

**METHOD FOR PRODUCING  
ANION-EXCHANGING LAYERED DOUBLE  
HYDROXIDE AND METHOD FOR  
SUBSTITUTING CARBONATE ION OF  
LAYERED DOUBLE HYDROXIDE**

TECHNICAL FIELD

[0001] The present invention relates to a method for producing an anion-exchanging layered double hydroxide having easily ion-exchangeable anions ( $X^-$ ) between layers. More specifically, the present invention relates to a method for producing an anion-exchanging layered double hydroxide by substituting carbonate ions, using a layered double hydroxide containing hardly ion-exchangeable carbonate ions ( $CO_3^{2-}$ ) between layers as a starting material, and a method for substituting carbonate ions of the carbonate-ion-containing layered double hydroxide.

BACKGROUND ART

[0002] Many layered compounds have been developed by using layered compounds such as clay minerals, and by allowing various types of cations or cationic functional organic substances to be included in such layered compounds. This method capitalizes on the fact that clay mineral layers have negative charge, and that cations existing between layers are easily ion-exchangeable. The layered double hydroxide (hereinafter referred to as LDH) has, unlike clay minerals, positively-charged layers, has anions between layers, and has anion-exchanging property. Since there are only a few types of inorganic anion-exchanging materials, LDHs are attracting attention (Non-patent Literature 1).

[0003] As a method for synthesizing a layered compound having anions between LDH layers, some methods for substituting carbonate ions by other anions using an LDH containing carbonate ions between layers (hereinafter referred to as carbonate ion-type LDH) are known.

[0004] Since the carbonate ion-type LDH can be synthesized easily and high-quality crystal having high crystallinity can be obtained, most of the LDHs manufactured industrially are this carbonate ion-type LDHs. However, the carbonate ion-type LDHs have extremely low ion-exchangeability, and therefore it is difficult to change them into LDHs containing anions other than carbonate ions by ordinary anion exchange (Non-patent Literature 2). If carbonate ion-type LDHs can be converted into anion-exchanging LDHs containing easily ion-exchangeable anions (such as perchlorate ions, nitrate ions, and chlorine ions) by simpler chemical process, broad application is expected both industrially and at research and test levels. A method for converting carbonate ion-type LDHs to anion-exchanging LDHs by simpler chemical process has therefore been desired.

[0005] The inventors have found that by allowing a mixed solution of hydrochloric acid and sodium chloride (NaCl) to react with a carbonate ion-type LDH at a room temperature, decarbonation occurs, converting the carbonate ion-type LDH into an LDH containing chlorine ions ( $Cl^-$ ) (Patent Literature 1, Non-patent Literature 3).

[0006] Decarbonation that uses a mixed chloric acid-NaCl solution is simple. However, since the solution is highly acidic, and in addition the LDH itself is easily soluble to an aqueous solution of acid, it is necessary to cause decarbonation to occur under the condition where LDH does not dissolve. Furthermore, in the decarbonation using a mixed chlo-

ric acid-NaCl solution, complete conversion into an anion-exchanging LDH other than  $Cl^-$  type (such as  $ClO_4^-$  and  $NO_3^-$ -types) was difficult (Non-patent Literature 4). As described above, the decarbonation using a mixed chloric acid-NaCl solution is groundbreaking as a method for producing LDHs containing chlorine ions, namely easily anion-exchangeable anions without affecting particle size or uniformity. Due to problems described previously, however, further improvement has been desired.

[0007] The inventors found that by using a mildly acidic acetic acid buffer solution and allowing a solution prepared by adding neutral salt such as sodium chloride (NaCl), sodium perchlorate, and sodium nitrate to this acetic acid buffer solution to react with carbonate ion-type LDH at a room temperature, decarbonation occurred, causing conversion into an LDH containing anions that had been added (Patent Literature 2, Non-patent Literatures 5 and 6). This method has also ensured conversion into an anion-exchanging LDH of a type other than  $Cl^-$  type (such as  $ClO_4^-$  and  $NO_3^-$ -types).

[0008] With this reaction, however, since ion exchange reaction due to chemical equilibrium also occurs, a largely excessive amount of anions to be inserted in LDH layers must exist in the reaction system. In particular, since perchlorate ions and nitrate ions are low in affinity to LDHs, an excessive amount of salt was needed to introduce these anions (Non-patent Literature 6). Furthermore, as a result of using acetic acid buffer solution to adjust the acidity, anionic acetate ions exist in the system. Consequently, depending on the type of the LDH, there was a risk of entry of acetate ions between layers. As described above, the method using an acetic acid buffer solution has allowed decarbonation to occur under stable pH conditions. However, many types of reagents must be used in largely excessive amounts, and depending on the type of LDH, there was a risk of allowing entry of acetate ions existing in the system. Solving these problems has been necessary.

CITATION LIST

Patent Literature

- [0009] Patent Literature 1: JP 4228077 B
- [0010] Patent Literature 2: WO 2009/072488
- [0011] Patent Literature 3: JP 2005 335965 A

Non-Patent Literature

- [0012] Non-patent Literature 1: Cavani, F., Trifiro, F., Vaccari, A., Catal. Today 11, 173-301 (1991)
- [0013] Non-patent Literature 2: Miyata, S., Clays Clay Miner. 31, 305-311 (1983)
- [0014] Non-patent Literature 3: Iyi, Nobuo, Matsumoto, T., Kaneko, Y., Kitamura, K., Chem. Mater. 16, 2926-2932 (2004)
- [0015] Non-patent Literature 4: Iyi, Nobuo, Okamoto, K., Kaneko, Y., Matsumoto, T., Chem. Lett. 34, 932-933 (2005)
- [0016] Non-patent Literature 5: Iyi, Nobuo, Sasaki, Takayoshi, J. Colloid Interface Sci. 322, 237-245 (2008)
- [0017] Non-patent Literature 6: Iyi, Nobuo, Yamada, Hirohisa, Chem. Lett. 39, 591-593 (2010)
- [0018] Non-patent Literature 7: Iyi, N., Fujii, K., Okamoto, K., Sasaki, Takayoshi, Appl. Clay Sci. 35, 218-227 (2007)