

DESCRIPTION

Title of Invention

METHOD FOR REGENERATING CARBONATE-TYPE LAYERED
DOUBLE HYDROXIDE AND ACIDIC EXHAUST GAS TREATMENT FACILITY

Technical Field

[0001] The present invention relates to a method for regenerating a carbonate-type layered double hydroxide used in treatment of acidic exhaust gas generated from a combustion facility of thermal power plants, incineration facilities and the like, as well as an acidic exhaust gas treatment facility comprising means of regeneration thereof.

Background Art

[0002] In combustion exhaust gas generated in thermal power generation, waste incineration and the like, there are contained hazardous acidic substances such as hydrogen chloride, sulfur oxide and nitrogen oxide. Hence, treatment by various methods in order to remove the acidic substances is carried out on acidic exhaust gas containing the acidic substances.

[0003] In a method for removing such acidic substances, the present applicant proposes, as an efficient treatment technology capable of simultaneously treating and removing plural kinds of acidic substances, a treatment method and a treatment agent and the like of acidic exhaust gas utilizing a carbonate-type Mg-Al layered double hydroxide (hereinafter, referred to also as Mg-Al LDH (Layered Double Hydroxide)) (see PTL1).

[0004] The Mg-Al LDH is a treatment agent capable of being regenerated and repeatedly used, and conventionally, as described in PTL1, in the case where the carbonate-type Mg-Al LDH is used for acidic exhaust gas treatment and converted to an anion-type Mg-Al LDH, this spent layered double hydroxide is regenerated by being mixed with a carbonic acid aqueous solution.

Citation List

Patent Literature

[0005]

PTL1: JP 2016-190199 A

Summary of Invention

Technical Problem

[0006] Means of mixing the spent layered double hydroxide and the carbonic acid aqueous solution as described above can be carried out in a layered double hydroxide regeneration facility installed out of a waste incineration facility. This case, however, has a problem of high labor and cost burdens on transport of the spent layered double hydroxide between the waste incineration facility and the layered double hydroxide regeneration facility and of a regenerated layered double hydroxide, and on installation of another outside facility other than the waste incineration facility and the like.

Further, in the case where a regeneration facility of the spent layered double hydroxide is installed inside the waste incineration facility, a storage tank and a mixing tank of the carbonic acid aqueous solution, and the like need to be installed and connected, inevitably needing to make large the scale of the whole of the facilities.

[0007] The present invention has been made in order to solve the above technical problems, and has an object to provide a method for regenerating a carbonate-type layered double hydroxide, the method being capable of efficiently regenerating a spent anion-type Mg-Al LDH in an acidic exhaust gas treatment into a carbonate-type Mg-Al LDH, and provide an acidic exhaust gas treatment facility.

Solution to Problem

[0008] The present invention is based on the finding that by bringing a spent layered double hydroxide in an acidic exhaust gas treatment into contact with a gas containing water and a predetermined amount of carbon dioxide, particularly a treated gas from the acidic exhaust gas treatment, the spent layered double hydroxide can efficiently be regenerated into a carbonate-type layered double hydroxide.

[0009] That is, the present invention provides the following [1] to [4].

[1] A method for regenerating a carbonate-type layered double hydroxide, comprising bringing an anion-type Mg-Al layered double hydroxide formed in an acidic exhaust gas treatment using the carbonate-type Mg-Al layered double hydroxide into contact with a mixed gas at 70°C or higher containing water and

carbon dioxide at a concentration of 5% by volume or higher to thereby regenerate the carbonate-type Mg-Al layered double hydroxide.

[2] The method for regenerating a carbonate-type layered double hydroxide according to the above [1], wherein the moisture content of the mixed gas is 10% or larger.

[3] The method for regenerating a carbonate-type layered double hydroxide according to the above [1] or [2], wherein the acidic exhaust gas treatment is a treatment of an acidic exhaust gas generated in a combustion facility, and a treated gas from the treatment in which an acidic gas excluding carbon dioxide has been removed is used for the mixed gas.

[0010]

[4] An acidic exhaust gas treatment facility, comprising means (1) of carrying out an acidic exhaust gas treatment using a carbonate-type Mg-Al layered double hydroxide, and means (2) of carrying out regeneration of the carbonate-type Mg-Al layered double hydroxide by the regeneration method according to any one of the above [1] to [3].

Advantageous Effects of Invention

[0011] According to the present invention, it becomes enabled to regenerate onsite a spent layered double hydroxide in an acidic exhaust gas treatment into a carbonate-type layered double hydroxide without needing a large-scale facility, and this onsite regeneration is advantageous over regeneration treatment in an offsite regeneration facility also from the viewpoint of facility, labor and cost burdens.

Further, a treated gas from the acidic exhaust gas treatment can also be utilized, and according to the acidic exhaust gas treatment facility of the present invention, the carbonate-type layered double hydroxide can efficiently be regenerated.

Brief Description of Drawing

[0012]

[Fig. 1] Fig. 1 is a schematic flow diagram of an acidic exhaust gas treatment process using an acidic exhaust gas facility of one embodiment of the present invention.

Description of Embodiments

[0013] Hereinafter, there will be described the method for regenerating a carbonate-type layered double hydroxide of the present invention, and the acidic exhaust gas treatment facility of the present invention partially by reference to the drawing.

[0014] [Method for regenerating a carbonate-type layered double hydroxide]

The method for regenerating a carbonate-type layered double hydroxide of the present invention is characterized by bringing an anion-type Mg-Al LDH formed in an acidic exhaust gas treatment using the carbonate-type Mg-Al LDH into contact with a mixed gas at 70°C or higher containing water and carbon dioxide at a concentration of 5% by volume or higher to thereby regenerate the carbonate-type Mg-Al LDH.

By thus carrying out the regeneration treatment of the anion-type Mg-Al LDH after the acidic exhaust gas treatment by contact with a gas containing water and a predetermined amount of carbon dioxide, the regeneration into the carbonate-type Mg-Al LDH can efficiently be carried out.

[0015] <Carbonate-type Mg-Al LDH>

The carbonate-type Mg-Al LDH is a nanoparticle having a structure in which a hydroxide base layer ($[\text{Mg}^{2+}_{1-x}\text{Al}^{3+}_x(\text{OH})_2]$) and a middle layer ($[(\text{CO}_3^{2-})_{x/2} \cdot y\text{H}_2\text{O}]$) constituted of interlayer carbonate ions and interlayer water are alternatively laminated. The carbonate-type Mg-Al LDH is a nonstoichiometric compound in which the hydroxide base layer has a positive charge equivalent to x , and the carbonate ions are present, as anions having a negative charge compensating the positive charge, in the middle layer.

The carbonate-type Mg-Al LDH, while holding the hydroxide base layer, can entrap acidic gas, for example, hydrogen chloride, sulfur dioxide and nitrogen dioxide into the interlayer. Hence, the carbonate-type Mg-Al LDH can suitably be used for the acidic exhaust gas treatment removing the acidic gas.

[0016] Then, when the carbonate-type Mg-Al LDH is used in the acidic exhaust gas treatment, there may concurrently be used layered double hydroxides other than the carbonate-type Mg-Al LDH and/or chemical agents other than the layered double hydroxides, for example, calcium hydroxide (slaked lime), calcium oxide, sodium bicarbonate, sodium carbonate, dolomite hydroxide, soft-burned dolomite, aluminum hydroxide, aluminum oxide, magnesium hydroxide, and magnesium oxide. From the viewpoint of efficiently regenerating and reutilizing

the carbonate-type Mg-Al LDH, however, it is preferable that the carbonate-type Mg-Al LDH is not present mixed with the other layered double hydroxides and chemical agents.

[0017] As the carbonate-type Mg-Al LDH, there is also a clay mineral naturally produced as hydrotalcite, but a synthetic powder is usually used. A synthesis method thereof is not especially limited, and a well-known method (for example, a method described in PTL1) can be used.

The carbonate-type Mg-Al LDH can be obtained, for example, by dropwise charging an aqueous solution in which magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$) and aluminum nitrate ($\text{Al}(\text{NO}_3)_3$) are mixed in $\text{Mg}/\text{Al} = 2/1$ (in molar ratio) to a sodium carbonate (Na_2CO_3) aqueous solution while the pH is held at 10.5.

[0018] The carbonate-type Mg-Al LDH used in the acidic exhaust gas treatment, when the acidic gas is entrapped in the interlayer, turns to the anion-type Mg-Al LDH in which interlayer carbonate ions have been exchanged for other anions originated from acidic exhaust gas, such as chloride ions, sulfate ions and nitrate ions. The anion-type Mg-Al LDH thus formed has no capability of further removing acidic exhaust gas. Hence, the anion-type Mg-Al LDH is regenerated again into the carbonate-type Mg-Al LDH by anion exchange and provided for reutilization.

[0019] <Mixed gas>

In the method for regenerating the carbonate-type layered double hydroxide, by anion exchanging the anion-type Mg-Al LDH, which is a spent layered double hydroxide in the acidic exhaust gas treatment, by using the mixed gas at 70°C or higher containing water and carbon dioxide at a concentration of 5% by volume or higher, the anion-type Mg-Al LDH is regenerated into the carbonate-type Mg-Al LDH.

Such a regeneration method using gas contact, as compared with conventional regeneration methods using a carbonic acid aqueous solution being a liquid, is efficient as means of regeneration into the carbonate-type Mg-Al LDH.

[0020] The mixed gas contains water and carbon dioxide at a concentration of 5% by volume or higher.

In order to regenerate into the carbonate-type Mg-Al LDH having interlayer carbonate ions and interlayer water in the middle layer by exchanging interlayer anions originated from acidic exhaust gas for carbonate ions, such a mixed gas containing water and carbon dioxide is used.

Here, "water" used here means gaseous water, that is, steam.

[0021] The content of carbon dioxide in the mixed gas is 5% by volume or higher, preferably 10 to 75% by volume and more preferably 10 to 30% by volume.

When the content is 10% by volume or higher, interlayer anions of the anion-type Mg-Al LDH are efficiently caused to be desorbed and exchanged for interlayer carbonate ions to thereby be able to carry out the regeneration of the carbonate-type Mg-Al LDH.

[0022] The moisture content of the mixed gas is preferably 10% or larger, more preferably 15 to 30% and still more preferably 20 to 25%.

When the moisture content is 10% or larger, interlayer anions of the anion-type Mg-Al LDH are efficiently caused to be desorbed, and there can be carried out the regeneration of the carbonate-type Mg-Al LDH having interlayer carbonate ions and interlayer water in the middle layer.

Here, "moisture content" used in the present invention refers to an equivalence to the volume fraction [%] of steam contained in exhaust gas in JIS Z 8808:2013, and can be measured by a method according to a method using a moisture-absorbing tube described in the JIS Standard.

[0023] The mixed gas may contain gas other than water and carbon dioxide, but it is preferable that the mixed gas contains no acidic gas other than carbon dioxide. It is preferable that the mixed gas is prepared by mixing air, from the viewpoint of simplicity, costs and the like in the preparation of the mixed gas containing predetermined amounts of water and carbon dioxide.

[0024] The temperature of the mixed gas is made to be 70°C or higher, preferably 75 to 100°C and more preferably 80 to 90°C.

When the temperature is 70°C or higher, the regeneration of the anion-type Mg-Al LDH into the carbonate-type Mg-Al LDH can efficiently be carried out.

[0025] For the mixed gas, it is preferable to use a treated gas in which there has been removed acidic gas other than carbon dioxide after the treatment of acidic exhaust gas generated in the combustion facility.

By using such a treated gas, gas formed in the combustion facility can effectively be utilized, and there becomes enabled the onsite regeneration of the anion-type Mg-Al LDH into the carbonate-type Mg-Al LDH, and the

improvement in efficiency of the regeneration treatment can further be accomplished.

[0026] [Acidic exhaust gas treatment facility]

The acidic exhaust gas treatment facility of the present invention is characterized by comprising means (1) of carrying out an acidic exhaust gas treatment using the carbonate-type Mg-Al layered double hydroxide, and means (2) of carrying out regeneration of the carbonate-type Mg-Al layered double hydroxide by the above regeneration method of the present invention.

According to such an acidic exhaust gas treatment facility, while the acidic exhaust gas treatment is carried out, there can be carried out onsite the regeneration of the carbonate-type layered double hydroxide to be used for the acidic exhaust gas treatment.

[0027] Fig. 1 shows an acidic exhaust gas treatment process flow using an acidic exhaust gas treatment facility of one embodiment of the present invention. In the acidic exhaust gas treatment process flow shown in Fig. 1, first an acidic exhaust gas a discharged from a combustion facility 10 is introduced to a layered double hydroxide-housing container 20 in which a carbonate-type Mg-Al LDH is housed. Then, in the layered double hydroxide-housing container 20, the acidic exhaust gas a is brought into contact with the carbonate-type Mg-Al LDH to carry out acidic exhaust gas treatment, and a treated gas b is conveyed to an exhaust gas duct 50 by an induced-draft fan or the like (not shown in figure) and released into the air.

Then, as the acidic exhaust gas a, for example, in the case where the combustion facility 10 is a waste incineration furnace, suitably used is a gas that is an exhaust gas at a high temperature from the incineration furnace main body, which is cooled through a heat exchanger such as a boiler and from which dust and the like are removed by a dust collector.

[0028] In the case where along with an elapse of time of the acidic exhaust gas treatment, the carbonate-type Mg-Al LDH changes to the anion-type Mg-Al LDH and the acidic exhaust gas treatment capability decreases, lines are switched by a switching valve V1 so that the acidic exhaust gas a is introduced to a layered double hydroxide-housing container 21 separately installed. Then, by operating a switching valve V2, part of the treated gas b is introduced to the layered double hydroxide-housing container 20 through a bypath line 40 by an induced-draft fan or the like. There is thus carried out the regeneration treatment into the

carbonate-type Mg-Al LDH by bringing the treated gas b, that is, the mixed gas is brought into contact with the anion-type Mg-Al LDH.

In the regeneration treatment, anions desorbed from the anion-type Mg-Al LDH are absorbed in water (liquid) being a condensate of moisture in the acidic exhaust gas a, and are stored as a regeneration treatment drainage water c in a regeneration treatment drainage water-recovering container 30.

When the regeneration treatment is finished, the switching valve V1 and the switching valve V2 are returned to their original states, and the acidic exhaust gas treatment in the layered double hydroxide-housing container 20 is restarted. Then, the judgement of the finish of the regeneration treatment of the carbonate-type Mg-Al LDH can be carried out based on the concentration analysis and the like of anion components contained in the regeneration treatment drainage water c.

If a similar regeneration treatment is carried out also in the layered double hydroxide-housing container 21 separately installed, by switching lines by the switching valve V1, the layered double hydroxide-housing container 20 and the layered double hydroxide-housing container 21 can be used alternately; and the acidic exhaust gas treatment can continuously and efficiently be carried out without stopping the flow of the acidic exhaust gas a.

Examples

[0029] Hereinafter, the present invention will be described in more detail based on Example, but the present invention is not any more limited by the following Example.

[0030] [Regeneration treatment test of a carbonate-type layered double hydroxide]

In the following Preparation Example 1, a chloride-type Mg-Al LDH (anion-type Mg-Al LDH sample) in which interlayer carbonate ions had been exchanged for interlayer chloride ions was prepared by bringing a hydrogen chloride gas as an acidic exhaust gas for test into contact with a carbonate-type Mg-Al LDH. 20 g of the chloride-type Mg-Al LDH was packed in an acrylic resin-made column having an inner diameter of 40 mm, and was subjected to a regeneration treatment test under each condition of the following Example and Comparative Examples.

The regeneration efficiency of the carbonate-type layered double hydroxide was evaluated by measuring the contents of chlorine in the Mg-Al LDH before and after the regeneration treatment test by ion chromatography and determining the desorption rate of chloride ions. It can be said that the higher the desorption rate of chloride ions, the higher the regeneration efficiency from the chloride-type Mg-Al LDH into the carbonate-type Mg-Al LDH.

[0031] (Preparation Example 1)

The carbonate-type Mg-Al LDH ("Kyowaad(Registered trade mark) 500 PL", manufactured by Kyowa Chemical Industry Co., Ltd., synthetic hydrotalcite) was packed in the acrylic resin-made column having an inner diameter of 40 mm; and a hydrogen chloride-containing gas regulated at a hydrogen chloride concentration of about 1000 ppm and at 100°C by introducing a hydrogen chloride gas into air, was allowed to pass through the column until hydrogen chloride was detected at the column outlet port to thereby obtain the chloride-type Mg-Al LDH.

Here, the formation of the chloride-type Mg-Al LDH was confirmed by powder X-ray diffractometry and ion chromatography.

[0032] (Example 1)

The regeneration treatment test was carried out by making a mixed gas regulated at a moisture content of 20%, a carbon dioxide concentration of 30% by volume and at 80°C by introducing water and carbon dioxide in air to pass through the column packed with the chloride-type Mg-Al LDH for 8 hours.

The desorption rate of chloride ions in the regeneration treatment test was 96%.

[0033] (Comparative Example 1)

The regeneration treatment test was carried out by making a mixed gas regulated at a carbon dioxide concentration of 30% by volume and at room temperature (25°C) by introducing carbon dioxide in air to pass through the column packed with the chloride-type Mg-Al LDH for 24 hours.

The desorption rate of chloride ions in the regeneration treatment test was 6%.

[0034] (Comparative Example 2)

The regeneration treatment test was carried out by making a mixed gas regulated at a moisture content of 20% and at 80°C by introducing water in air to pass through the column packed with the chloride-type Mg-Al LDH for 8 hours.

The desorption rate of chloride ions in the regeneration treatment test was 37%.

[0035] (Comparative Example 3)

The regeneration treatment test was carried out by making a mixed gas regulated at a carbon dioxide concentration of 30% by volume and at 80°C by introducing carbon dioxide in air to pass through the column packed with the chloride-type Mg-Al LDH for 8 hours.

The desorption rate of chloride ions in the regeneration treatment test was 30%.

[0036] From each test result of the above Example and Comparative Examples, it was recognized that by bringing the anion-type Mg-Al LDH into contact with a gas containing water and a predetermined amount of carbon dioxide, the anion-type Mg-Al LDH was able to be efficiently regenerated into the carbonate-type Mg-Al LDH.

Reference Signs List

[0037]

10 Combustion facility

20, 21 Layered double hydroxide-housing container

30 Regeneration treatment drainage water-recovering container

40 Bypass line

50 Exhaust gas duct

v1, v2 Switching valve

a Acidic exhaust gas

b Treated gas

c Regeneration treatment drainage water

CLAIMS

[Claim 1]

A method for regenerating a carbonate-type layered double hydroxide, comprising bringing an anion-type Mg-Al layered double hydroxide formed in an acidic exhaust gas treatment using the carbonate-type Mg-Al layered double hydroxide into contact with a mixed gas at 70°C or higher containing water and carbon dioxide at a concentration of 5% by volume or higher to thereby regenerate the carbonate-type Mg-Al layered double hydroxide.

[Claim 2]

The method for regenerating a carbonate-type layered double hydroxide according to claim 1, wherein a moisture content of the mixed gas is 10% or larger.

[Claim 3]

The method for regenerating a carbonate-type layered double hydroxide according to claim 1 or 2, wherein

the acidic exhaust gas treatment is a treatment of an acidic exhaust gas generated in a combustion facility, and

a treated gas from the treatment in which an acidic gas excluding carbon dioxide has been removed is used for the mixed gas.

[Claim 4]

An acidic exhaust gas treatment facility, comprising means (1) of carrying out an acidic exhaust gas treatment using a carbonate-type Mg-Al layered double hydroxide, and means (2) of carrying out regeneration of the carbonate-type Mg-Al layered double hydroxide by the regeneration method according to any one of claims 1 to 3.