DESCRIPTION

TITLE OF INVENTION: METHOD FOR PRODUCING METAL SALT OF ALICYCLIC DICARBOXYLIC ACID

TECHNICAL FIELD

[0001]

The present invention relates to methods for producing metal salts of alicyclic dicarboxylic acids.

BACKGROUND ART

[0002]

The present inventor and others have previously conducted extensive studies on metal salts of various carboxylic acids for use as nucleating agents for crystalline thermoplastic resins. As a result, it has been found out that metal salts of alkyl-substituted cyclohexane-1,2-dicarboxylic acids exhibit excellent nucleating performance in resins such as polyolefins.

[0003]

Moreover, the present inventor and others conducted detailed investigations into the effect of the structure of metal salts of alkyl-substituted cyclohexane-1,2-dicarboxylic acids on nucleating performance, and confirmed that excellent nucleating performance is exhibited when the metal species forming the metal salt is calcium or sodium.

The present inventor and others also found out that the stereochemical configuration of the alkyl substituent and the oxycarbonyl group forming the metal salt on the cyclohexane ring has a significant influence on nucleating performance, and ultimately found out that the nucleating performance is improved in correlation with the molar ratio of the cis isomer thereof (see Patent Literature 1).

CITATION LIST

- PATENT LITERATURE

[0004]

Patent Literature 1: WO 2020/054492

[0005]

In general, the metal salts of the alkyl-substituted cyclohexane-1,2-dicarboxylic

acids described above have been produced through the following steps (1) to (3).

(1) An alkyl-substituted 4-cyclohexene-1,2-dicarboxylic acid anhydride is obtained by a Diels-Alder reaction between a conjugated diene compound and maleic anhydride. Alternatively, an alkyl-substituted phthalic anhydride is obtained by a method such as introducing an alkyl substituent into phthalic anhydride.

(2) The alkyl-substituted 4-cyclohexene-1,2-dicarboxylic acid anhydride or the alkyl-substituted phthalic anhydride is subjected to a hydrogenation reaction to obtain an alkyl-substituted cyclohexane-1,2-dicarboxylic acid anhydride.

(3) The alkyl-substituted cyclohexane-1,2-dicarboxylic acid anhydride is reacted with an oxide, hydroxide, or chloride of a metal species that forms the target metal salt.

[0006]

In the reaction system described above, the stereochemical configuration of the alkyl substituent and the oxycarbonyl group forming the metal salt on the cyclohexane ring, which greatly affects the nucleating performance as described above, is represented by the molar ratio of cis-trans isomers. When an alkyl-substituted phthalic anhydride is used as the raw material for the hydrogenation reaction, the molar ratio is established during the hydrogenation reaction (the step (2) above).

[0007]

When the hydrogenation reaction is carried out using an alkyl-substituted 4-cyclohexene-1,2-dicarboxylic acid anhydride, the molar ratio of isomers having an alkyl substituent at the 3-position or the 6-position is determined during the Diels-Alder reaction and the hydrogenation reaction. In addition, the molar ratio of isomers having an alkyl substituent at the 4-position or the 5-position is determined during the hydrogenation reaction. In other words, the cis-trans isomer ratio has already been determined before conversion to the metal salt (i.e., before the step (3) above).

[0008]

In both the Diels-Alder reaction and the hydrogenation reaction described above, formation of the cis isomer is stereochemically favored, and alkyl-substituted cyclohexane-1,2-dicarboxylic acids having a molar ratio of the cis isomer of 60 to 70% or more can be obtained even under ordinary reaction conditions. Moreover, it has been confirmed that, by optimizing the reaction conditions, alkyl-substituted cyclohexane-1,2-dicarboxylic acids having a molar ratio of the cis isomer close to 100% can be obtained in the reaction system.

[0009]

However, the alkyl-substituted 4-cyclohexene-1,2-dicarboxylic acid anhydride used as a raw material readily undergoes double-bond migration upon heating or the like (for example, such migration readily occurs during the step (2) (hydrogenation reaction) of the conventional process). As a result, impurities (ring-structure isomers such as the Δ1 type) are formed and the selectivity is reduced. Consequently, the molar ratio of the cis isomer at the completion of the reaction is generally limited to about 85%, and it has been difficult to achieve a molar ratio of the cis isomer of 90% even under special conditions employing a large amount of solvent or the like.

[0010]

In addition, since the relative volatility of the cis isomer and the trans isomer of the alkyl-substituted cyclohexane-1,2-dicarboxylic acid is substantially the same, removal of the trans isomer requires a distillation column having 100 or more theoretical stages. As a result, there have been problems in that a large amount of heat energy is required and that disposal losses are increased due to the low recovery rate.

SUMMARY OF INVENTION

- Technical Problem

[0011]

In light of this situation, the present invention aims to provide a method for producing a metal salt of an alicyclic dicarboxylic acid (a calcium salt, hydroxyaluminum salt, disodium salt, or dilithium salt of an alkyl-substituted 1,2-dicarboxylic acid), which can reduce disposal losses and can readily produce the metal salt with excellent selectivity (i.e., a high molar ratio of the cis isomer).

- Solution to Problem

[0012]

As a result of intensive studies to solve the above problems, the present inventor found out that all the above problems can be solved by employing a method for producing a metal salt of an alicyclic dicarboxylic acid, the method including: step (1) of obtaining an alkali metal salt or an ammonium salt from cyclohexene-1,2-dicarboxylic acid anhydride having a C1-C4 linear or branched alkyl substituent, or from phthalic anhydride having a C1-C4 linear or branched alkyl substituent; and step (2) of subjecting the alkali metal salt or the ammonium salt obtained in the step (1) to a hydrogenation reaction, thereby completing the present invention.

[0013]

Specifically, the present invention relates to a method for producing a metal salt of an alicyclic dicarboxylic acid, the alicyclic dicarboxylic acid being a metal salt of cyclohexane-1,2-dicarboxylic acid having at least one alkyl substituent directly bound to a cyclohexane ring, the alkyl substituent being a C1-C4 linear or branched alkyl group, the metal salt being a calcium salt, a hydroxyaluminum salt, a disodium salt, or a dilithium salt, the method including the following step (1) and step (2),

step (1): obtaining an alkali metal salt or an ammonium salt from cyclohexene-1,2-dicarboxylic acid anhydride having a C1-C4 linear or branched alkyl substituent, or from phthalic anhydride having a C1-C4 linear or branched alkyl substituent; and

step (2): subjecting the alkali metal salt or the ammonium salt obtained in the step (1) to a hydrogenation reaction.

[0014]

In the method for producing a metal salt of an alicyclic dicarboxylic acid of the present invention, preferably, the alkali metal salt in the step (1) is at least one selected from the group consisting of a sodium salt, a potassium salt, and a lithium salt.

The alkali metal salt in the step (1) is more preferably a sodium salt.

Preferably, a catalyst for the hydrogenation reaction in the step (2) is at least one selected from the group consisting of palladium, rhodium, and ruthenium.

Preferably, a temperature of the hydrogenation reaction in the step (2) is 80°C or lower.

Preferably, the method further includes the following step (3),

step (3): converting the alkali metal salt or the ammonium salt obtained by the hydrogenation in the step (2) into a calcium salt or a disodium salt.

Preferably, the method further includes the following step (4) after the step (2),

step (4): crystallizing the alkali metal salt or the ammonium salt obtained by the hydrogenation in the step (2).

The alkali metal salt subjected to the crystallization in the step (4) is preferably a monoalkali metal salt.

The alkyl substituent is preferably located at the 3-position or the 4-position of the cyclohexane ring.

The alkyl substituent is preferably a methyl group.

The molar ratio of a cis isomer among stereoisomers of the alicyclic dicarboxylic acid with respect to the alkyl substituent and an oxycarbonyl group constituting the metal salt on the cyclohexane ring is preferably 90.0% or more, more preferably 93.0% or more, still more preferably 95% or more.

ADVANTAGEOUS EFFECTS OF INVENTION

[0015]

The present invention provides a method for producing a metal salt of an alicyclic dicarboxylic acid (a calcium salt, hydroxyaluminum salt, disodium salt, or dilithium salt of an alkyl-substituted 1,2-dicarboxylic acid), which can reduce disposal losses and can readily produce the metal salt with excellent selectivity (i.e., a high molar ratio of the cis isomer).

DESCRIPTION OF EMBODIMENTS

[0016]

The method for producing a metal salt of an alicyclic dicarboxylic acid of the present invention is a method for producing a metal salt of an alicyclic dicarboxylic acid, the alicyclic dicarboxylic acid being a metal salt of cyclohexane-1,2-dicarboxylic acid having at least one alkyl substituent directly bound to a cyclohexane ring, the alkyl substituent being a C1-C4 linear or branched alkyl group, the metal salt being a calcium salt, a hydroxyaluminum salt, a disodium salt, or a dilithium salt, the method including the following step (1) and step (2),

step (1): obtaining an alkali metal salt or an ammonium salt from cyclohexene-1,2-dicarboxylic acid anhydride having a C1-C4 linear or branched alkyl substituent, or from phthalic anhydride having a C1-C4 linear or branched alkyl substituent; and

step (2): subjecting the alkali metal salt or the ammonium salt obtained in the step (1) to a hydrogenation reaction.

[0017]

Including the step (1) and the step (2) described above, the method for producing a metal salt of an alicyclic dicarboxylic acid enables production of a metal salt of an alicyclic dicarboxylic acid (a calcium salt, hydroxyaluminum salt, disodium salt, or dilithium salt of an alkyl-substituted 1,2-dicarboxylic acid) having a high molar ratio of the target cis isomer in a high yield.

Moreover, since a purification step (e.g., a distillation step) can be omitted, disposal losses can be reduced.

[0018]

As used herein, the term “cis isomer” in the calcium salt, hydroxyaluminum salt, disodium salt, or dilithium salt of an alkyl-substituted 1,2-dicarboxylic acid means that the alkyl substituent on the cyclohexane ring and two oxycarbonyl groups

constituting the metal salt are all oriented in the same direction.

[0019]

Each step is described hereinbelow.

[0020]

<Step (1)>

The method for producing a metal salt of an alicyclic dicarboxylic acid includes the following step (1).

Step (1): obtaining an alkali metal salt or an ammonium salt from cyclohexene-1,2-dicarboxylic acid anhydride having a C1-C4 linear or branched alkyl substituent (also referred to as an alkyl-substituted cyclohexene-1,2-dicarboxylic acid anhydride), or from phthalic anhydride having a C1-C4 linear or branched alkyl substituent (also referred to as an alkyl-substituted phthalic anhydride).

[0021]

The alkyl-substituted cyclohexene-1,2-dicarboxylic acid anhydride preferably has a C1-C4 linear or branched alkyl substituent at the 3-position or the 4-position, more preferably at the 4-position.

[0022]

Examples of the C1-C4 linear or branched alkyl substituent in the alkyl-substituted cyclohexene-1,2-dicarboxylic acid anhydride include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, and a tert-butyl group.

Among these, a methyl group or a tert-butyl group is preferred from the viewpoint of the crystallization-promoting effect when the resulting metal salt of the alicyclic dicarboxylic acid is used as a nucleating agent.

[0023]

The alkyl-substituted phthalic anhydride preferably has a C1-C4 linear or branched alkyl substituent at the 3-position or the 4-position, more preferably at the 4-position.

[0024]

Examples of the C1-C4 linear or branched alkyl substituent in the alkyl-substituted phthalic anhydride include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, and a tert-butyl group.

Among these, a methyl group or a tert-butyl group is preferred from the viewpoint of the crystallization-promoting effect when the resulting metal salt of the

alicyclic dicarboxylic acid is used as a nucleating agent.

[0025]

The alkali metal salt or the ammonium salt obtained in the step (1) can be prepared by reacting the alkyl-substituted cyclohexene-1,2-dicarboxylic acid anhydride or the alkyl-substituted phthalic anhydride with an alkali metal hydroxide or an amine to open the acid anhydride ring.

[0026]

Examples of the alkali metal hydroxide include sodium hydroxide, potassium hydroxide, and lithium hydroxide.

[0027]

Examples of the amine include triethylamine, ammonia, and trimethylamine.

[0028]

The amount of the alkali metal hydroxide or amine used is preferably 1 equivalent or more and 2 equivalents or less, more preferably 1.1 equivalents or more and 1.9 equivalents or less, relative to the alkyl-substituted cyclohexene-1,2-dicarboxylic acid anhydride or the alkyl-substituted phthalic anhydride, from the viewpoint of stereoselectivity.

[0029]

The alkali metal salt or the ammonium salt obtained in the step (1) is preferably at least one selected from the group consisting of a sodium salt, a potassium salt, and a lithium salt, more preferably a sodium salt or a potassium salt, still more preferably a sodium salt.

[0030]

In the step (1), the reaction method and reaction conditions are not limited as long as an alkali metal salt or an ammonium salt can be obtained.

As a general method, the alkali metal salt or the ammonium salt can be readily obtained by adding the alkyl-substituted cyclohexene-1,2-dicarboxylic acid anhydride or the alkyl-substituted phthalic anhydride to a solution prepared by dissolving the alkali metal hydroxide or amine in water, followed by stirring at room temperature or under slight heating.

[0031]

By carrying out the step (1), the reaction system in the subsequent step (2) can be maintained in a homogeneous state from the beginning of the reaction even when ordinary water is used. This effect becomes more remarkable particularly when the reaction temperature is lowered in order to increase the molar ratio of the cis isomer.

Accordingly, inclusion of the step (1) eliminates the need for a special solvent, thereby enabling simplification of the production process and reduction of production costs.

[0032]

<Step (2)>

The method for producing a metal salt of an alicyclic dicarboxylic acid include the following step (2).

Step (2): subjecting the alkali metal salt or the ammonium salt obtained in the step (1) to a hydrogenation reaction.

[0033]

The hydrogenation reaction in the step (2) is preferably carried out under the following conditions.

[0034]

(a) Concentration

In the step (2), a solution of the alkali metal salt or the ammonium salt obtained in the step (1) (also referred to as a substrate) is used.

The concentration of the substrate is not limited, and is preferably 1% by mass or more and 25% by mass or less, more preferably 5% by mass or more and 20% by mass or less.

[0035]

(b) Reaction catalyst

As the reaction catalyst, preferred are palladium, ruthenium, and rhodium from the viewpoint of increasing the molar ratio of the resulting cis isomer.

A further preferred reaction catalyst is selected depending on the location and type of the alkyl substituent of the alkali metal salt or the ammonium salt obtained in the step (1), or depending on the type of acid anhydride. For example, when the alkyl-substituted cyclohexene-1,2-dicarboxylic acid anhydride is used, palladium and ruthenium are preferred, whereas when the alkyl-substituted phthalic anhydride is used, rhodium and ruthenium are preferred.

[0036]

The reaction catalyst may be one supported on a carrier such as carbon, alumina, silica, zirconia, or zeolite.

In this case, the catalyst loading is preferably from 0.1 to 10% by mass.

[0037]

The amount of the reaction catalyst used is preferably 0.1 parts by mass or

more and 5 parts by mass or less relative to 100 parts by mass of the alkali metal salt or the ammonium salt obtained in the step (1).

[0038]

(c) Reaction temperature

The reaction temperature is preferably 80°C or lower from the viewpoint of suppressing the formation of the above-described impurities (ring-structure isomers such as Δ1 isomers) and preventing a decrease in selectivity.

When the reaction temperature is 80°C or lower, a metal salt of an alicyclic dicarboxylic acid having a molar ratio of the cis isomer of 90.0% or more can be suitably obtained.

The reaction temperature is more preferably 60°C or lower.

[0039]

(d) Reaction pressure

The reaction pressure is preferably 0.1 MPa or higher, more preferably 0.9 MPa or higher, still more preferably 1.8 MPa or higher, particularly preferably 4 MPa or higher in terms of hydrogen pressure (gauge pressure), from the viewpoint of suppressing the formation of the above-described impurities (ring-structure isomers such as Δ1 isomers) and preventing a decrease in selectivity.

In consideration of the disadvantageous need for high-pressure gas facilities, the reaction pressure may be less than 1.0 MPa in terms of hydrogen pressure (gauge pressure). By setting the hydrogen pressure (gauge pressure) to less than 1.0 MPa, the process can be carried out advantageously on an industrial scale.

[0040]

(e) Reaction time

The reaction time is not limited, and is preferably, for example, 30 minutes or more and 5 hours or less.

The reaction time herein refers to the period from when the reaction temperature reaches the above-described reaction temperature until the reaction is terminated.

[0041]

(f) Reaction solvent

Water may be used as the solvent.

[0042]

<Step (3)>

The method for producing a metal salt of an alicyclic dicarboxylic acid

preferably further includes the following step (3) as needed.

Step (3): converting the alkali metal salt or the ammonium salt obtained by the hydrogenation in the step (2) (also simply referred to as a hydrogenated compound) into a calcium salt, a hydroxyaluminum salt, a disodium salt, or a dilithium salt.

[0043]

In the case where the target metal salt of the alicyclic dicarboxylic acid is a disodium salt, when the alkali metal salt obtained in the step (1) is a sodium salt, the sodium salt may be reacted with an aqueous sodium hydroxide solution as appropriate after the step (2) to form a disodium salt, and the step (3) can be omitted.

When the alkali metal salt obtained in the step (1) is a salt other than a sodium salt, the hydrogenated compound obtained in the step (2) may first be converted back to the corresponding carboxylic acid and then reacted with an aqueous sodium hydroxide solution.

[0044]

In the case where the target metal salt of the alicyclic dicarboxylic acid is a dilithium salt, when the alkali metal salt obtained in the step (1) is a lithium salt, the lithium salt may be reacted with an aqueous lithium hydroxide solution as appropriate after the step (2) to form a dilithium salt, and the step (3) can be omitted.

When the alkali metal salt obtained in the step (1) is a salt other than a lithium salt, the hydrogenated compound obtained in the step (2) may first be converted back to the corresponding carboxylic acid and then reacted with an aqueous lithium hydroxide solution.

[0045]

In the case where the target metal salt of the alicyclic dicarboxylic acid is a calcium salt or a hydroxyaluminum salt, it can be readily produced by a so-called double decomposition method or the like, in which the hydrogenated compound obtained in the step (2) is reacted with a hydroxide, oxide, chloride, or the like of calcium or hydroxyaluminum.

[0046]

When a solvent is used in the step (3), water is preferably used.

[0047]

<Step (4)>

The method for producing a metal salt of an alicyclic dicarboxylic acid preferably further includes the following step (4) after the step (2) as needed.

Step (4): crystallizing the hydrogenated compound obtained in the step (2).

[0048]

Inclusion of the step (4) can suitably increase the molar ratio of the cis isomer in the target metal salt of the alicyclic dicarboxylic acid.

When the step (3) is included, the step (4) is preferably performed prior to the step (3).

[0049]

The step (4) may be carried out, for example, by dissolving the hydrogenated compound obtained in the step (2) in a solvent such as water under heating, followed by cooling to crystallize the cis isomer. Alternatively, the solution of the hydrogenated compound obtained in the step (2) may be used as such.

[0050]

From the viewpoint of solubility in water, the alkali metal salt or the ammonium salt crystallized in the step (4) is preferably a monoalkali metal salt or a monoammonium salt.

Specifically, the equivalent amount of the alkali metal salt or the ammonium salt crystallized in the step (4) (i.e., the equivalent amount of the alkali metal salt or the ammonium salt relative to the alicyclic dicarboxylic acid) is preferably from 1.0 equivalents to 1.3 equivalents.

[0051]

The step (4) is preferably carried out under the following conditions.

[0052]

(a) Solvent

The solvent is preferably a solvent that provides relatively low solubility for the cis isomer and allows selective precipitation of the cis isomer. From the viewpoint of environmental considerations and the like, water is more preferred.

[0053]

(b) Concentration

The concentration of the hydrogenated compound during crystallization (also referred to as the substrate concentration) may be appropriately selected in consideration of the selectivity and yield of the cis isomer. From the viewpoint of industrially favorable production, the concentration is preferably 15 to 20% by mass.

[0054]

<Metal salt of an alicyclic dicarboxylic acid>

A metal salt of an alicyclic dicarboxylic acid produced by the method for producing a metal salt of an alicyclic dicarboxylic acid of the present invention will

now be described.

[0055]

The metal salt of an alicyclic dicarboxylic acid is a metal salt of cyclohexane-1,2-dicarboxylic acid having at least one alkyl substituent directly bound to the cyclohexane ring, wherein the alkyl substituent is a C1-C4 linear or branched alkyl group, and the metal salt is a calcium salt, a hydroxyaluminum salt, a disodium salt, or a dilithium salt.

[0056]

Examples of the C1-C4 linear or branched alkyl group include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, and a tert-butyl group.

Among these, a methyl group or a tert-butyl group is preferred from the viewpoint of the crystallization-promoting effect when the metal salt of the alicyclic dicarboxylic acid is used as a nucleating agent.

[0057]

The alkyl substituent is preferably located at the 3-position or the 4-position of the cyclohexane ring, more preferably at the 4-position, from the viewpoint of the crystallization-promoting effect when the metal salt of the alicyclic dicarboxylic acid is used as a nucleating agent.

[0058]

The metal salt is preferably a calcium salt from the viewpoint of the crystallization-promoting effect when the metal salt of the alicyclic dicarboxylic acid is used as a nucleating agent.

[0059]

Specific examples of the metal salt of an alicyclic dicarboxylic acid include disodium salts of 3-methylcyclohexane-1,2-dicarboxylic acid, calcium salts of 3-methylcyclohexane-1,2-dicarboxylic acid, hydroxyaluminum salts of 3-methylcyclohexane-1,2-dicarboxylic acid, dilithium salts of 3-methylcyclohexane-1,2-dicarboxylic acid, disodium salts of 3-ethylcyclohexane-1,2-dicarboxylic acid, calcium salts of 3-ethylcyclohexane-1,2-dicarboxylic acid, hydroxyaluminum salts of 3-ethylcyclohexane-1,2-dicarboxylic acid, dilithium salts of 3-ethylcyclohexane-1,2-dicarboxylic acid, disodium salts of 3-n-propylcyclohexane-1,2-dicarboxylic acid, calcium salts of 3-n-propylcyclohexane-1,2-dicarboxylic acid, hydroxyaluminum salts of 3-n-propylcyclohexane-1,2-dicarboxylic acid, dilithium salts of 3-n-propylcyclohexane-1,2-dicarboxylic acid, disodium salts of 3-isopropylcyclohexane-

1,2-dicarboxylic acid, calcium salts of 3-isopropylcyclohexane-1,2-dicarboxylic acid, hydroxyaluminum salts of 3-isopropylcyclohexane-1,2-dicarboxylic acid, dilithium salts of 3-isopropylcyclohexane-1,2-dicarboxylic acid, disodium salts of 3-n-butylcyclohexane-1,2-dicarboxylic acid, calcium salts of 3-n-butylcyclohexane-1,2-dicarboxylic acid, hydroxyaluminum salts of 3-n-butylcyclohexane-1,2-dicarboxylic acid, dilithium salts of 3-n-butylcyclohexane-1,2-dicarboxylic acid, disodium salts of 3-tert-butylcyclohexane-1,2-dicarboxylic acid, calcium salts of 3-isobutylcyclohexane-1,2-dicarboxylic acid, hydroxy aluminum salts of 3-isobutylcyclohexane-1,2-dicarboxylic acid, dilithium salts of 3-isobutylcyclohexane-1,2-dicarboxylic acid, disodium salts of 4-methylcyclohexane-1,2-dicarboxylic acid, calcium salts of 4-methylcyclohexane-1,2-dicarboxylic acid, hydroxyaluminum salts of 4-methylcyclohexane-1,2-dicarboxylic acid, dilithium salts of 4-methylcyclohexane-1,2-dicarboxylic acid, disodium salts of 4-ethylcyclohexane-1,2-dicarboxylic acid, calcium salts of 4-ethylcyclohexane-1,2-dicarboxylic acid, hydroxy aluminum salts of 4-ethylcyclohexane-1,2-dicarboxylic acid, dilithium salts of 4-ethylcyclohexane-1,2-dicarboxylic acid, disodium salts of 4-n-propylcyclohexane-1,2-dicarboxylic acid, calcium salts of 4-n-propylcyclohexane-1,2-dicarboxylic acid, hydroxyaluminum salts of 4-n-propylcyclohexane-1,2-dicarboxylic acid, dilithium salts of 4-n-propylcyclohexane-1,2-dicarboxylic acid, disodium salts of 4-isopropylcyclohexane-1,2-dicarboxylic acid, calcium salts of 4-isopropylcyclohexane-1,2-dicarboxylic acid, hydroxy aluminum salts of 4-isopropylcyclohexane-1,2-dicarboxylic acid, dilithium salts of 4-isopropylcyclohexane-1,2-dicarboxylic acid, disodium salts of 4-n-butylcyclohexane-1,2-dicarboxylic acid, calcium salts of 4-n-butylcyclohexane-1,2-dicarboxylic acid, hydroxyaluminum salts of 4-n-butylcyclohexane-1,2-dicarboxylic acid, dilithium salts of 4-n-butylcyclohexane-1,2-dicarboxylic acid, disodium salts of 4-tert-butylcyclohexane-1,2-dicarboxylic acid, calcium salts of 4-tert-butylcyclohexane-1,2-dicarboxylic acid, hydroxyaluminum salts of 4-tert-butylcyclohexane-1,2-dicarboxylic acid, dilithium salts of 4-tert-butylcyclohexane-1,2-dicarboxylic acid, disodium salts of 4-isobutylcyclohexane-1,2-dicarboxylic acid, calcium salts of 4-isobutylcyclohexane-1,2-dicarboxylic acid, hydroxyaluminum salts of 4-isobutylcyclohexane-1,2-dicarboxylic acid, and dilithium salts of 4-isobutylcyclohexane-1,2-dicarboxylic acid. Preferred are, for example, disodium salts of 3-methylcyclohexane-1,2-dicarboxylic acid, calcium salts of 4-methylcyclohexane-1,2-dicarboxylic acid, and calcium salts of 4-tert-butylcyclohexane-1,2-dicarboxylic acid.

[0060]

The molar ratio of the cis isomer, among stereoisomers of the alicyclic dicarboxylic acid with respect to the alkyl substituent and the oxycarbonyl group constituting the metal salt on the cyclohexane ring, is preferably 90.0% or more, more preferably 93.0% or more, still more preferably 95.0% or more, particularly preferably 97.0% or more, most preferably 99.0% or more, from the viewpoint of the crystallization-promoting effect when the metal salt of the alicyclic dicarboxylic acid is used as a nucleating agent.

[0061]

The following are disclosed herein.

[0062]

The present disclosure (1) relates to a method for producing a metal salt of an alicyclic dicarboxylic acid, the alicyclic dicarboxylic acid being a metal salt of cyclohexane-1,2-dicarboxylic acid having at least one alkyl substituent directly bound to a cyclohexane ring, the alkyl substituent being a C1-C4 linear or branched alkyl group, the metal salt being a calcium salt, a hydroxyaluminum salt, a disodium salt, or a dilithium salt, the method including the following step (1) and step (2),

step (1): obtaining an alkali metal salt or an ammonium salt from cyclohexene-1,2-dicarboxylic acid anhydride having a C1-C4 linear or branched alkyl substituent, or from phthalic anhydride having a C1-C4 linear or branched alkyl substituent; and

step (2): subjecting the alkali metal salt or the ammonium salt obtained in the step (1) to a hydrogenation reaction.

The present disclosure (2) relates to the method for producing a metal salt of an alicyclic dicarboxylic acid according to the present disclosure (1), wherein the alkali metal salt in the step (1) is at least one selected from the group consisting of a sodium salt, a potassium salt, and a lithium salt.

The present disclosure (3) relates to the method for producing a metal salt of an alicyclic dicarboxylic acid according to the present disclosure (2), wherein the alkali metal salt in the step (1) is a sodium salt.

The present disclosure (4) relates to the method for producing a metal salt of an alicyclic dicarboxylic acid according to any one of the present disclosures (1) to (3), wherein a catalyst for the hydrogenation reaction in the step (2) is at least one selected from the group consisting of palladium, rhodium, and ruthenium.

The present disclosure (5) relates to the method for producing a metal salt of an alicyclic dicarboxylic acid according to any one of the disclosures (1) to (4), wherein a

temperature of the hydrogenation reaction in the step (2) is 80°C or lower.

The present disclosure (6) relates to the method for producing a metal salt of an alicyclic dicarboxylic acid according to any one of the present disclosures (1) to (5), further including the following step (3),

step (3): converting the alkali metal salt or the ammonium salt obtained by the hydrogenation in the step (2) into a calcium salt or a disodium salt.

The present disclosure (7) relates to the method for producing a metal salt of an alicyclic dicarboxylic acid according to any one of the present disclosures (1) to (6), further including the following step (4) after the step (2),

step (4): crystallizing the alkali metal salt or the ammonium salt obtained by the hydrogenation in the step (2).

The present disclosure (8) relates to the method for producing a metal salt of an alicyclic dicarboxylic acid according to the present disclosure (7), wherein the alkali metal salt or the ammonium salt subjected to the crystallization in the step (4) is a monoalkali metal salt.

The present disclosure (9) relates to the method for producing a metal salt of an alicyclic dicarboxylic acid according to any one of the present disclosures (1) to (8), wherein the alkyl substituent is located at 3-position or 4-position on the cyclohexane ring.

The present disclosure (10) relates to the method for producing a metal salt of an alicyclic dicarboxylic acid according to any one of the present disclosures (1) to (9), wherein the alkyl substituent is a methyl group.

The present disclosure (11) relates to the method for producing a metal salt of an alicyclic dicarboxylic acid according to any one of the present disclosures (1) to (10), wherein stereoisomers of the alicyclic dicarboxylic acid with respect to the alkyl substituent and an oxycarbonyl group constituting the metal salt on the cyclohexane ring includes a cis isomer at a molar ratio of 90.0% or more.

The present disclosure (12) relates to the method for producing a metal salt of an alicyclic dicarboxylic acid according to any one of the present disclosures (1) to (11), wherein the molar ratio of the cis isomer is 93.0% or more.

The present disclosure (13) relates to the method for producing a metal salt of an alicyclic dicarboxylic acid according to the present disclosure (7) or (8), wherein the molar ratio of the cis isomer is 95.0% or more.

EXAMPLES

[0063]

The present invention will be described in more detail with reference to, but not limited to, the following examples. The abbreviations of compounds used in the examples and the methods for measuring the respective properties are as follows.

[0064]

[Method for analyzing obtained compound]

(1) Gas chromatography analysis (GC analysis)

In each step, the molar ratio of the cis isomer among stereoisomers of the alicyclic dicarboxylic acid with respect to the alkyl substituent and the oxycarbonyl group constituting the metal salt on the cyclohexane ring was measured by GC analysis. The GC measurement conditions were as follows.

In the case of an alicyclic dicarboxylic acid, the compound was cyclized with acetic anhydride and analyzed as the corresponding acid anhydride. In the case of a metal salt or an ammonium salt of an alicyclic dicarboxylic acid, the compound was first converted back to the corresponding acid using concentrated hydrochloric acid, then cyclized with acetic anhydride, and analyzed as the corresponding acid anhydride.

<GC measurement conditions>

Type of equipment: Gas chromatograph GC-2010 (available from Shimadzu Corporation)

Detector: FID, 280°C

Column: DB-1701 (60 m × 0.25 mmφ × 0.25 μm)

Column temperature: 145°C

Injection temperature: 280°C

Carrier gas: helium (line speed: 30 cm/sec)

Injection amount: 0.1 μL (sprit ratio: 1/35)

[0065]

After the GC analysis, the area ratios of the peaks were calculated by an area percentage method, and the molar ratio of the cis isomer among stereoisomers of the alicyclic dicarboxylic acid with respect to the alkyl substituent and the oxycarbonyl group constituting the metal salt on the cyclohexane ring was determined using the expression: [(area ratio of cis isomer)/(area ratio of cis isomer + area ratio of trans isomer)] × 100.

Comparison of the above molar ratio with the result of the similar measurement performed after converting the obtained metal salt of the alicyclic dicarboxylic acid back to an acid anhydride thereof revealed that the molar ratio of the cis isomer among

the stereoisomers did not change before and after the step [compound obtained in the step (3)] of reacting the alicyclic dicarboxylic acid or a derivative thereof [compound obtained in the step (2) or (4)] with a metal oxide, a metal hydroxide, or a metal chloride.

[0066]

In the examples and comparative examples below, the molar ratio of the cis isomer was evaluated according to the following criteria.

○○: 93% or more.

○: 90% or more and less than 93%.

×: less than 90%.

[0067]

In addition, nuclear magnetic resonance spectroscopy analysis described below confirmed that the compounds corresponding to the respective retention times were alicyclic dicarboxylic acid anhydrides or derivatives thereof, and that the corresponding isomers were the cis isomer and the trans isomer among the above-mentioned stereoisomers.

[0068]

(2) Nuclear magnetic resonance spectroscopy (NMR analysis)

The structures of the respective isomers identified in the gas chromatography analysis were confirmed by nuclear magnetic resonance spectroscopy (NMR) analysis. Conditions for the NMR analysis are described below.

NMR analysis apparatus: trade name “DRX-500” available from Bruker

Solvent: deuterated dimethylsulfoxide (DMSO-d6)

Internal standard: tetramethylsilane (TMS)

Sample tube: 5 mm

^{1}H-NMR ... resonance frequency: 500.1 MHz, number of scans: 4

^{13}C-NMR ... resonance frequency: 125.8 MHz, number of scans: 23

The measurement sample was prepared by diluting 30 mg of a sample with 0.8 ml of the solvent.

The stereochemical configuration of each isomer was determined by measuring HMBC, HHCOYS, HMQC, and NOESY spectra.

[0069]

(3) Infrared spectroscopy (IR analysis)

FT-IR apparatus: trade name “Spectrum One” available from PerkinElmer, measurement range: 650 to 4000 cm^{-1}, measurement method: ATR method, number of

scans: 3, resolution: 4.00 cm^{-1}

The measurement was performed with the sample pressed onto a cell of the apparatus.

[0070]

(4) Inductively coupled plasma analysis (ICP analysis)

ICP apparatus: trade name "iCAP 6500Duo" available from Thermo Fisher SCIENTIFIC

Spray chamber: cyclone sprayer

Plasma conditions: plasma/aid/carrier = 15/1.0/0.6

Plasma observation direction: three times in axial direction

Prior to measurement, the sample was pretreated by a microwave digestion method to prepare a sample for analysis.

Microwave apparatus: "Multiwave PRO" available from Anton Paar

Digestion conditions: About 0.05 g of the sample was digested with 6 mL of nitric acid (reagent grade) and then diluted with distilled water.

[0071]

(Example 1)

<Step (1)>

Into a 500-mL four-neck flask equipped with a stirrer and a reflux condenser were charged 6.0 g (150 mmol) of sodium hydroxide and 125 g of ion-exchanged water, and the mixture was stirred at room temperature until a homogeneous solution was obtained. Homogeneity of the solution was confirmed visually.

Subsequently, 25 g (150 mmol) of 4-methyl-4-cyclohexene-1,2-dicarboxylic acid anhydride (also referred to as "4-MT"; available from New Japan Chemical Co., Ltd.; trade name: "Rikacid MT") was added, and the mixture was stirred with heating until a homogeneous solution was obtained, thereby providing an aqueous solution of a metal salt (sodium salt) of 4-methyl-4-cyclohexene-1,2-dicarboxylic acid at a concentration of 20% by mass.

[0072]

<Step (2)>

Into a 500-mL autoclave were charged 150 g of the aqueous solution of a metal salt of 4-methyl-4-cyclohexene-1,2-dicarboxylic acid at a concentration of 20% by mass (also referred to as the substrate concentration) obtained in the step (1), and 0.3 g (1% by mass relative to the substrate) of a palladium-on-alumina catalyst (also referred to as "Pd/Al_2O_3") as a hydrogenation catalyst. The system was purged with hydrogen three

times.

Subsequently, the reaction was carried out at 60°C for one hour under a hydrogen atmosphere at 3 MPa (gauge pressure). After completion of the reaction, the hydrogenation catalyst was removed by hot filtration.

Thereafter, water was distilled off using an evaporator, and the residue was vacuum-dried at 80°C to obtain a monosodium salt of 4-methylcyclohexane-1,2-dicarboxylic acid.

GC analysis described above confirmed that the resulting monosodium salt of 4-methylcyclohexane-1,2-dicarboxylic acid had a molar ratio of the cis isomer of 93.5%.

[0073]

<Step (3)>

Into a 500-mL four-neck flask equipped with a stirrer, a reflux condenser, and a dropping funnel were charged 1.92 g (48 mmol) of sodium hydroxide and 225 g of ion-exchanged water, and the mixture was stirred at room temperature until a homogeneous solution was obtained.

After confirming dissolution visually, 10 g (48 mmol) of the monosodium salt of 4-methylcyclohexane-1,2-dicarboxylic acid obtained in the step (2) was added, and the mixture was stirred until a homogeneous solution was obtained, thereby providing an aqueous solution of the disodium salt of 4-methylcyclohexane-1,2-dicarboxylic acid.

The resulting aqueous solution was heated to 80°C, and 21.2 g of an aqueous calcium chloride solution prepared separately (an aqueous solution prepared by homogeneously dissolving 6.2 g (48 mmol) of calcium chloride dihydrate in 15 g of ion-exchanged water) was added dropwise over one hour. During the dropwise addition of the aqueous calcium chloride solution, formation of a white solid precipitate was observed almost simultaneously with the addition.

After completion of the dropwise addition of the aqueous calcium chloride solution, the reaction mixture was heated to 80°C and further stirred with heating for 1.5 hours, followed by hot filtration. The resulting solid was washed with a small amount of water and then vacuum-dried at 150°C for 10 hours, thereby obtaining 10.3 g (yield: 95.7%) of the desired calcium salt of 4-methylcyclohexane-1,2-dicarboxylic acid.

The structure of the obtained compound was confirmed to be that of the target compound by IR analysis and ICP analysis. In addition, the obtained calcium salt was converted back to the corresponding acid and analyzed by GC, confirming that the molar ratio of the cis isomer was 93.5%.

[0074]

(Examples 2 to 27)

The type of the acid anhydride, and the types and amounts of the alkali metal hydroxide and amine (also collectively referred to as alkali metal and the like) used in the step (1) were changed as shown in the tables.

The concentration of the aqueous solution of the metal salt of 4-methyl-4-cyclohexene-1,2-dicarboxylic acid used in the step (2) (also referred to as the substrate concentration), the type and amount of the catalyst, and the reaction conditions (hydrogen pressure, reaction temperature, and reaction time) were changed as shown in the tables.

Except for the above changes, a calcium salt of 4-methylcyclohexane-1,2-dicarboxylic acid was prepared as in Example 1.

[0075]

The catalysts used in the step (2) in the above examples were as follows.

<Catalyst>

Palladium-on-carbon catalyst (also referred to as "Pd/C")

Rhodium-on-alumina catalyst (also referred to as "Rh/Al_2O_3")

Ruthenium-on-alumina catalyst (also referred to as "Ru/Al_2O_3")

Trimethylamine is also referred to as "Me_3N", and triethylamine is also referred to as "Et_3N".

[0076]

(Examples 28 and 29)

In the step (1), 4-methylphthalic anhydride (also referred to as "4-MePA") was used in place of 4-methyl-4-cyclohexene-1,2-dicarboxylic acid anhydride, and the amount of the alkali metal and the like was changed as shown in the table.

The type of the catalyst used in the step (2) was changed as shown in the table.

Except for the above changes, a calcium salt of 4-methylcyclohexane-1,2-dicarboxylic acid was prepared as in Example 1.

[0077]

(Example 30)

In the step (1), 3-methyl-4-cyclohexene-1,2-dicarboxylic acid anhydride (also referred to as "3-MT") was used in place of 4-methyl-4-cyclohexene-1,2-dicarboxylic acid anhydride, and the amount of the alkali metal and the like was changed as shown in the table.

The type of the catalyst used in the step (2) was changed as shown in the table.

Except for the above changes, a calcium salt of 3-methylcyclohexane-1,2-dicarboxylic acid was prepared as in Example 1.

[0078]

(Example 31)

In the step (1), 4-(1-propyl)phthalic anhydride (also referred to as "4-(1-Pr)PA") was used in place of 4-methyl-4-cyclohexene-1,2-dicarboxylic acid anhydride, and the amount of the alkali metal and the like was changed as shown in the table.

Except for the above changes, a calcium salt of 4-(1-propyl)cyclohexane-1,2-dicarboxylic acid was prepared as in Example 1.

[0079]

(Example 32)

In the step (1), 4-tert-butylphthalic anhydride (also referred to as "4-t-BuPA") was used in place of 4-methyl-4-cyclohexene-1,2-dicarboxylic acid anhydride, and the amount of the alkali metal and the like was changed as shown in the table.

Except for the above changes, a calcium salt of 4-tert-butylcyclohexane-1,2-dicarboxylic acid was prepared as in Example 1.

[0080]

(Comparative Examples 1 to 3)

The step (1) was omitted. In the step (2), an aqueous solution of 4-methyl-4-cyclohexene-1,2-dicarboxylic acid (substrate concentration: 5% by mass) was used.

In the step (2), the type of the catalyst was changed as shown in the table.

Except for the above changes, the procedure of Example 1 was followed.

[0081]

(Comparative Example 4)

The step (1) was omitted, and 4-methyl-4-cyclohexene-1,2-dicarboxylic acid anhydride (substrate concentration: 100% by mass) was used.

Into a 500-mL autoclave were charged 150 g of 4-MT and 1.5 g (1% by mass relative to the substrate) of a palladium catalyst as a hydrogenation catalyst, and the system was purged with hydrogen three times.

Subsequently, the reaction was carried out at 150°C for five hours under a hydrogen atmosphere at 3 MPa (gauge pressure). After completion of the reaction, the hydrogenation catalyst was removed by hot filtration.

In the step (2), the reaction conditions (reaction temperature) were changed as shown in the table.

Except for the above changes, the procedure of Example 1 was followed.

[0082]

[Table 1]

	Step (1)			Step (2)						Evaluation results	
	Acid anhydride	Alkali metal and the like		Substrate	Catalyst		Hydrogen pressure	Reaction temperature	Reaction time	Molar ratio of cis isomer (%)	Evaluation
	Type	Type	Equivalent amount	Concentration (% by mass)	Type	Amount (% by mass)	(MPa)	(°C)	(h)		
Example 1	4-MT	NaOH	1	20	Pd/Al_2O_3	1	3	60	1	93.5	○○
Example 2	4-MT	NaOH	0.8	20	Pd/Al_2O_3	1	3	60	1	90.0	○
Example 3	4-MT	NaOH	1.5	20	Pd/Al_2O_3	1	3	60	1	93.5	○○
Example 4	4-MT	NaOH	2	20	Pd/Al_2O_3	1	3	60	1	93.5	○○
Example 5	4-MT	NaOH	2	20	Pd/Al_2O_3	1	3	80	1	92.6	○
Example 6	4-MT	KOH	2	20	Pd/Al_2O_3	1	3	60	1	93.5	○○
Example 7	4-MT	LiOH	2	20	Pd/Al_2O_3	1	3	60	1	93.5	○○
Example 8	4-MT	NH_3	2	20	Pd/Al_2O_3	1	3	60	1	93.5	○○
Example 9	4-MT	Me_3N	2	20	Pd/Al_2O_3	1	3	60	1	93.5	○○
Example 10	4-MT	Et_3N	2	20	Pd/Al_2O_3	1	3	60	1	93.5	○○
Example 11	4-MT	NaOH	2	20	Pd/Al_2O_3	1	3	30	1	95.3	○○
Example 12	4-MT	NaOH	2	20	Pd/Al_2O_3	1	3	80	1	92.8	○○
Example 13	4-MT	NaOH	2	20	Pd/Al_2O_3	1	3	100	1	91.0	○○
Example 14	4-MT	NaOH	2	5	Pd/Al_2O_3	1	3	30	1	96.1	○○
Example 15	4-MT	NaOH	2	5	Pd/Al_2O_3	1	3	60	1	94.6	○○
Example 16	4-MT	NaOH	2	5	Pd/Al_2O_3	1	3	80	1	93.4	○○
Example 17	4-MT	NaOH	2	20	Pd/Al_2O_3	10	3	60	1	94.3	○○

[0083]

[Table 2]

	Step (1)			Step (2)						Evaluation results	
	Acid anhydride	Alkali metal and the like		Substrate	Catalyst		Hydrogen pressure	Reaction temperature	Reaction time	Molar ratio of cis isomer (%)	Evaluation
	Type	Type	Equivalent amount	Concentration (% by mass)	Type	Amount (% by mass)	(MPa)	(°C)	(h)		
Example 18	4-MT	NaOH	2	20	Pd/Al_2O_3	0.5	3	60	1	93.0	○○
Example 19	4-MT	NaOH	2	20	Pd/C	1	3	60	1	93.6	○○
Example 20	4-MT	NaOH	2	20	Rh/Al_2O_3	1	3	60	1	92.4	○
Example 21	4-MT	NaOH	2.2	20	Rh/Al_2O_3	1	3	60	1	90.9	○
Example 22	4-MT	NaOH	2	20	Ru/Al_2O_3	1	3	60	1	91.3	○
Example 23	4-MT	NaOH	2	20	Pd/Al_2O_3	1	0.1	60	5	93.2	○○
Example 24	4-MT	NaOH	2	20	Pd/Al_2O_3	1	0.9	60	1	93.5	○○
Example 25	4-MT	NaOH	2	20	Pd/Al_2O_3	1	1.8	60	1	93.5	○○
Example 26	4-MT	NaOH	2	20	Pd/Al_2O_3	1	4	60	1	94.2	○○
Example 27	4-MT	NaOH	2	20	Pd/Al_2O_3	1	10	60	1	94.2	○○
Example 28	4-MePA	NaOH	2	20	Rh/Al_2O_3	1	3	60	1	97.8	○○
Example 29	4-MePA	NaOH	2	20	Ru/Al_2O_3	1	3	60	1	96.9	○○
Example 30	3-MT	NaOH	1	10	Pd/Al_2O_3	1	3	60	1	98.5	○○
Example 31	4-(1-Pr)PA	NaOH	2	20	Pd/Al_2O_3	1	3	60	1	98.4	○○
Example 32	4-t-BuPA	NaOH	2	20	Pd/Al_2O_3	1	3	60	1	99.9	○○
Comparative Example 1	4-MT	-	-	5	Pd/Al_2O_3	1	3	60	1	82.0	×
Comparative Example 2	4-MT	-	-	5	Rh/Al_2O_3	1	3	60	1	82.0	×
Comparative Example 3	4-MT	-	-	5	Ru/Al_2O_3	1	3	60	1	82.0	×
Comparative Example 4	4-MT	-	-	100	Pd/Al_2O_3	1	3	150	1	82.5	×

[0084]

(Example 33)

The step (1) and the step (2) were carried out as in Example 1.

<Step (4)>

The monosodium salt of 4-methylcyclohexane-1,2-dicarboxylic acid obtained in the step (2) was dissolved in water heated to 60°C to prepare an aqueous solution having a substrate concentration of 20% by mass.

Next, the aqueous solution was gradually cooled to 30°C to crystallize the cis isomer of the monosodium salt of 4-methylcyclohexane-1,2-dicarboxylic acid.

Thereafter, the crystals were collected by suction filtration and washed with a small amount of water to obtain a wet cake. The wet cake was then vacuum-dried at 80°C to obtain crystals.

The filtrate obtained by suction filtration was concentrated, and crystallization was carried out again in the same manner to obtain additional crystals.

[0085]

<Step (3)>

Into a 500-mL four-neck flask equipped with a stirrer, a reflux condenser, and a dropping funnel were charged 1.92 g (48 mmol) of sodium hydroxide and 225 g of ion-exchanged water, and the mixture was stirred at room temperature until a homogeneous solution was obtained.

After confirming dissolution visually, 10 g (48 mmol) of the crystals of the monosodium salt of 4-methylcyclohexane-1,2-dicarboxylic acid obtained in the step (4) was added, and the mixture was stirred until a homogeneous solution was obtained, thereby providing an aqueous solution of the disodium salt of 4-methylcyclohexane-1,2-dicarboxylic acid.

The resulting aqueous solution was heated to 80°C, and 21.2 g of an aqueous calcium chloride solution prepared separately (an aqueous solution prepared by homogeneously dissolving 6.2 g (48 mmol) of calcium chloride dihydrate in 15 g of ion-exchanged water) was added dropwise over one hour. During the dropwise addition of the aqueous calcium chloride solution, formation of a white solid precipitate was observed almost simultaneously with the addition.

After completion of the dropwise addition of the aqueous calcium chloride solution, the reaction mixture was heated to 80°C and further stirred with heating for 1.5 hours, followed by hot filtration. The resulting solid was washed with a small amount of water and then vacuum-dried at 150°C for 10 hours, thereby obtaining 10.3 g (yield: 95.7%) of the desired calcium salt of 4-methylcyclohexane-1,2-dicarboxylic acid.

The structure of the obtained compound was confirmed to be that of the target compound by IR analysis and ICP analysis. In addition, the obtained calcium salt was converted back to the corresponding acid and analyzed by GC, confirming that the molar ratio of the cis isomer was 99.9% or higher.

[0086]

From the examples, it was confirmed that, by employing a method for producing a metal salt of an alicyclic dicarboxylic acid including: step (1) of obtaining an alkali metal salt or an ammonium salt from cyclohexene-1,2-dicarboxylic acid anhydride having a C1-C4 linear or branched alkyl substituent, or from phthalic anhydride having a C1-C4 linear or branched alkyl substituent; and step (2) of subjecting the alkali metal salt or the ammonium salt obtained in the step (1) to a hydrogenation reaction, disposal losses can be reduced and a metal salt of an alicyclic dicarboxylic acid having a high molar ratio of the cis isomer can be obtained.

INDUSTRIAL APPLICABILITY

[0087]

The present invention provides a method for producing a metal salt of an alicyclic dicarboxylic acid (a calcium salt, hydroxyaluminum salt, disodium salt, or dilithium salt of an alkyl-substituted 1,2-dicarboxylic acid), which can reduce disposal losses and can readily produce the metal salt with excellent selectivity (i.e., a high molar ratio of the cis isomer).

The metal salt of the alicyclic dicarboxylic acid (a calcium salt, hydroxyaluminum salt, disodium salt, or dilithium salt of an alkyl-substituted 1,2-dicarboxylic acid) exhibits excellent performance as a nucleating agent for polyolefin resins and other resins. For example, it can significantly improve the crystallization rate, that is, the crystallization temperature, of thermoplastic resins such as polyolefin resins. As a result, molding cycles, particularly for large molded articles, can be significantly shortened, thereby contributing to cost reduction and prevention of processing troubles. Moreover, by improving the degree of crystallinity, not only are mechanical properties such as rigidity and thermal properties such as heat resistance of the resulting molded articles improved, but sink marks and warpage are also reduced, making it possible to stably produce molded articles having complex shapes.

CLAIMS

[Claim 1] A method for producing a metal salt of an alicyclic dicarboxylic acid,

the alicyclic dicarboxylic acid being a metal salt of cyclohexane-1,2-dicarboxylic acid having at least one alkyl substituent directly bound to a cyclohexane ring,

the alkyl substituent being a C1-C4 linear or branched alkyl group,

the metal salt being a calcium salt, a hydroxyaluminum salt, a disodium salt, or a dilithium salt,

the method comprising the following step (1) and step (2),

step (1): obtaining an alkali metal salt or an ammonium salt from cyclohexene-1,2-dicarboxylic acid anhydride having a C1-C4 linear or branched alkyl substituent, or from phthalic anhydride having a C1-C4 linear or branched alkyl substituent; and

step (2): subjecting the alkali metal salt or the ammonium salt obtained in the step (1) to a hydrogenation reaction.

[Claim 2] The method for producing a metal salt of an alicyclic dicarboxylic acid according to claim 1,

wherein the alkali metal salt in the step (1) is at least one selected from the group consisting of a sodium salt, a potassium salt, and a lithium salt.

[Claim 3] The method for producing a metal salt of an alicyclic dicarboxylic acid according to claim 2,

wherein the alkali metal salt in the step (1) is a sodium salt.

[Claim 4] The method for producing a metal salt of an alicyclic dicarboxylic acid according to any one of claims 1 to 3,

wherein a catalyst for the hydrogenation reaction in the step (2) is at least one selected from the group consisting of palladium, rhodium, and ruthenium.

[Claim 5] The method for producing a metal salt of an alicyclic dicarboxylic acid according to any one of claims 1 to 3,

wherein a temperature of the hydrogenation reaction in the step (2) is 80°C or lower.

[Claim 6] The method for producing a metal salt of an alicyclic dicarboxylic acid according to any one of claims 1 to 3, further comprising the following step (3),

step 3: converting the alkali metal salt or the ammonium salt obtained by the hydrogenation in the step (2) into a calcium salt, a hydroxyaluminum salt, a disodium salt, or a dilithium salt.

[Claim 7] The method for producing a metal salt of an alicyclic dicarboxylic acid according to claim 1 or 2, further comprising the following step (4) after the step (2),

step (4): crystallizing the alkali metal salt or the ammonium salt obtained by the hydrogenation in the step (2).

[Claim 8] The method for producing a metal salt of an alicyclic dicarboxylic acid according to claim 7,

wherein the alkali metal salt or the ammonium salt subjected to the crystallization in the step (4) is a monoalkali metal salt.

[Claim 9] The method for producing a metal salt of an alicyclic dicarboxylic acid according to any one of claims 1 to 3,

wherein the alkyl substituent is located at 3-position or 4-position on the cyclohexane ring.

[Claim 10] The method for producing a metal salt of an alicyclic dicarboxylic acid according to any one of claims 1 to 3,

wherein the alkyl substituent is a methyl group.

[Claim 11] The method for producing a metal salt of an alicyclic dicarboxylic acid according to any one of claims 1 to 3,

wherein stereoisomers of the alicyclic dicarboxylic acid with respect to the alkyl substituent and an oxycarbonyl group constituting the metal salt on the cyclohexane ring include a cis isomer at a molar ratio of 90.0% or more.

[Claim 12] The method for producing a metal salt of an alicyclic dicarboxylic acid according to claim 11,

wherein the molar ratio of the cis isomer is 93.0% or more.

[Claim 13] The method for producing a metal salt of an alicyclic dicarboxylic acid according to claim 7,

wherein stereoisomers of the alicyclic dicarboxylic acid with respect to the alkyl substituent and an oxycarbonyl group constituting the metal salt on the cyclohexane ring include a cis isomer at a molar ratio of 95.0% or more.