

Use of Layered Double Hydroxides to Create New Environmental Technologies

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Abstract

This review surveys recent advances in the applications of layered double hydroxides [LDHs] in sorption processes. By virtue of the flexible tunability and uniform distribution of metal cations in the brucite-like layers and the facile exchangeability of intercalated anions, LDHs-both as directly prepared or after thermal treatment or rehydrated have found many applications as stable and recyclable sorbents for environmental protection in industrial regions. This paper presents data on the structure and properties of LDHs, the production of sorbents with fixed and labile dimensions of interplanar spaces. Technologies for the removal of organic and inorganic substances using LDHs sorbents have been developed.

Keywords: layered double hydroxides; sorbent; environmental protection;

Introduction

Layered Double Hydroxides [1, 2] is a class of inorganic compounds consisting of positively charged layers of metal hydroxides, as well as anions and solvent molecules in the interplanar space. Hydroxides form a system of octahedral cavities, statistically filled with cations of metals of different valencies [Figure 1].

LDHs have the ability of capturing and exchange both organic and inorganic anions and cations, and these properties make these compounds unique. All LDHs show increased selectivity to the carbonate ions, because of the flat location in the interlayer space, parallel to the layers of the matrix. Therefore, the most common salt form of LDH is carbonate [Figure 2].

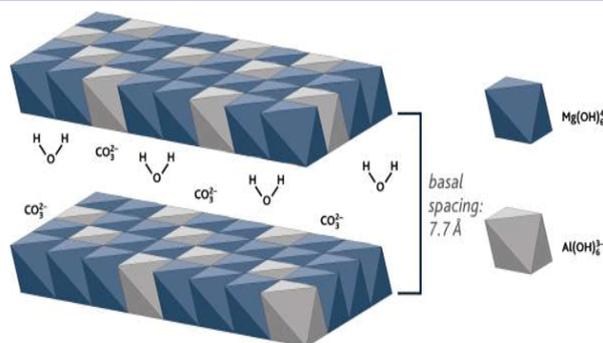


Figure 1: Schematic picture of the LDH

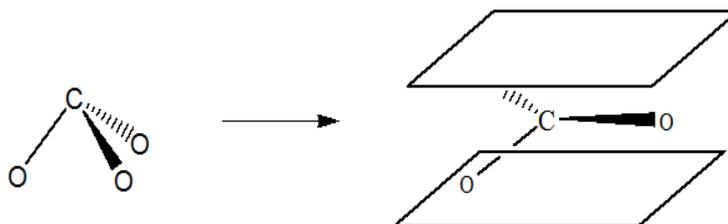


Figure 2: Plane-parallel arrangement of CO₃²⁻ ions in the inner space of LDHs

Anions in the interplanar space easily reacting of ion exchange. Varying the composition of internal anions, it is possible to increase interplanar distance between layers [from 2 to 50 Å]. LDHs have different basic sites. These are weak Brunsted sites and strong Lewis sites. The basicity of LDHs depends on the temperature of calcination, composition and structure, and the ratio of cations. The Brönsted basic sites in such compounds is a hydroxyl localized on tetrahedral aluminum. Lewis' basic sites are an undivided electron pair of oxygen [Figure 3] [3].

The main factor determining the number of basic sites and their strength is the number of isomorphous substitutions and their frequency. That is, all LDHs are bifunctional substances in which both basic and acid sites are present. Of course, the number and strength of the sites strongly depend on the degree of isomorphous substitution. The most important property, thanks to which LDH surpasses all other basic sorbents and catalysts, is the ability to control the pore size. This allows to create structures corresponding to the sizes of molecules and ions that must be

sorbed, that is, to create narrow-selective sorbents. And at the same time, it is possible to create LDH with a wide distribution of pores, capable of absorbing the molecules of different sizes. Finally, it is possible to create LDHs capable of changing their structure, adjusting to the size of the molecules and ions present in the solution [4].

The structure of the internal space of LDH depends on many factors - matrix cations, anions and molecules in the interior space, processing temperatures. Located in the inner space of LDH molecules change their orientation, releasing the blocked active sites. Pillared clays are two-dimensional LDH with a given size of interlayered distances .

Ordinary LDHs change the size of their pores, adjusting to the size of molecules in solution. Creating columns that fix the distance between layers completely eliminates these shortcomings. The general scheme for creating columns in the pillared LDHs is shown in the figure [Figure 4].

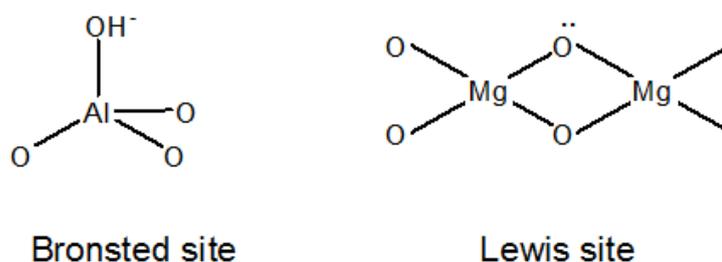


Figure 3: Brønsted and Lewis sites in LDHs

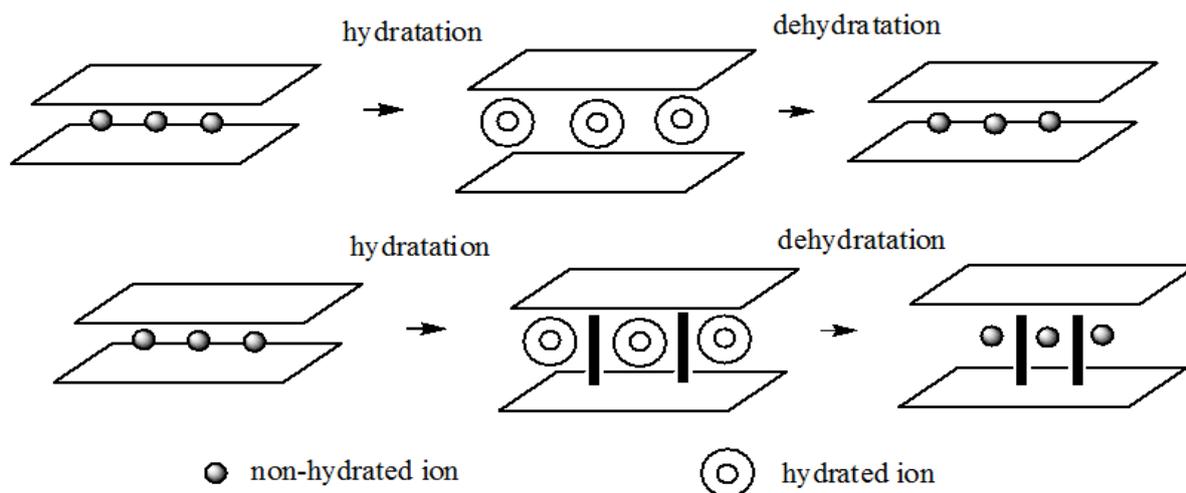


Figure 4: Pillared layered double hydroxides preparation

The process of obtaining columnar clays consists of the main stages: ion exchange of small cations for larger ions; calcination for the transformation of polyhydroxocations to metal oxide clusters in the form of columns; restoration of the initial hydroxide structure of the base layers. The use of various pillarizing substances makes it possible to create LDHs with a given, fixed size of interplanar distances.

To bind the layers in clays, oxides of an acidic nature are mostly often used. The uniqueness of LDH is that, although they are basic sorbents, they always have acid sites, which make it possible to create columnar clays from LDH. A typical curve of the mass loss at the calcination is shown in the [Figure 5].

The peak in the temperature 200-250°C corresponds to the loss of crystallization water, at the 450°C to the transition of the LDHs from the hydroxide form to the oxide one. And one more unique property of LDHs. Up to a certain temperature of calcination LDHs have a “memory effect”, that is, they can restore the layered structure from the oxide by hydration [5]. This allows us to use LDH many times, restoring the structure after burning of the sorbed organic material. But LDHs are very effective for burial after sorption of inorganic substances. When calculating LDHs at temperatures above 550°C, a spinel is formed, which retains the contaminants [Figure 6 and 7] [6].

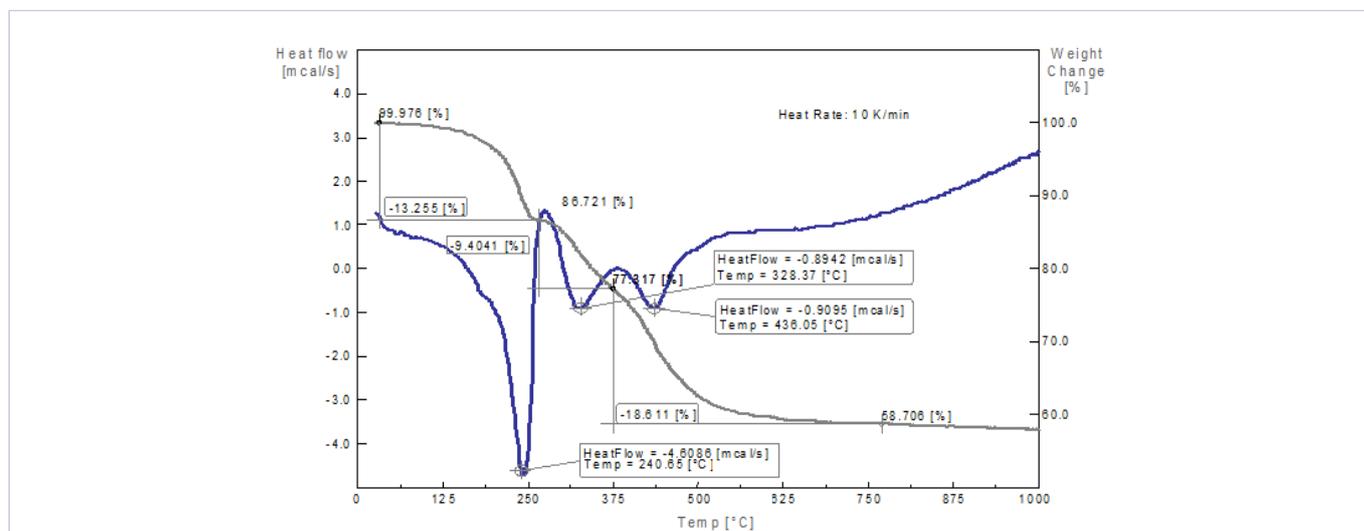


Figure 5: Calcining of Layered Double Hydroxides

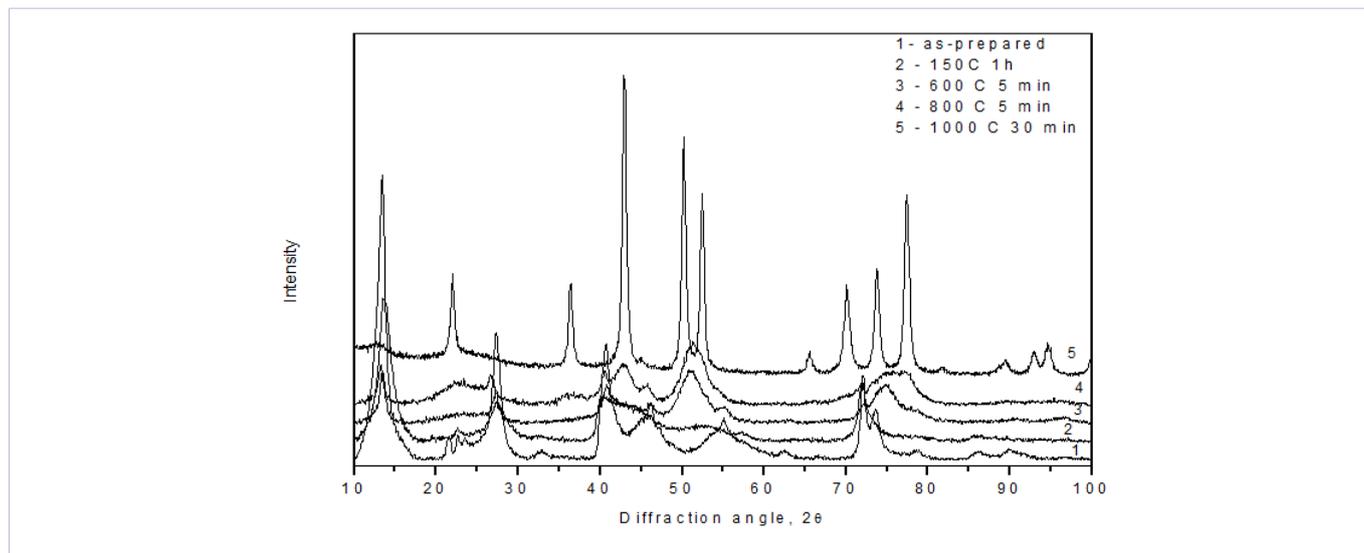


Figure 6: Calcining of LDH at difference temperature

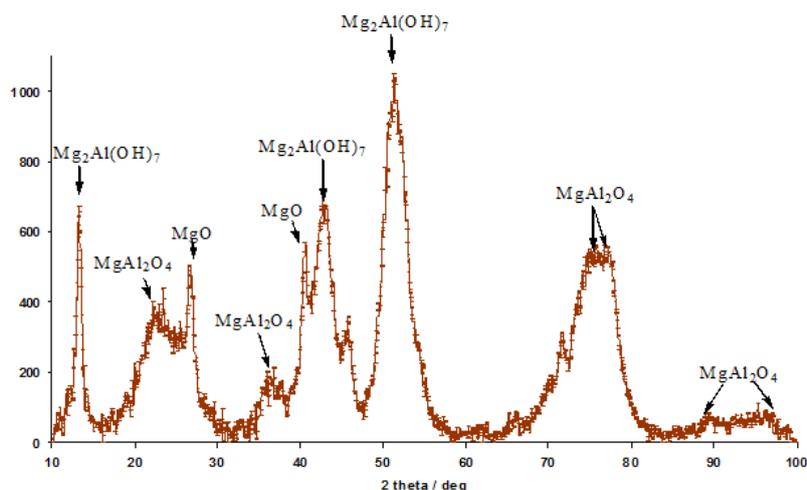


Figure 7: Transformation of LDHs into spinel at 800°C

We carried out thermal studies to establish the structures formed during heat treatment of LDH; to establish the areas of existence of these structures to safe disposal of sorbents with sorbed substances [7].

As an example, consider the removal of naphthalenes and naphthols. Sorption experiments were carried out by comparing the sorption of naphthalene and β -naphthol in the LDHs. The sorption of β -naphthol and naphthalene undergoing via different mechanisms [8]. After sorption, the specific surface was determined and the interplanar distances were measured. The results are shown in the Figure 8.

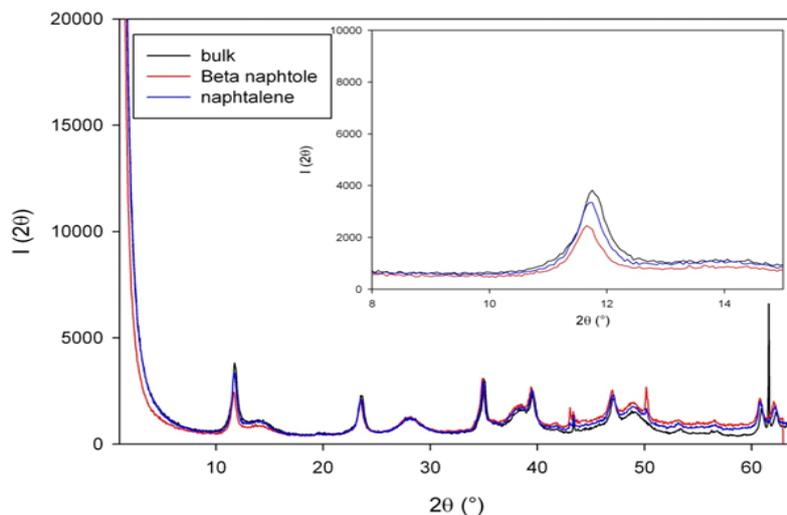
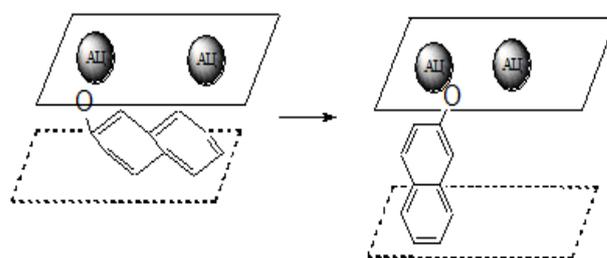


Figure 8: X-ray patterns of LDH $Mg/(Mg+Al) = 0,52$ mol/molC

From the presented X-ray patterns you can see that the maximum deviations are observed at the sorption of β -naphthol. The reason is that the aromatic rings of adsorbed naphthalene are located parallel to the inorganic layers, regardless of the concentration of active sites [9].

The interplanar distance in LDHs is about 7 Å. This value is comparable to the “thickness” of the aromatic ring of about 3 Å, whereas the diameter of the benzene molecule is 7 Å. And for β -naphthol, the plane-parallel arrangement is observed only in the initial stage of ion exchange. Natural and synthetic LDHs have similar compositions and structures, identical basic and acid properties, and identical series of selectivity. The processes of sorption occur at different rates and with different degrees of adsorption. X-ray diffraction data show that the synthetic LDH has small crystal dimensions and significant stress, whereas in natural LDH, large crystals with low stress predominate. The dimensions of the crystals, in turn, influence the geometry of the inner space of LDHs [10,11].

When the aromatic rings of naphthalene are arranged parallel to the inorganic layers, the interplanar distance is 9 Å, and at perpendicular position is 19 Å. Using LDH allowed us to reach final concentrations of naphthalene at 12 mg/m³, which is the best result in the world and better than the limit concentration at 20 mg/m³. So, the following properties of LDHs make them unique for use for protecting the environment. Creation of LDHs with a rigid structure, with a fixed pore size or sorbents with varying pore size with automatically adjusting to the size of the contaminant. Creation of LDHs that “remember” their original structure and reconstruct it after rehydration. That is, creation of LDHs sorbents, absorbing all contaminants, or sorbents selective to certain pollutants. Creation of LDHs with a given type of sites, acidic or basic, Bronsted or Lewis. After the sorption of contaminants, LDHs can be safely disposed of or restored for repeated use.

Theoretical studies of LDHs and laboratory experiments allowed the development of the following new technologies for environmental protection:

- Removal of chromium compounds, both cationic and anionic [12]
- Removal of sulphides [13]
- Removal of naphthols and naphthalene [14]
- Removal of phenols [15]

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