that a fluidized-bed apparatus, a rotary heating apparatus, and the like are used wherein the support carrier is fluidized. In the case where vaporization of water occurs during heating, it is believed that when the support carrier is fluidized, the amount of vaporization of water does not vary on a particle of the support carrier basis and, therefore, the uniformity is further improved.

[0279]

If vaporization of water during heating is too fast, the entire water may be removed before the hydrolysis of the base precursor is completed and, thereby, the precipitant may not be supplied sufficiently. Therefore, usually,

complete removal of water is conducted desirably in such a way that the water is removed completely over 1 hour or more, preferably 3 hours or more, and further preferably 6 hours or more after the heating is started and the precipitation generation reaction is finished.

[0280]

If necessary, the resulting catalyst is washed with water, an alkaline aqueous solution, an acid aqueous solution, an organic solvent, or the like and is dried. Thereafter, firing is conducted in an atmosphere of an inert gas, e.g., nitrogen or argon, or an atmosphere of an oxidizing gas, e.g., air or a diluted oxygen gas, so that a catalyst having a desired performance can be obtained. The heating and firing temperature at this time is usually 100°C to 1,200°C, preferably 300°C to 1,100°C, and further preferably 500°C to 1,000°C. The catalyst activity and the stability of the resulting catalyst, that is, a solid acid catalyst, to which specific metal elements have been added, can be improved by conducting the above-described heating and firing.

[0281]

However, all the above-described steps are not always necessary insofar as a catalyst, in which at least one type of metal element not contained in the solid acid catalyst and selected from the group consisting of the groups 3, 5,

10, and 11 in the periodic table has been added to the solid acid catalyst, is obtained finally. Therefore, the production steps thereof are not specifically limited.

[0282]

<Amount of supported metal>

In the catalyst obtained by the above-described process, usually, the additive element in the state of an oxide is added to the solid acid catalyst.

[0283]

In the case where the catalyst to be used in the present invention is a catalyst in which a metal oxide, e.g., zirconia, is supported by a carrier, e.g., silica in a solid acid catalyst and an additive element, e.g., Ni, Cu, Ce, or the like is added to the solid acid catalyst, the amount of supported metal serving as the solid acid catalyst is preferably 0.1 to 15 percent by mole, and in particular 0.5 to 10 percent by mole relative to the carrier. If the amount of support is larger than this range, it becomes difficult to support the metal in a uniform, highly dispersed state. If the amount is small, a sufficient amount of acid is not generated. Preferably, the amount of supported specific metal element is 0.01 to 10 percent by mole, and in particular 0.05 to 5 percent by mole relative to the carrier. Preferably, the mole ratio of additive element/solid acid catalyst metal is 0.01 to 5, and in

particular 0.05 to 3.

[0284]

If the amount of supported additive element is larger than this range, the performance other than the average molecular weight may be adversely affected. If the amount is small, an effect of changing the average molecular weight is not exerted sufficiently.

[0285]

In the case where the catalyst to be used in the present invention is a catalyst in which an additive element is added to a clay catalyst serving as a solid acid catalyst, preferably, the amount of addition of additive element is 0.01 to 20 percent by weight, and in particular 0.05 to 15 percent by weight relative to the clay catalyst. If the amount of supported additive element is larger than this range, the performance other than the average molecular weight may be adversely affected. If the amount is small, an effect of changing the average molecular weight is not exerted sufficiently.

[0286]

[Process for production of polyether]

The process for production of a polyether according to the present invention, in which the solid acid catalyst produced as described above and containing the additive element is used as the catalyst for polymerization, will be

described below.

[0287]

This process for production of a polyether is conducted by a ring-opening polymerization reaction of cyclic ethers. That is, the cyclic ethers are used as raw materials for the reaction, and polyethers are produced by subjecting them to the ring-opening polymerization reaction.

[0288]

In the case where polyethers are produced by ring-opening polymerization reaction of cyclic ethers, examples of cyclic ethers to be used as the raw materials for the reaction include cyclic ethers in which the number of carbon constituting the ring is 3 to 10. Furthermore, cyclic ethers including alkyl groups, halogen groups, acyl groups, and the like as substituents can also be used. Specifically, tetrahydrofuran, oxetane, oxepane, 1,4-dioxane, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, and the like are used. Any one of homogeneous polymerization by using merely one type of cyclic ether and copolymerization by using at least two types of cyclic ethers can be conducted.

[0289]

At least one type of the solid acid catalyst containing the additive element, as described above, is used as the catalyst.

[0290]

Preferably, the ring-opening polymerization reaction of the cyclic ether is conducted in the presence of a carboxylic anhydride and/or a carboxylic acid from the viewpoint of the molecular weight control. In general, aliphatic or aromatic carboxylic anhydrides and/or carboxylic acids having 2 to 12 carbon atoms are used, and preferably those having 2 to 8 carbon atoms are used. These carboxylic anhydrides and/or carboxylic acids may be used alone or at least two types may be used in combination. It is favorable that the carboxylic anhydride and/or the carboxylic acid is added usually at within the range of 0.01 to 1.0 (mole ratio) relative to the cyclic ether.

[0291]

In the polymerization reaction, a solvent inactive to the reaction can also be used. In general, at least one type of aliphatic hydrocarbons, aromatic hydrocarbons, and the like inactive to the ring-opening polymerization reaction is used as the solvent.

[0292]

A generally adopted reaction form, e.g., a vessel type or a tower type, is used, and any one of a batch system and a continuous system is adopted. Examples thereof include a method in which the cyclic ether, the catalyst, and the carboxylic anhydride and/or the carboxylic acid are charged and polymerized with agitation (batch system) and a method

in which the cyclic ether and the carboxylic anhydride and/or the carboxylic acid are continuously supplied to a reactor including the catalyst and a reaction liquid is continuously taken out (continuous system). The continuous system is preferable from the viewpoint of the productivity. [0293]

The usage of the catalyst is determined on the basis of the type thereof, and is not specifically limited. For example, in the batch type reactor, if the amount of catalyst is too small, the polymerization rate is reduced. Conversely, if the amount is too large, removal of a polymerization heat becomes difficult. Furthermore, since the slurry concentration of the reaction system increases, agitation becomes difficult, and a problem tends to occur in separation of the catalyst and the reaction liquid after the completion of the polymerization reaction. Therefore, the usage of the catalyst is usually selected within the range of 0.001 to 50 times on a weight basis relative to the liquid phase, preferably the range of 0.01 to 20 times on a weight basis in consideration of the reaction form being the batch reaction or the flow reaction. For the flow reaction, the usage of the catalyst refers to the amount of the catalyst relative to the amount of supply of the liquid phase per unit time.

[0294]

The reaction temperature is usually 0°C to 200°C, and preferably 10°C to 80°C.

The reaction pressure may be any pressure insofar as the reaction system is allowed to maintain a liquid phase at that pressure. Usually, the pressure is selected within the range of normal pressure to 10 MPa, and preferably normal pressure to 5 MPa.

The reaction time is not specifically limited. However, in consideration of both the reaction time and the amount of catalyst and in consideration of the yield and the economic efficiency, preferably, the reaction time is within the range of 0.1 to 20 hours, and preferably within the range of 0.5 to 15 hours. In the batch system, the reaction time refers to a period from the point in time when the temperature is raised to the reaction temperature until the reaction is finished and the cooling is started. In the continuous system, the reaction time refers to a residence time of a reaction composition liquid in the reactor.

[0295]

The molecular weight distribution of the resulting polyether is depending on the type of the raw material compound. However, in the case where a ring-opening polymerization reaction of tetrahydrofuran (THF) is conducted, a polyether having a number average molecular weight (M_n) of 200 to 80,000 and, in particular, a low to

middle molecular weight of about 200 to 40,000 can be obtained. Furthermore, it is one of the features that a polyether having a narrow molecular weight distribution can be easily produced. That is, there is a great demand for a polyether exhibiting M_w/M_n of 1.3 to 2.5 industrially. A polyether exhibiting M_w/M_n of less than 3, for example, 1.1 to 3.0, can be obtained by using the solid acid catalyst according to the present invention. In particular, when a preferable condition of the present invention is selected, a polyether having a very narrow molecular weight distribution M_w/M_n of about 1.3 to 2.0 can also be obtained.

[0296]

The relationship between the amount of addition of additive element relative to the solid acid catalyst and the average molecular weight of the resulting polyether of the catalyst to be used cannot be univocally specified. Polyethers having various average molecular weights are obtained depending on the type of the additive element. In general, in the case where the same additive element is added to the same solid acid catalyst, a polyether having a larger average molecular weight tends to be obtained as the amount of addition of additive element increases.

[0297]

The polyethers produced according to the present invention can be used for applications to elastic fibers,

thermoplastic polyester elastomers, thermoplastic polyurethane elastomers, coating materials, and the like.

[Examples and comparative examples]

[0298]

The fourth aspect will be further specifically described below with reference to examples and comparative examples. However the following examples do not limit the scope of the fourth aspect.

[0299]

In the following description, the degree of conversion of tetrahydrofuran (THF), and the number average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of polytetramethylene ether glycol acetic acid ester (PTME) were determined with GPC (gel permeation chromatography) described below.

GPC apparatus: GPC 8220 produced by Tosoh Corporation

Column: TSK-GEL H (30 cm) $\times$ 2 units

Detection method: RI

Column temperature: 40°C

Moving bed: THF

Flow rate: 1 ml/min

Amount of injection of sample: 500 μ l

Sample concentration: adjusted in such a way that the concentration of a polyether becomes about 0.1 percent by weight

[0300]

[Comparative example 3-1]

<Preparation of solid acid catalyst>

Preparation of 12.1 ml of homogeneous solution was conducted by dissolving 2.84 g of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and 0.957 g of urea into desalted water. The resulting impregnation solution was blended with 10.0 g of silica carrier (produced by Fuji Silysia Chemical Ltd., CARIAMIT Q30, particle diameter 75 to 500 μm , average particle diameter 200 μm , pore volume 1.21 ml/g, average pore diameter 30 nm) at room temperature, and impregnation was conducted by standing for 1 hour while mixing was conducted by shaking sometimes. The impregnated carrier was put in a 100-ml Erlenmeyer flask, a lid was put, and this was treated in a drier at 110°C for 6 hours. After a lapse of 6 hours, the lid of the flask was removed, and drying was conducted in the as-is status in the drier at 110°C for 16 hours. This was further dried at 140°C for 4 hours and was stood for cooling. The resulting product was added to a solution, in which 7.2 g of ammonium bicarbonate (content of 20 percent by weight in terms of ammonia) was dissolved in 72 ml of desalted water, at room temperature and agitation was conducted for 1 hour. Thereafter, filtration was conducted, suspension washing was conducted three times with 84 ml of desalted water. After drying at 120°C, firing was conducted at 900°C while the air

was passed so as to prepare a catalyst.

[0301]

<Polymerization reaction>

In a nitrogen atmosphere, 133.5 g of THF and 6.85 g of acetic anhydride were put in a 500-ml four-neck flask and were mixed with agitation. In a nitrogen atmosphere, 4.68 g of the above-described catalyst was weighed and added to the resulting mixed solution with agitation. Thereafter, a reaction was conducted at 40°C for 5 hours. The reaction liquid was analyzed with GPC so as to measure the degree of conversion of THF, the number average molecular weight (M_n) of PTME, and the molecular weight distribution (M_w/M_n). As a result, the degree of conversion was 32%, M_n was 3,002, and M_w/M_n was 1.84.

[0302]

[Example 3-1]

A solid acid catalyst containing an additive element was prepared as in Comparative example 3-1 except that an impregnation solution was prepared by dissolving 2.86 g of $ZrO(NO_3)_2 \cdot 2H_2O$, 0.464 g of $Ce(NO_3)_3 \cdot 6H_2O$, and 1.108 g of urea into desalted water so as to produce 12.1 ml of homogeneous solution. The polymerization reaction was conducted in the same manner by using the resulting catalyst.

As a result, the degree of conversion was 28%, M_n was 2,664, and M_w/M_n was 1.84.

[0303]

[Example 3-2]

A solid acid catalyst containing an additive element was prepared as in Comparative example 3-1 except that an impregnation solution was prepared by dissolving 2.86 g of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, 0.432 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 1.108 g of urea into desalted water so as to produce 12.1 ml of homogeneous solution. The polymerization reaction was conducted in the same manner by using the resulting catalyst.

As a result, the degree of conversion was 36%, Mn was 3,241, and Mw/Mn was 1.82.

[0304]

[Example 3-3]

A solid acid catalyst containing an additive element was prepared as in Comparative example 3-1 except that an impregnation solution was prepared by dissolving 2.86 g of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, 0.311 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 1.06 g of urea into desalted water so as to produce 12.1 ml of homogeneous solution. The polymerization reaction was conducted in the same manner by using the resulting catalyst.

As a result, the degree of conversion was 34%, Mn was 4,137, and Mw/Mn was 1.83.

[0305]

[Example 3-4]

A solid acid catalyst containing an additive element

was prepared as in Comparative example 3-1 except that an impregnation solution was prepared by dissolving 2.86 g of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, 0.258 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and 1.059 g of urea into desalted water so as to produce 12.1 ml of homogeneous solution. The polymerization reaction was conducted in the same manner by using the resulting catalyst.

As a result, the degree of conversion was 30%, Mn was 4,059, and Mw/Mn was 1.76.

[Comparative example 3-2]

<Preparation of solid acid catalyst>

After 88.01 g of zirconium oxynitrate aqueous solution (18.46 percent by weight in terms of ZrO_2) produced by Shin Nippon Metal & Chemical Co., Ltd., was blended with 22.35 g of desalted water, mixing was conducted homogeneously. The resulting mixture was blended with 11.89 g of urea and mixing was conducted homogeneously so as to prepare an impregnation solution. The resulting solution was blended with 80 g of silica carrier (produced by Fuji Silysia Chemical Ltd., CARIACT Q15, particle diameter 75 to 500 μm , average particle diameter 200 μm , pore volume 1.16 ml/g, average pore diameter 15 nm), and impregnation was conducted by pore-filling (the amount of impregnation solution was 100% of the carrier pore volume) while mixing was conducted by shaking for about 1 hour.

[0306]

This was put into a 500-ml pear-shaped flask, and a joint and a curved tube filled with glass wool were connected to the upper portion of the flask. Thereafter, the flask was fixed with a clamp to a rotating shaft of a rotary drier. The rotating shaft was rotated at a speed of 10 rpm, the temperature of the drier was set at 105°C, and heating was conducted for 2 hours. After the curved tube filled with glass wool at the upper portion was removed, the temperature of the drier was set at 120°C, and heating was conducted for 16 hours. After the joint at the upper portion was removed, the temperature of the drier was set at 140°C, and heating was conducted for 4 hours. The heating and rotation were terminated after a lapse of 4 hours, and the catalyst was taken out. The catalyst was transferred to a 500-ml beaker and stood for cooling to room temperature. After about 300 ml of desalted water was added, suspension washing for about 10 minutes was repeated three times. The catalyst was air-dried and dried with a drier at 120°C for a night. Subsequently, firing was conducted at 900°C while the air was passed so as to produce a catalyst.

[0307]

<Polymerization reaction>

The polymerization reaction was conducted as in Comparative example 3-1 by using the solid acid catalyst, which was obtained as described above, as a catalyst. As a

result, the degree of conversion was 43%, Mn was 2,116, and Mw/Mn was 1.75.

[0308]

[Example 3-5]

A solid acid catalyst containing an additive element was prepared as in Comparative example 3-2 except that 77.52 g of zirconium oxynitrate aqueous solution (18.46 percent by weight in terms of ZrO_2) produced by Shin Nippon Metal & Chemical Co., Ltd., was blended with 23.22 g of desalted water, mixing was conducted homogeneously, 1.03 g of $Ca(NO_3)_2 \cdot 4H_2O$ was added thereto, mixing was conducted homogeneously, 10.92 g of urea was further added thereto, and mixing was conducted homogeneously so as to prepare an impregnation solution. The polymerization reaction was conducted in the same manner by using the resulting catalyst.

As a result, the degree of conversion was 46%, Mn was 2,279, and Mw/Mn was 1.75.

[0309]

[Example 3-6]

A solid acid catalyst containing an additive element was prepared as in Comparative example 3-2 except that 77.69 g of zirconium oxynitrate aqueous solution (18.46 percent by weight in terms of ZrO_2) produced by Shin Nippon Metal & Chemical Co., Ltd., was blended with 20.31 g of desalted water, mixing was conducted homogeneously, 2.12 g of

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added thereto, mixing was conducted homogeneously, 11.81 g of urea was further added thereto, and mixing was conducted homogeneously so as to prepare an impregnation solution. The polymerization reaction was conducted in the same manner by using the resulting catalyst.

As a result, the degree of conversion was 47%, Mn was 2,687, and Mw/Mn was 1.76.

[0310]

[Example 3-7]

A solid acid catalyst containing an additive element was prepared as in Comparative example 3-2 except that 77.52 g of zirconium oxynitrate aqueous solution (18.46 percent by weight in terms of ZrO_2) produced by Shin Nippon Metal & Chemical Co., Ltd., was blended with 23.22 g of desalted water, mixing was conducted homogeneously, 1.05 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was added thereto, mixing was conducted homogeneously, 10.92 g of urea was further added thereto, and mixing was conducted homogeneously so as to prepare an impregnation solution. The polymerization reaction was conducted in the same manner by using the resulting catalyst.

As a result, the degree of conversion was 47%, Mn was 2,983, and Mw/Mn was 1.74.

[0311]

[Example 3-8]

A solid acid catalyst containing an additive element

was prepared as in Comparative example 3-2 except that 77.56 g of zirconium oxynitrate aqueous solution (18.46 percent by weight in terms of ZrO_2) produced by Shin Nippon Metal & Chemical Co., Ltd., was blended with 20.95 g of desalted water, mixing was conducted homogeneously, 0.35 g of $Cu(NO_3)_2 \cdot 3H_2O$ and 1.70 g of $Ni(NO_3)_2 \cdot 6H_2O$ was added thereto, mixing was conducted homogeneously, 11.13 g of urea was further added thereto, and mixing was conducted homogeneously so as to prepare an impregnation solution. The polymerization reaction was conducted in the same manner by using the resulting catalyst.

As a result, the degree of conversion was 46%, Mn was 2,667, and Mw/Mn was 1.74.

[0312]

[Comparative example 3-3]

A polymerization reaction was conducted as in Comparative example 3-1 except that a catalyst prepared by firing 20 g of Tonsil OptimumFF, which was a clay (activated clay) catalyst produced by Sued Chemie, at 400°C for 1 hour while the air was passed was used as the catalyst. The polymerization reaction was conducted in the same manner by using the resulting catalyst.

As a result, the degree of conversion was 42%, Mn was 3,497, and Mw/Mn was 2.01.

[0313]

[Example 3-9]

After 0.35 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved into 10 g of desalted water, mixing was conducted homogeneously.

Subsequently, 20 g of Tonsil OptimumFF, which was a clay catalyst produced by Sued Chemie, was impregnated with the resulting solution, and standing was conducted for 1 hour. Thereafter, a solid acid catalyst containing an additive element was prepared by conducting firing at 400°C for 1 hour while the air was passed as in Comparative example 3-3. The polymerization reaction was conducted in the same manner by using the resulting catalyst.

As a result, the degree of conversion was 42%, Mn was 4,002, and Mw/Mn was 2.00.

[0314]

[Example 3-10]

After 0.78 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved into 10 g of desalted water, mixing was conducted homogeneously.

Subsequently, 20 g of Tonsil OptimumFF, which was a clay catalyst produced by Sued Chemie, was impregnated with the resulting solution, and standing was conducted for 1 hour. Thereafter, a solid acid catalyst containing an additive element was prepared by conducting firing at 400°C for 1 hour while the air was passed as in Comparative example 3-3. The polymerization reaction was conducted in the same manner by using the resulting catalyst.

As a result, the degree of conversion was 39%, Mn was 4,380, and Mw/Mn was 2.01.

[0315]

The results of the above-described examples and comparative examples are shown in Tables 3-1 to 3-3 collectively.

[0316]

[Table 3-1]

	Catalyst composition		Percentage of support relative to SiO ₂ carrier (mol%)	Degree of conversion (%)	Mn	Mw/Mn
	Solid acid catalyst	Additive element (oxide)				
Comparative example3-1	ZrO ₂ /SiO ₂	—	Zr=6	32	3002	1.83
Example3-1		Ce ₂ O ₃	Zr/Ce=6/0.6	28	2664	1.84
Example3-2		Fe ₂ O ₃	Zr/Fe=6/0.6	36	3241	1.82
Example3-3		NiO	Zr/Ni=6/0.6	34	4137	1.83
Example3-4		CuO	Zr/Cu=6/0.6	30	4059	1.76

[0317]

[Table 3-2]

	Catalyst composition		Percentage of support relative to SiO ₂ carrier (mol%)	Degree of conversion (%)	Mn	Mw/Mn
	Solid acid catalyst	Additive element (oxide)				
Comparative example3-2	ZrO ₂ /SiO ₂	—	Zr=8	43	2116	1.75
Example3-5		CaO	Zr/Ca=8/0.3	46	2279	1.75
Example3-6		NiO	Zr/Ni=8/0.5	47	2687	1.76
Example3-7		CuO	Zr/Cu=8/0.3	47	2983	1.74
Example3-8		CuO/NiO	Zr/Cu/Ni=8/0.1/0.4	46	2667	1.74

[0318]

[Table 3-3]

	Catalyst composition		Percentage of support relative to clay (percent by weight)	Degree of conversion (%)	Mn	Mw/Mn
	Solid acid catalyst	Additive element (oxide)				
Comparative example3-3	clay (Tonsil)	-	-	42	3497	2.01
Example3-9		CuO	CuO=0.6	42	4002	2.00
Example3-10		NiO	NiO=1.0	39	4380	2.01

[0319]

As is clear from comparisons between Comparative example 3-1 and Examples 3-1 to 3-4, when the solid acid catalyst is allowed to contain the additive element of the groups 3, 5, 8, 10, and 11 in the periodic table, merely the average molecular weight can be changed at the same condition without adversely affecting the other performance.

As is clear from comparisons between Comparative example 3-2 and Examples 3-5 to 3-8, the same goes for the case where the production condition of the solid acid catalyst is changed and the case where at least two types of metal elements are added.

Furthermore, as is clear from comparisons between Comparative example 3-3 and Examples 3-9 and 3-10, the same goes for the case where the metal element is added to the solid acid catalyst afterward.

[0320]

The present invention has been described in detail with reference to specific forms. However, it is apparent to those skilled in the art that various modifications could be made without departing from the spirit or scope of the invention.

The present invention contains subject matters related to Japanese Patent Application (Japanese Patent Application No. 2005-258055) filed on September 6, 2005 and Japanese Patent Application (Japanese Patent Application No. 2005-258056) filed on September 6, 2005, the entire contents of which are incorporated herein by reference.

CLAIMS

[1] A solid acid catalyst for producing a polyether, characterized in that the amount of surface hydroxyl group is 0.1 to 2.5 $\mu\text{mol}/\text{m}^2$ and the amount of acid exhibiting pKa of -5.6 or less is 20 $\mu\text{mol}/\text{g}$ or more.

[2] A process for production of a polyether, characterized by comprising the step of subjecting a raw material compound to a polymerization reaction or a condensation reaction in the presence of a solid acid catalyst so as to produce a polyether,

wherein a solid acid catalyst having the amount of surface hydroxyl group of 0.1 to 2.5 $\mu\text{mol}/\text{m}^2$ and the amount of acid exhibiting pKa of -5.6 or less of 20 $\mu\text{mol}/\text{g}$ or more is used as the solid acid catalyst.

[3] A process for production of a polyether, characterized by comprising the step of subjecting a raw material compound to a polymerization reaction or a condensation reaction in the presence of a solid acid catalyst so as to produce a polyether,

wherein a solid acid catalyst having surface hydroxyl groups is allowed to contact with an organic compound and/or an inorganic compound, which can react or interact with the surface hydroxyl groups and which is other than the polyether, and is used for the polymerization reaction or the condensation reaction.

[4] The process for production of a polyether according to Claim 1, characterized in that the solid acid catalyst comprises at least one type selected from the group consisting of composite metal oxide catalysts, metal oxide catalysts, and clay catalysts.

[5] The process for production of a polyether according to Claim 3, characterized in that the solid acid catalyst comprises at least one type selected from the group consisting of composite metal oxide catalysts, metal oxide catalysts, and clay catalysts.

[6] The process for production of a polyether according to Claim 2, characterized in that the solid acid catalyst comprises at least one type of metal element selected from the group consisting of the group 2, the group 3, the group 4, the group 5, the group 8, the group 10, the group 11, the group 13, and the group 14 in the periodic table.

[7] The process for production of a polyether according to Claim 3, characterized in that the solid acid catalyst comprises at least one type of metal element selected from the group consisting of the group 2, the group 3, the group 4, the group 5, the group 8, the group 10, the group 11, the group 13, and the group 14 in the periodic table.

[8] The process for production of a polyether according to Claim 3, characterized in that the organic compound comprises at least one type selected from the group

consisting of alcohols, silylating agents, and carbonates.

[9] The process for production of a polyether according to Claim 2, characterized in that a cyclic ether is subjected to a ring-opening polymerization reaction so as to produce a polyether.

[10] The process for production of a polyether according to Claim 3, characterized in that a cyclic ether is subjected to a ring-opening polymerization reaction so as to produce a polyether.

[11] The process for production of a polyether according to Claim 9, characterized in that a cyclic ether is subjected to a ring-opening polymerization reaction in the presence of a carboxylic anhydride and/or a carboxylic acid so as to produce a polyether.

[12] The process for production of a polyether according to Claim 10, characterized in that a cyclic ether is subjected to a ring-opening polymerization reaction in the presence of a carboxylic anhydride and/or a carboxylic acid so as to produce a polyether.

[13] The process for production of a polyether according to Claim 2, characterized in that the solid acid catalyst is produced by conducting a homogeneous precipitation method in carrier pores.

[14] The process for production of a polyether according to Claim 3, characterized in that the solid acid catalyst is

produced by conducting a homogeneous precipitation method in carrier pores.

[15] A process for production of a solid acid catalyst in which a metal hydroxide and/or a metal oxide is supported by a carrier, the process characterized by comprising the step of allowing the metal hydroxide and/or the metal oxide to be supported in pores of the carrier by conducting a homogeneous precipitation method in the carrier pores.

[16] The process for production of a solid acid catalyst according to Claim 15, characterized in that the homogeneous precipitation method comprises a homogeneous precipitation method by using a precipitant precursor.

[17] The process for production of a solid acid catalyst according to Claim 15, characterized in that the precipitant precursor is a base precursor.

[18] The process for production of a solid acid catalyst according to Claim 15, characterized in that the metal hydroxide and/or the metal oxide comprises a hydroxide and/or an oxide of at least one type of metal element selected from the group consisting of the group 3, the group 4, the group 5, the group 13, and the group 14 in the periodic table.

[19] The process for production of a solid acid catalyst according to Claim 17, characterized in that the base precursor is urea.

[20] A process for production of a polyether, the process characterized by comprising the step of subjecting a cyclic ether to ring-opening polymerization in the presence of a catalyst,

wherein a catalyst, in which a solid acid catalyst containing at least one type of element selected from the group consisting of the groups 1, 2, 4, 6, 8, 9, 12, 13, 14, 15, 16, and 17 in the periodic table and being capable of subjecting by itself a cyclic ether to ring-opening polymerization is allowed to contain at least one type of metal element not contained in the solid acid catalyst and selected from the group consisting of the groups 3, 5, 10, and 11 in the periodic table, is used as the catalyst.

[21] The process for production of a polyether according to Claim 20, characterized in that at least one type of solid acid catalyst selected from the group consisting of metal oxide catalysts, composite metal oxide catalysts, clay catalysts, and zeolite catalysts is used as the solid acid catalyst capable of subjecting by itself a cyclic ether to ring-opening polymerization.

[22] The process for production of a polyether according to Claim 20, characterized in that copper and/or nickel is used as the metal element not contained in the solid acid catalyst and selected from the group consisting of the groups 3, 5, 10, and 11 in the periodic table.

[23] The process for production of a polyether according to Claim 20, characterized in that at least one type of solid acid catalyst selected from the group consisting of clay catalysts, silica-alumina, silica-titania, and silica-zirconia is used as the solid acid catalyst capable of subjecting a cyclic ether to ring-opening polymerization.

[24] The process for production of a polyether according to Claim 20, characterized in that the catalyst is produced by allowing the metal hydroxide and/or the metal oxide to be supported in pores of a carrier by conducting a homogeneous precipitation method in the carrier pores.