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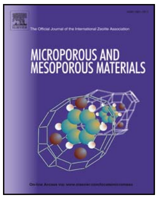

Intercalation and *in situ* formation of coordination compounds with ligand 8-hydroxyquinoline-5-sulfonic acid in the interlayer space of layered silicate magadiite by solid-solid reactions

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ABSTRACT

Intercalation and *in situ* formation of three fluorescent complexes, Al(III)-, Ca(II)- and Zn(II)-8-hydroxyquinoline-5-sulfonic acid (M-8HqS, M = Al, Ca and Zn) in the interlayer spaces of magadiite (mag) were synthesized by solid-solid reactions between metal ions exchanged mags (M-mag, M = Al, Ca and Zn) and 8HqS at room temperature. The intercalation and *in situ* formation of 8HqS molecules into the interlayer spaces of M-mags were evaluated by XRD, ICP-AES, EDS, elemental mappings, TG/DTA, elemental analysis, FE-SEM, FTIR, UV-Vis, PL and XPS. Results show that the basal spacings of the intercalated composites increase after the intercalation of 8HqS into M-mags. A new peak at 1461 cm^{-1} is observed, supporting the formation of the coordination complexes between 8HqS and metal cations. The slight shift of the absorption and luminescence bands of the complexes suggests the different microstructures including molecular packing of the complexes in the interlayer spaces of mags, which indicating that the process is a host-guest interaction. The amount of 8HqS in the intercalated compounds is different due to the diversification of coordination ability of metal ions, and the order of the coordination ability of these three metal ions is $Ca^{2+} > Zn^{2+} > Al^{3+}$. The amount of the metal cations (Al^{3+}, Ca^{2+} and Zn^{2+}) in the interlayer of mag is enough for the *in situ* complex formation of M-8HqS complexes. Thus, the intercalation and *in situ* formation of M-8HqS complexes (M = Al, Ca and Zn) in the interlayer space of mag are successfully achieved in the present work.

1. Introduction

Intercalation of organic guest species into layered silicates is considered to be a fascinating topic from the viewpoints of scientific interests as well as the practical applications because it is an elegant process of constructing nanocomposite materials based on the combination of vast varieties of inorganic and organic substances [1–7]. The organization of photo and electroluminescent metal complexes within layered silicates has attracted a lot of attention owing to the excellent luminescent properties towards the scientific study and potential application for light emitting diodes [8–10]. The hybrid materials of various inorganic substances containing metal complexes were fabricated, and their properties and applications were investigated [11–17]. The confinements of metal complexes in nanospace have been done by using *in situ* complex formation and/or immobilization of pre-synthesized metal complexes into the layered silicates [3].

Intercalation chemistry of layered clay minerals such as smectites has been studied extensively because they possess various attractive features including swelling behavior, ion exchange property, large surface area and adsorptive properties [8,18–23]. In the past decades, Makoto Ogawa's group paid huge attention to the intercalation chemistry of montmorillonite including the preparations, characterizations, properties and applications [4,9,24,25]. Accordingly, intercalation compounds of montmorillonite with various metal complexes, such as the complexation of 8-hydroxyquinoline and 4,4′-bipyridine with zinc (II) [4], a series of group XIII metal-quinolate complexes [26], two ligands (8-hydroxyquinoline and 2,2′-bipyridine or 1,10-phenanthroline) with zinc (II) [9] and so on, were synthesized and their properties of the intercalates were examined extensively. They found that the solid-solid reaction is a promising way to immobilize organic guest species in the interlayer spaces of layered silicates. The solid-solid reaction is one of the most suitable techniques for the intercalated process due to its facile operation and possibility to prepare compounds, which are not accessible from solutions [27,28]. The solid-solid intercalation of both cationic and nonionic species into various inorganic solids, such as layered clay minerals, layered zirconium phosphate, and zeolites, was reported [2,4,25–28]. Because of the advantages of this synthetic methodology, the effect of solid-sate intercalation of metal complexes

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into layered silicates on their structures and properties is worth investigating [9,21,25]. Therefore, the intercalation of organic guest species into other layered silicates like magadiite, which has been less studied, may bear scientific importance and novel chemical and physical properties. Based on this point, we moved our interest to the intercalation of organic guest species into the interlayer space of magadiite in this study.

Magadiite ($Na_2Si_{14}O_{29}{\cdot}xH_2O$, abbreviated as mag) comes from the phyllosilicate family, which constitutes of kenyaite ($Na_2Si_{20}O_{41}{\cdot}xH_2O$), kanemite ($NaHSi_2O_5{\cdot}3H_2O$) and makatite ($Na_2Si_4O_{10}{\cdot}5H_2O$). Mag was first found in the deposits of Lake Magadi in Kenya and described by Eugster 1967 [29]. It has a layered appearance which consists of agglomerated particles with an irregular shape and partly sharp grain boundaries. It also possesses a high aspect ratio and a high strength. The structure of mag is composed of one or multiple negatively charged sheets of SiO_4 tetrahedra with abundant silanol-terminated surfaces. Negative charges in the layers of mag are counterbalanced by hydrated cations (Na^+ or H^+ et al.) in the interlayer spaces [14,30–32]. Mag has a high cation exchange capacity (CEC) and can be applied to ion exchange. The sodium ions can be replaced by protons, other cations or large quaternary ammonium ions [33,34]. These properties of mag prove it to be a good candidate for the formation of organic-inorganic nanocomposites as the host material. So far, some reports have been synthesized mag intercalation compounds containing various organic guests. Pastore et al. synthesized a sorbent combining mag and polyethylenimine [35]. Chen et al. synthesized a photochromic composite using mag as host material and polytungstate as guest molecule [36]. Blanchard et al. used CTAB as intercalation agent to exfoliate mag and achieve a high-surface area material [37]. However, these products were normally synthesized by ion-exchange and few species of molecule were intercalated into the mag. Additionally, the differentiation of bulk, complicated structural metal-chelates remains a challenge for mag derived using the traditional approach [38]. In our report [39], self-assembly of 8-hydroxyquinoline-Li(I), Al(III) and Cu(II) complexes into the interlayer surfaces of mag. In this study, we are interested in extending the previous study to the intercalation of 8-hydroxyquinoline-5-sulfonic acid (abbreviated as 8HqS, the molecular structure is shown in Scheme 1a) into the interlayer space of metal ions exchanged mags (abbreviated as M-mags, M = Al, Ca and Zn). To the best of our knowledge, the intercalation of 8HqS into the layered inorganic solids has not been fabricated so far [40].

In the present work, intercalation and *in situ* complex formation of 8HqS with the interlayer metal cations (Al^{3+}, Ca^{2+} and Zn^{2+}) were investigated to form coordination complexes in the interlayer space. Metal-8HqS and substituted 8HqS complexes have attracted attention owing to the useful luminescence properties especially in the use for organic light-emitting devices [41–43]. It was reported that the developments in designing metal chelates as organic electroluminescent materials could tune the electroluminescent colors, operating the stability and enhance the overall electroluminescent efficiency. The choice of these three metals is owing to these metals complexes with 8HqS showing strong luminescence properties [44]. Thus, the formation of coordination complexes between 8HqS and metal cations (Al^{3+}, Ca^{2+} and Zn^{2+}) in the interlayer space of mag is meaningful and useful. Herein, we carried out the solid-solid reaction between M-mags (M = Al, Ca and Zn) and 8HqS to incorporate the complexes with ligand 8HqS (Scheme 1b–d) into the interlayer spaces of mag.

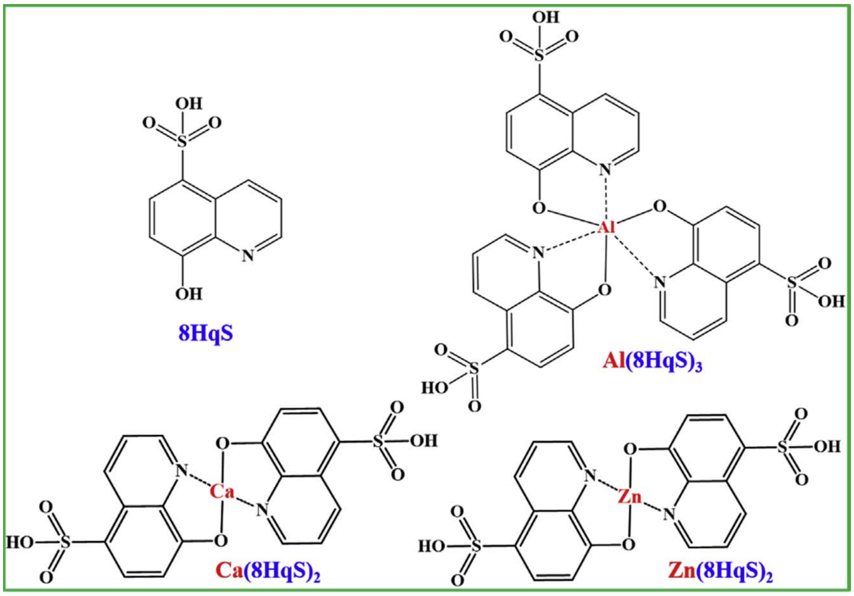
2. Experimental section

2.1. Materials

All chemicals with analytical grade, including sodium hydroxide (NaOH), zinc acetate dehydrate ($C_4H_6O_4Zn{\cdot}2H_2O$), calcium chloride ($CaCl_2$), aluminum sulfate ($Al_2(SO_4)_3{\cdot}18H_2O$), 8-hydroxyquinoline-5-sulfonic acid ($C_9H_7NO_4S$, denoted as 8HqS) and silica gel (40 wt.% Aldrich), were purchased from Sinopharm Chemical Reagent Co., Ltd and used without any further purification. Initial magadiite (mag) was hydrothermally synthesized based on our previous report [39]. In a typical synthesis, the mixtures of colloidal silica (Ludox) and NaOH with a molar ratio SiO_2: NaOH: H_2O = 9: 3: 162 were sealed in a Teflon-lined autoclave and hydrothermally treated at 150 °C for 48 h. After the reaction, the suspension was filtered and washed with distilled water to remove excess NaOH, and dried at 80 °C for 24 h. The empirical chemical formula of the obtained mag can be expressed as $Na_2Si_{14}O_{29}{\cdot}9H_2O$. Cation exchange capacity (CEC) of mag was 200 meq/100 g [33].

2.2. Intercalation of coordination compounds with ligand 8HqS in the interlayer space of mag

Intercalation of coordination compounds with ligand 8HqS in the interlayer space of mag mainly composed of two steps, as depicted in Scheme 2. (1) Synthesis of metal ions exchanged mags. Metal ions



Scheme 1. The molecular structure of 8HqS, Al(III)-8HqS, Ca(II)-8HqS and Zn(II)-8HqS.