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Experimental and theoretical investigation into the elimination of organic pollutants from solution by layered double hydroxides

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ABSTRACT

This work aims at revealing the role of pristine layered double hydroxide (LDH) materials in the elimination of organic pollutants from solution. Typical LDH samples, ZnCr- and MgAl-LDHs (with Zn^{2+}/Cr^{3+} or Mg^{2+}/Al^{3+} molar ratio 2), are prepared and used for the removal of methylene blue (MB), methyl orange (MO), and formaldehyde. The systematic investigations of structural characterization and periodic density functional theory (DFT) calculation of the LDH samples demonstrate that: (1) no electron–hole pairs could be generated for MgAl-LDHs under the irradiation of visible light due to the large calculated gap energy above 5.0 eV. (2) ZnCr-LDHs are sensitive to the irradiation of visible light with the calculated gap energy between 2.0 and 3.0 eV, but the rapid charge recombination and low efficiency in electron/hole separation would suggest that photocatalytic activity of ZnCr-LDHs would be greatly limited. In the experimental work, ZnCr- and MgAl-LDHs show no photocatalytic activity for the removal of formaldehyde under the visible light. The disposal of the organic dyes molecules in the solution would be caused by the photoassisted degradation and surface adsorption effect rather than the photocatalysis impact for both LDH samples. This is confirmed by the elimination tests that carry out in the dark condition with the similar procedure under visible light irradiation. Moreover, the two types of LDH samples exhibit the different adsorption capability for the MB and MO molecules due to the different colloidal properties of the LDH samples, which is revealed by Zeta potential measurement. The above finding that elimination of organic dyes from solution by the pristine LDH samples through photoassisted degradation and adsorption processes would be important for the rational design and use of clay-like materials for the treatment of sewage containing toxic compounds.

1. Introduction

Over the past few decades, there have been increasing demands for solutions to the multiple environmental problems associated with sewage containing toxic compounds. Organic pollutants have been extensively used with high toxicity and hard-degradation. Therefore, many efforts have been made to developing methods for the elimination of such organic compounds from wastewater by means of biological and physical–chemical techniques [1]. One important branch refers to the development of suitable adsorbents used in the elimination of organic pollutants, including activated carbons [2], zeolites [3], and layered double hydroxide (LDH)-derived materials [4]. LDH is a family of two-dimensional anionic clays with the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]A^{n-}_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are di- and trivalent cations, respectively; the value of the coefficient x is equal to the molar ratio of $M^{3+}/(M^{2+}+M^{3+})$; and A^{n-} is an anion [5–9]. LDH and their calcination products have been successfully employed as adsorbent materials for a variety of anion species and/or pollutants, including sulfur oxides [10], sodium dodecylsulfate [11], synthetic dyes [12], and pesticides [13–15]. Based on the structure and intercalation characters of LDH, there are three kinds of uptaking mechanisms presented: surface adsorption, interlayer anion exchange, and reconstruction of calcined LDH by the "memory effect" [16].

Another effective strategy for the elimination of organic pollutants from wastewater is the photocatalytic performance of semiconductor materials such as TiO_2 [17–19], ZnO [20–23], and CdS [24–26] have been intensively investigated. All these semiconductors could act as sensitizers for light-reduced redox processes due to their electronic structure, which is characterized by a filled valence band (VB) and an empty conduction band (CB) [27,28]. When a photon with energy of $h\nu$ matches or exceeds the band gap energy, E_g, of the semiconductor, the electrons transferred from the VB to the CB and generated the photogenerated charge carriers, i.e., electrons (e^-) and holes (h^+) pairs, which are powerful reductants and oxidants, respectively. Considering the di- and trivalent metal ions on the main layers of LDH could

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be varied in a wide range without altering the structure [29], LDH would be envisioned as providing the opportunity of having doped semiconductors or semiconductor composite materials after thermal treatment at high temperature and such semiconductor composites could be served as excellent photocatalytic materials [30–32]. Some investigations about the elimination of organic dyes from wastewater over LDH-related materials believe that LDH could be regarded as semiconductor materials and photocatalytic degradation processes may take place. For instance, Mantilla et al. [33] investigated the photocatalytic properties of series of ZnAlFe-LDHs materials. It was revealed that, after the reconstruction of LDH by calcination/rehydration processes, the activated ZnAlFe-LDHs could play the role of photocatalyst for the degradation of 2,4-dichloropenoxyacetic. They pointed out that Fe^{3+} ions in the ZnAlFe-LDHs provoke important variations in the semiconductor properties of the materials which accounted for the photocatalytic activity. They also reported the photoassited activities of MgAl-LDHs, and this activity was explained by a photo excitation which produced mobility charges in the lamellar structure of MgAl-LDHs [34]. Shao et al. demonstrated the applications of ZnTi-LDHs displayed superior photocatalytic activity in the visible light for decomposition of MB [35], but the MB might be not suit for photocatalytic activity test, since the photoinduced reaction by MB photoadsorption would mislead into believing that a given semiconductor material has visible-light photocatalytic activity [36]. On the other hand, the investigations about series of MgZnAl-LDHs demonstrated that [37] the large band gap values of such materials indicated a diminished semiconducting capacity, but they still exhibited photocatalytic activity for the degradation of pollutants. The authors also suggested that the residual small amount of ZnO after the reconstruction of MgZnAl-LDHs led to the photocatalytic activity. Moreover, the higher specific surface area presented by the materials could not be overlooked. Although Silva et al. proposed that ZnCr-LDHs could be used as excellent photocatalyst for oxygen generation from splitting of water under visible light irritation, special sacrificial acceptor solution (i.e., $AgNO_3$) was necessary [38]. Naturally, one question comes to us: whether the removal pathways of pollutant molecules are carried out over LDH materials through intrinsic photocatalytic processes as a result of the textual characters of LDH?

Herein, in order to disclose the reason for the above question, two typical pristine LDH samples, ZnCr-LDHs (which is viewed as semiconductor (mixed oxides) and exhibited adsorption peaks in the visible region [38,39]), and MgAl-LDHs (which is not considered to be capable of generating the e^- and h^+ pairs by band gap under visible light irradiation [34,37]) are prepared and applied for the elimination of different pollutants, methylene blue (MB), methyl orange (MO), and formaldehyde with or without irradiation of visible light. The periodic density functional theory (DFT) calculations which have been applied in the photocatalyst design and analysis [40,41] is also performed to predict the electronic band structure of ZnCr- and MgAl-LDHs. The structural and optical properties of both LDH samples are characterized by powder X-ray diffraction (XRD), room temperature Fourier transform infrared spectra (FT-IR), N_2 sorption measurements, and ultraviolet–visible spectra (UV–vis). The elimination results are carefully discussed and compared with the DFT calculation results of LDH samples.

2. Experimental

2.1. Models and computational methods

The parent LDH material is the naturally occurring mineral MgAl-LDHs whose microstructure with Mg^{2+}/Al^{3+} ratio of two or three has been studied by using quantum chemistry methods

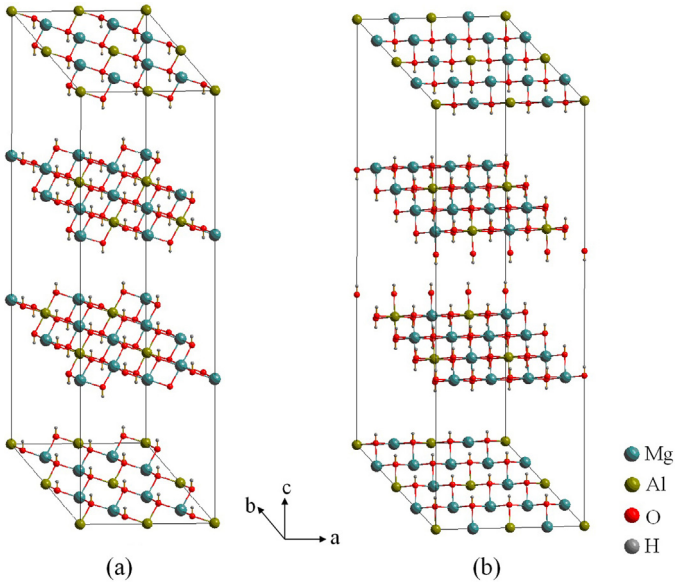

Fig. 1. Sub-lattices of MgAl-LDHs with Mg/Al ratio of two (a) and three (b).

[1,42,43]. The typical structure is the $Mg^{2+}/Al^{3+} = 2$ and 3 with *R-3m* space-group [6], of which the Al^{3+} exists with highly dispersed form. Both two structures are three laminates as a repeating unit, shown in Fig. 1. The previous study [44] shows that the intercalated CO_3^{2-} anions could affect the original space-group for LDH structure, if the symmetry of the incoming anions matches the local symmetry of the interlayer site (D_{3h} or O_h). However, it needs to meet two conditions in order to maintain the same space group after introduction of CO_3^{2-} group: the plane containing the four atoms of CO_3^{2-} need to parallel to the layer of LDH and CO_3^{2-} group need to be in the middle of the triangular pyramid-shaped (as shown in Fig. 2, the four vertices of the triangular pyramid as Al^{3+}, and three of which as an equilateral triangle in a lamellae). Accordingly, the CO_3^{2-} group has two spatial orientations in the interlayer as shown in Fig. 2(I) and (II). The calculation results indicate that the structure (II) is less stable and most likely becomes the type (I). The models of ZnCr-LDHs with CO_3^{2-} in the interlayer are obtained as the same approach.

All calculations are performed with the DFT method using Dmol3 [45,46] module in Material Studio software package [47]. The initial configuration is fully optimized by using Perdew–Wang (PW91) [48] generalized gradient approximation (GGA) method with the double numerical basis sets plus polarization function

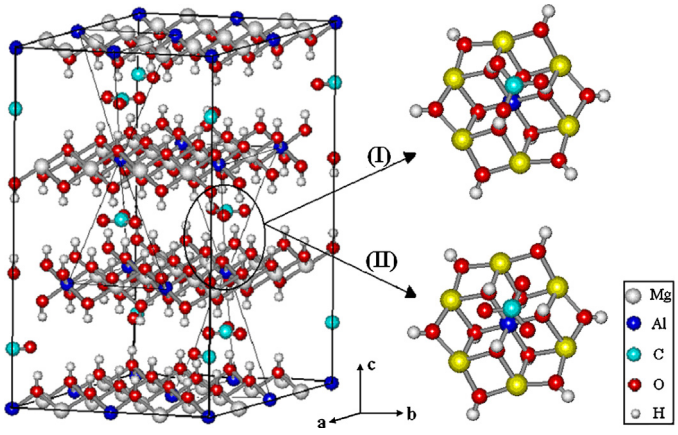

Fig. 2. Crystal structure of MgAl-LDHs (Mg/Al ratio of three) with CO_3^{2-} in the interlayer.