The present inventors have disclosed a method for producing an aluminotitanosilicate by contacting an aluminosilicate compound with a liquid halogenated titanium compound (Patent Literature 5).

Citation List

Patent Literature

[0007]

[Patent Literature 1] JP4254009

[Patent Literature 2] WO2015/041137

[Patent Literature 3] JP2008-050186A

[Patent Literature 4] JP2017-057126A

[Patent Literature 5] WO2019/225549

Summary

Technical Problem

[0008]

The aluminotitanosilicate obtained in Patent Literature 5 suggests that it can be an excellent catalyst for producing an aromatic dihydroxide compound. The aforementioned literature discloses that among them, the aluminotitanosilicate with a titanium source introduced by using titanium tetrachloride gives an aromatic dihydroxide compound with particularly high selectivity. Moreover,

according to an X-ray crystal structure analysis (X-ray diffraction (XRD) pattern) by the present inventors, the aluminotitanosilicate is a compound that exhibits a maximum peak at 23° to 24°.

[0009]

According to investigations conducted by the present inventors, it has been found that a massy solid material may be generated in gel-like silica used as an intermediate raw material. From an industrial perspective, such a solid present may cause a problem in stably and quantitatively transferring the contents upon transferring them to a reaction apparatus (for example, an autoclave) for hydrothermal synthesis in the next step, and has a possibility to reduce, for example, reactivity due to being solid in a subsequent step. For this reason, it may be disadvantageous from the viewpoint of stable production. Pulverization of the solid material can practically solve the above problem, but carrying out the pulverization requires a special apparatus that leads to an increase in fixed costs and reduction of production speed, which may complicate a manufacturing step for industrial production.

[0010]

An object of the present disclosure is to provide a method for producing a modified aluminosilicate such as an

aluminotitanosilicate, capable of producing hydroquinones preferably with higher selectivity and a higher yield, for example, by reacting phenols with, for example, hydrogen peroxide, under more industrially advantageous conditions than before. The other object of the present disclosure is also to provide a catalyst capable of stably and highly selectively producing hydroquinones, for example, by reacting phenols with, for example, hydrogen peroxide under more industrially advantageous conditions, a method for producing an aromatic polyhydroxide compound using the catalyst, and a modified aluminosilicate.

Solution to Problem

[0011]

The present inventors have found as a result of investigations on the aforementioned objects that a silicate source such as silica in sol state containing water was contacted with an aluminum source such as a zeolite, in sol state, and thereafter a molar ratio of water to silica (H_2O/SiO_2) (hereinafter may be referred to as "HMR") was controlled, as a result of which the HMR value greatly affects performance of solid material described above. Providing a step of controlling the HMR value within a specific range has been found to allow a suitable

aluminosilicate to be efficiently produced even from sol state which has better flowability than a gel. Via an acid treatment step or a contact treatment step with a transition metal compound such as a titanium compound, this aluminosilicate has also been found to be able to be converted into a modified aluminosilicate such as aluminotitanosilicate capable of producing hydroquinones with extremely high selectivity, then to complete the present application.

[0012]

That is, the present disclosure includes the following items [1] to [10].

[1] A method for producing a modified aluminosilicate, comprising

a first step of preparing liquid in which sol-like silica containing water was contacted with a metal compound (AL) containing aluminum and oxygen to obtain an aluminosilicate in which a molar ratio of water to silica (H_2O/SiO_2: HMR) is in a range of 0.1 to 8.0,

a second step of treating the aluminosilicate obtained in the first step with an acid,

a third step of subjecting the treated product obtained in the second step to primary calcination at 550°C to 850°C, and

[7] A method for producing a catalyst for producing an aromatic polyhydroxide compound, the catalyst containing the modified aluminosilicate according to [5].

[8] A method for producing an aromatic polyhydroxide compound, comprising a step of reacting an aromatic hydroxide with hydroperoxide in the presence of the catalyst according to [6].

[9] A method for producing an aromatic polyhydroxide compound, comprising a step of reacting an aromatic hydroxide with hydroperoxide in the presence of the catalyst according to [7].

[10] A modified aluminosilicate, having a ratio of an absorbance at 300 nm (A[300]) in an ultraviolet-visible absorption spectrum to an absorbance at 210 nm (A[210]) in an ultraviolet-visible absorption spectrum (A[300]/A[210]) of 0.045 or more and 0.070 or less.

[0012a]

In an aspect of the present disclosure, there is provided a method for producing a modified aluminosilicate, comprising

a first step of preparing liquid in which sol-like silica containing water is contacted with a metal compound (AL) containing aluminum and oxygen to obtain an

aluminosilicate in which a molar ratio of water to silica (H_2O/SiO_2: HMR) is in a range of 0.1 to 8.0,

a second step of treating the aluminosilicate obtained in the first step with an acid,

a third step of subjecting the treated product obtained in the second step to primary calcination at 550°C to 850°C, and

a fourth step of contacting the calcined product obtained in the third step with liquid containing one or more elements selected from the group consisting of elements in Group 4 and Group 5 of the Periodic Table, followed by carrying out drying and secondary calcination.

[0012b]

In another aspect of the present disclosure, there is provided a method for producing a catalyst for producing an aromatic polyhydroxide compound, the catalyst containing the modified aluminosilicate as disclosed herein.

[0012c]

In a further aspect of the present disclosure, there is provided a method for producing an aromatic polyhydroxide compound, comprising a step of reacting an aromatic hydroxide with hydroperoxide in the presence of the catalyst as disclosed herein.

[0012d]

In another aspect of the present disclosure, there is provided a modified aluminosilicate, having a ratio of an absorbance at 300 nm (A[300]) in an ultraviolet-visible absorption spectrum to an absorbance at 210 nm (A[210]) in an ultraviolet-visible absorption spectrum (A[300]/A[210]), as measured by filling 0.1 g of a sample in a cell with an optical path length of 10 mm, of 0.045 or more and 0.070 or less.

Advantageous Effects

[0013]

According to the method for producing a modified aluminosilicate, one of the characteristics is to efficiently obtain an industrially useful aluminosilicate even though sol-like silica obtained, for example, by heating gel-like silica containing water, is used. In this manner, even sol-

like silica containing water has been contacted with a metal compound (AL) containing aluminum and oxygen, a representative example of which is a zeolite (aluminum-containing compound crystal) that is an aluminum source, and then when a ratio of water to silica which are moieties of raw materials, is controlled within a specific range to carry out production, for example, an alminosilicate suitable for production of the aluminotitanosilicate which will be described below can be efficiently produced. The aluminosilicate is also preferably an aluminosilicate having the specific structure determined by an X-ray diffraction pattern. Even though the aluminosilicate is contacted with liquid containing one or more elements selected from the group consisting of elements in Group 4 and Group 5 of the Periodic Table, for example, an aqueous solution of a titanium source under mild conditions, an aluminotitanosilicate for use as a catalyst suitable for producing an aromatic polyhydroxide compound can also be obtained. Such an aluminotitanosilicate may also exhibit an ultraviolet-visible light spectrum (UV-Vis) that meets specific requirements. For this reason, the present application is of industrial importance. Use of the modified aluminosilicate produced by the production method described above enables highly selectively producing an aromatic

particularly preferably 1.70. The upper limit value is, on the other hand, preferably 4.5 and more preferably 4.4.

[0053]

Such an aluminosilicate used makes it possible to obtain, for example, a suitable catalyst for aromatic polyhydroxide compounds by using a method for introducing, for example, a titanium source as described below, the reason for which is unknown at this stage. Therefore, an aluminosilicate with a structure having the diffraction pattern as measured by XRD as described above is some preferred aspects of the present invention.

[0054]

The aluminosilicate according to the present invention exhibits a crystal structure, but it is presumed that its crystal form is probably different from that of conventional aluminosilicates and is slightly unstable structure (in particular based on the results of the value of the peak intensity ratio of the peak (β) to the peak (γ)) or includes an unstable structure. It is also presumed that such instability may lead to excellent performance as a catalyst for producing aromatic polyhydroxide compounds when the modified aluminosilicate described below is formed.

[0055]