

Research Progress of Hydrotalcite-like compounds

Luyao Wang^{1, 2, 3, 4}, Lulu Zhang^{1, 2, 3, 4}

¹Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi'an 710075, China

²Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi'an 710075, China

³Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Natural Resources of China, Xi'an 710075, China

⁴Shaanxi Provincial Land Consolidation Engineering Technology Research Center, Xi'an 710075, China

Abstract: Hydrotalcite-like compounds has layered structure and unique properties. Rich surface hydroxyl groups and interlayer anions make it have excellent heavy metal adsorption capacity. The variable valence manganese element in the laminate gives it good catalytic performance. This paper introduces the concept, structure, preparation methods and application of hydrotalcite-like compounds in detail, in order to provide reference for academic research and industrial application of environment function material.

Keywords: LDHs, Negatively charged, Heavy metals, Catalytic oxidation.

1. Introduction

Hydrotalcite-like compounds, also known as anionic clay, although the content is not as much as cationic clay, it is common in nature. In 1842, Hochstetter discovered the presence of natural hydrotalcite-like compounds in Sweden. The main body of hydrotalcite-like compounds is usually composed of two kinds of metal hydroxides and has a layered structure, so it is also called layered double hydroxides (LDHs) [1]. LDHs have unique structure and physical and chemical properties, and can be synthesized artificially. The hydrotalcite-like compounds has been formed and is becoming more and more mature. The application of hydrotalcite-like materials in various fields including environmental remediation and pollution control has broad prospects.

2. Structure and Chemical Composition of LDHs

LDHs have a layered structure of brucite $Mg(OH)_2$, with a unit layer of MgO_6 octahedron sharing two-dimensional stretching. Due to the replacement of some divalent metal ions by trivalent metal ions on the hydrotalcite-like laminate, there is a residual positive charge. This charge generated by the crystal structure itself is called structural positive charge. There is residual positive charge in the interlayer channel of the anion balance layer [2].

The crystal structure of LDHs is the same as that of hydrotalcite, but its chemical composition such as the type and relative proportion of lamellar metal ions and interlayer anions are different, so these substances are called hydrotalcite-like compounds. The distance between two adjacent structural layers or unit layers is called the basal spacing, and the height of the gap between two layers is called the gallery height.

3. Physicochemical Properties of LDHs

The physical and chemical properties of LDHs depend on the type and content of lamellar elements and interlayer anions, interlayer water distribution and lamellar stacking. The physical and chemical properties of LDHs include acid-

base properties, thermal stability, memory effect, exchangeability of interlayer anions, controllability of lamellar chemical composition, and controllability of crystal size and distribution. The unique physical and chemical properties of LDHs make them have broad application prospects in many fields, such as polymer functional materials, ion exchange, adsorption, catalysis, medicine, biology, electrochemistry, photochemistry and military materials, and have attracted wide attention from scholars at home and abroad[3-5].

4. Synthesis of LDHs

Most of the minerals in nature are negatively charged and few of them are positively charged. Therefore, the synthesis of LDHs with positively charged structure has become a topic of concern. There are many synthetic methods of LDHs, including co-precipitation method, ion exchange method, structural reconstruction method, hydrothermal synthesis method, gas solvothermal method, mechanochemical method and so on[6].

5. Application of LDHs and Its Derivatives in Environmental Remediation

5.1. Removal of Heavy Metals

Manganese-based hydrotalcite is a layered manganese mineral, which exists in the natural environment and can also be artificially synthesized. It is often used as an environmental functional material for adsorption/catalysis. Manganese-based hydrotalcite/derivatives have attracted wide attention in the field of adsorption of heavy metals due to their unique structural properties. In recent years, manganese-based hydrotalcite/derivatives have been gradually applied to the removal of heavy metals in water. Otgonjargal et al.[7] prepared FeMn-LDH by co-precipitation method and used it to remove As (III) and As (V) from aqueous solution. The maximum adsorption capacities of FeMn-LDH for As (III) and As (V) were 112.5 and 52.5 mg/g, respectively. The removal mechanisms included oxidation, adsorption and ion exchange. In addition, the adsorption capacity of FeMn-LDH

remains unchanged in a wide pH range, and the column adsorption experiment also proves that FeMn-LDH has a good application prospect.

5.2. Catalytic Oxidation of Organic Matter

MnFe-LDH was prepared by Hou et al. [8] and used to activate PMS to degrade acid orange 7. It was found that the generated active radicals $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ were the key reasons for the efficient degradation of acid orange 7. MnFe-LDH has good activation performance for PMS, and can remove 85% of the new organic pollutant-octadecylamine (ODA, 10 mg/L) within 5 min. MnFe-LDH+PMS system has a good ability to remove ODA under alkaline conditions. MnFe-LDH also showed high reusability and low metal ion dissolution stability. MnFe-LDH can not only remove refractory organic pollutants, but also has environmental friendly characteristics, so it has good application potential.

6. Conclusion

Current research focuses on the design and development of highly efficient adsorbents and catalysts based on the adsorption and catalytic properties of divalent metals, such as the synthesis of LDH using highly oxidizing divalent metals (such as Cu^{2+} and Co^{2+}) as raw materials to improve the catalytic activity of materials. It can be speculated that the adsorbent (such as LDH) will affect the biological adsorption, catalysis and corresponding environmental effects of the adsorbent after immobilizing heavy metals. However, there is still a lack of necessary understanding of the changes in the structural properties of LDH during the immobilization of heavy metals. At the same time, it is not clear that the change of structure and surface reactivity may lead to the change of environmental functions (such as adsorption capacity, catalytic activity, etc.) of LDH.

Acknowledgment

This work was supported by Natural Science Basic

Research Program of Shaanxi (No.2021JQ-959) and the Shaanxi Provincial Land Engineering Construction Group Research Project (No. DJNY2022-38).

References

- [1] Abasi C Y, Ejidike I P, Dikio E D. Synthesis, characterisation of ternary layered double hydroxides (LDH) for sorption kinetics and thermodynamics of Cd^{2+} [J]. *International Journal of Environmental Studies*, 2019, 76(3): 441-455.
- [2] Goh K H, Lim T T, Dong Z. Application of layered double hydroxides for removal of oxyanions: a review[J]. *Water Research*, 2008, 42(6-7):1343-1368.
- [3] Chen M, Wu P, Huang Z, et al. Environmental application of MgMn-layered double oxide for simultaneous efficient removal of tetracycline and Cd pollution: Performance and mechanism[J]. *Journal of Environmental Management*, 2019, 246: 164-173.
- [4] Abdelkader N B, Bentouami A, Derriche Z, et al. Synthesis and characterization of Mg-Fe layer double hydroxides and its application on adsorption of Orange G from aqueous solution[J]. *Chemical Engineering Journal*, 2011, 169(1-3): 231-238.
- [5] Lv W, Mei Q, Fu H, et al. A general strategy for the synthesis of layered double hydroxide nanoscrolls on arbitrary substrates: its formation and multifunction[J]. *Journal of Materials Chemistry A*. 2017, 5(36): 19079-19090.
- [6] Li F, Duan X. Applications of Layered Double Hydroxides[J]. Springer Berlin Heidelberg, 2006,119:193-223.
- [7] Otgonjargal E, Kim Y, Park S, et al. Mn-Fe layered double hydroxides for adsorption of As (III) and As (V)[J]. *Separation Science and Technology*, 2012, 47(14-15):2192-2198.
- [8] Hou H, Li X, Yang Q, et al. Heterogeneous activation of peroxymonosulfate using Mn-Fe layered double hydroxide: Performance and mechanism for organic pollutant degradation[J]. *Science of the Total Environment*, 2019, 663: 453-464.