

Synthesis and characterization of Mg-Al-O hydrotalcite - type material

Nguyễn Tiến Thảo*

Faculty of Chemistry, VNU University of Science, 19 Lê Thánh Tông Str., Hoàn Kiếm Dist., Hanoi, Vietnam

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Abstract. Mg-Al layered double hydrotalcite (LDH) samples were prepared through the precipitation method. Both hydrotalcite samples and their calcined forms are characterized by XRD, BET, SEM, TEM and FTIR. The former shows a lamellar structure with the presence of carbonate ions in the interlayers. After calcination, the filaments of the parent solid were completely disappeared and the Mg-Al LDH is converted to the mutual mixture between MgO and AlOx. The latter yields a higher specific surface area and smaller particle domains.

Keywords: Mg-Al hydrotalcite, LDH, perclase, MgO, micropore.

1. Introduction

Layered double hydroxides (LDHs), named as anionic clays or hydrotalcite-type compounds, are a family of materials with general formula $[A_{1-x}B_x(OH)_2]^{x+}[Y^{n-}]_{x/n} \cdot yH_2O]^{x-}$ ($0 < x < 0.33$) where A^{2+} and B^{3+} are divalent and trivalent metal ions, and Y^{n-} is an anion with n - valent [1,2]. Their structure is composed of brucite-like layers $Mg(OH)_2$, where a partial A^{2+}/B^{3+} substitution has taken place, e.g. Mg^{2+} by Al^{3+} , resulting in a net positive charge, balanced by interlayer anions (generally carbonate, chlorate, sulfate, nitrate...) accompanied a variable amount of water [1]. Furthermore, some of the Mg^{2+} , as well as Al^{3+} ions can be replaced respectively

by other divalent (e.g. Cu, Ni, Co, Zn) and/or trivalent (Ni, Co, Fe, Cr, Ga, In) cations [1,3]. Thus, there have been used as potential materials in many applications such as ion exchangers, and absorbents... In the field of catalysis, hydrotalcites and their derivatives are of great interest due to their high surface area, phase purity, basic surface properties, and structural stability [2,3]. Mg-Al based hydrotalcites are, for example, used as a basic catalyst for the transesterification of poultry fat with methanol [5], propane dehydrogenation [6]. Hydrotalcite-derived oxides catalyze higher alcohol synthesis from CO/H₂, oxidation of mercaptan, water gas shift reactions [2-4]. Also, Mg-Al mixed oxides prepared by oxidative decomposition of hydrotalcite precursors have been used in base-catalyzed aldol condensations, alkylations, condensations,

* Tel: 84-4-39331605.

E-mail: nguyentienthao@gmail.com

double-bond isomerization, reforming of methanol [3,4,7-11].

In this study, we prepared some Mg-Al hydrotalcite-type materials with the Mg/Al molar ratio of 7/3 and studied their structure. Furthermore, the sample will be studied the structural change during heating condition.

2. Experimental

2.1. Synthesis of Mg-Al hydrotalcite

A desired amount of 1.60 g of sodium carbonate was dissolved in 25 ml of water in a 500-ml-beaker. The solution was heated to 65° C. Then, 11.25 g of aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99 %) and 17.92 g of magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%) were dissolved in 150 ml of deionized water. The resulting suspension was added drop-wise to the preheated Na_2CO_3 solution. The pH of the solution was adjusted to approximately 9.50 using 1.5 M NaOH. After completing addition of the metal nitrate solutions, the resulting suspension was kept at 65°C with stirring for 24 h. The precipitate was separated from the solution by filtering and washed with 1000 ml of hot deionied water. The filter cake was dried in an oven at 105 °C overnight and calcined at 450 °C for 2 hours in air to obtain the mixed $\text{Mg}(\text{Al})\text{O}_x$ oxides.

2.2. Material characterization

XRD patterns were collected in a range of 10-80° from a Philips X'pert diffractometer equipped using Cu $K\alpha$ radiation. Scanning electron microscope (SEM) images of the catalysts are acquired on a Hitachi S-800 operating at 10 kV. TEM observation was

conducted with a JEM-200CX electron microscope. The BET surface areas were determined by N_2 adsorption on a Micrometrics ASAP 2020 apparatus at -196 °C. Elemental analysis of Mg, Al was done at Columbia Service Center.

3. Results and discussion

Elemental analysis of hydrotalcite composition indicated that the Mg/Al molar ratio is close to a nominal value (Mg/Al = 2.06). Power X-ray diffraction patterns for the Mg-Al hydrotalcite (LDH) and its calcined product are presented in Figure 1.

The MgAl-LDH exhibits a single phase corresponding to the layered double hydroxide with a sharp and asymmetric reflections at 2-theta of 11.5, 23.2, 34.7, 38.8, 46.3, 60.7, 61.8° [3,9,10]. These peaks are well matched with the target composition of empirical formula $\text{Mg}_{0.7}\text{Al}_{0.3}(\text{OH})_2(\text{CO}_3)_{0.15} \cdot x\text{H}_2\text{O}$ hydrotalcite-type compound. Also, no peaks of other oxides detected were, indicating a pure substance of the synthesized hydrotalcite material. The structure of such a material is collapsed after calcination at 450°C and forms perclase MgO (JCPDS: 4-0829) [3] evidenced by its X-ray diffractions at 2- theta of 34.7, 42.9 and 62.5° [3,5]. In this case, neither residual hydrotalcite nor crystalline AlO_x phases were detected in addition to the presence of a single poorly crystalline MgO perclase [11]. The results let us suggest that Al^{3+} cations remain closely associated with MgO structure, in consistent with literature [1,2,10]. Therefore, the textural structure of the calcined oxides should be different from the parent one. To confirm this conduction, we have collected the physical adsorption/desorption of nitrogen at -196°C.

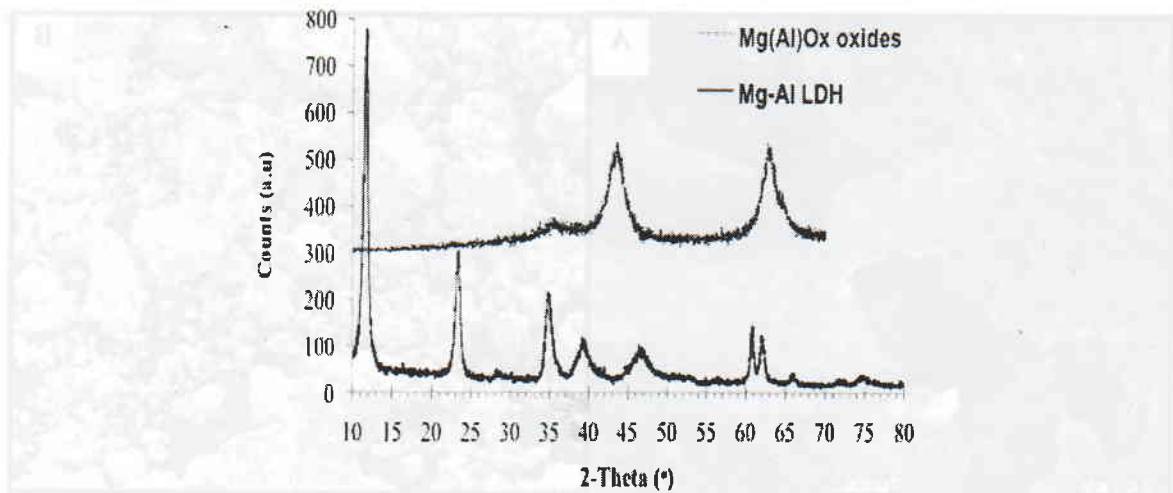


Figure 1. Power XRD patterns of MgAl-LDH and Mg(Al)Ox oxides.

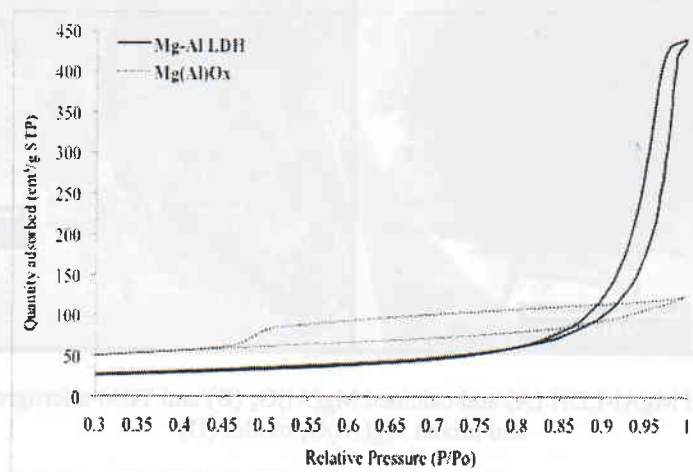


Figure 2. Isotherms of Mg-Al layered double hydroxide and calcined Mg(Al)Ox.

The isotherms of both patterns are presented in Figure 2. Firstly, the nitrogen adsorption – desorption isotherm of the MgAl-LDH closely resembles a type II isotherm. In this case, nitrogen absorption monotonically increases with P/P_0 value due to sorption in the hydrotalcite mesopores [12]. Meanwhile, the hysteresis loop resembles to type H3 hysteresis in the relative pressure range of 0.80–0.95, indicating the formation of a new interparticle

and intragallery porosity during calcination step (Fig. 2). Isotherm exhibits an H3- type hysteresis at high relative pressure, which is typical for aggregates of plate-like particles giving rise to slit-shaped pores. This kind of hysteresis is typical for the presence of open large pores, which allow easy diffusion of the reactants through the materials. Also, the solid contains not only mesopores but also some small amount of micropores.

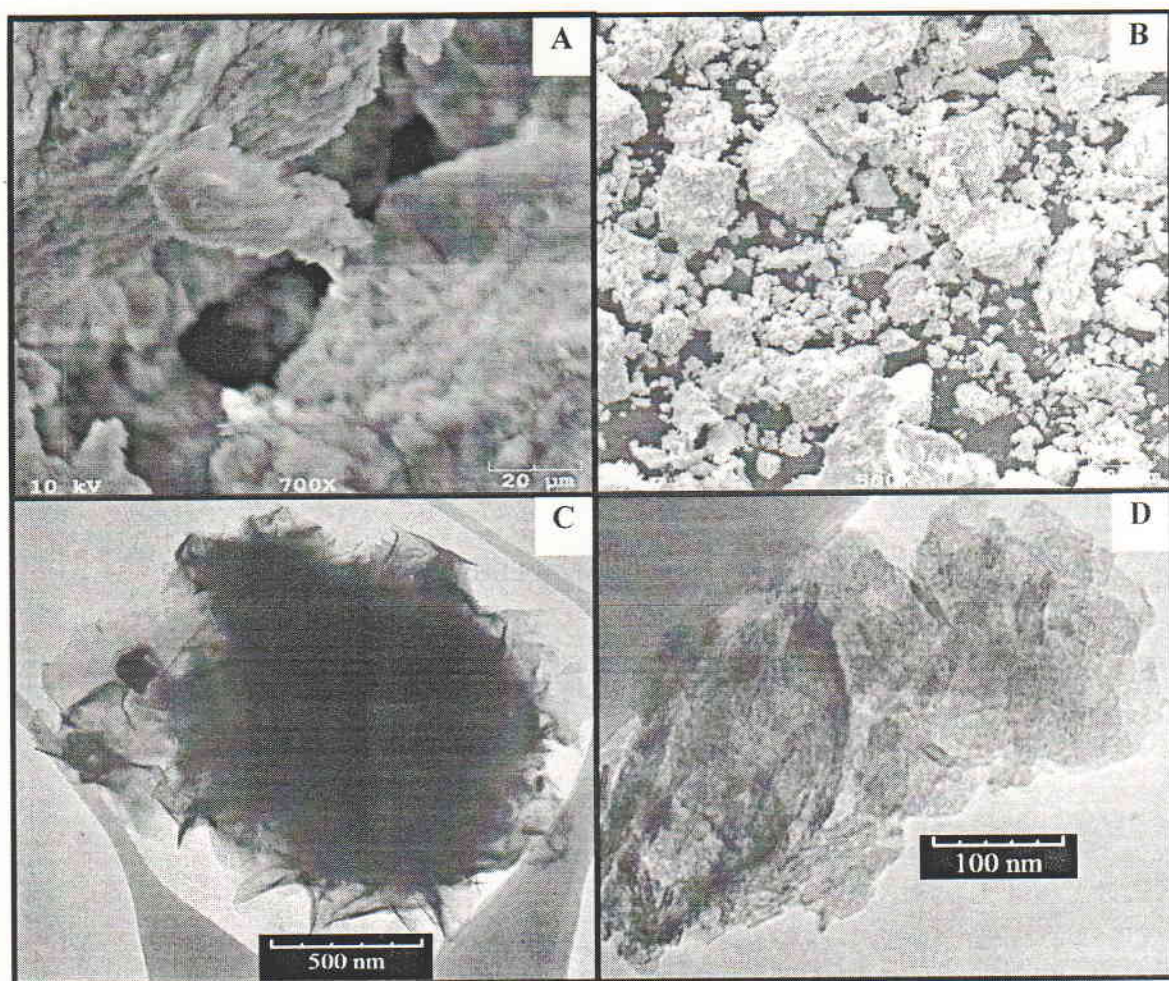


Figure 3. SEM images of MgAl-LDH (A) and calcined Mg(Al)O_x (B) and TEM micrographs of MgAl-LDH (C) and mixed Mg(Al)O_x oxides (D)

For Mg-Al-O mixed oxides, the physical adsorption/desorption describes the hysteresis loop shape of the calcined oxides shows a H4 hysteresis loop in the relative pressure range of 0.4-0.9. This is clearly characteristics for the microporous materials. Calcining at 400-500°C leads to the removals of carbonate ions and water possibly destroyed a layered structure of the hydrotalcite-like compounds. The BET surface areas of the parent one (MgAl-LDH) is about 83 m²/g while that of the calcined one is up to 153 m²/g [4]. During the thermal decomposition of Mg-Al hydrotalcites at 400°C,

water and CO₂ are formed by dehydroxylation of OH groups within brucite layers and by decarboxylation of interlayer carbonates, respectively. The release of these gaseous products creates a significant porous structure and substantially increases the surface area of calcined hydrotalcites [12].

Figure 3A reveals the lamellar structure of the Mg-Al LDH aggregates consisting of small crystallites with platelet morphology in the average diameter ranging between 25 and 50 µm (Fig. 3). In the case of the oxides, a diminution of the crystallinity of the materials

and of the diameter of crystallites was observed. The morphology of Mg(Al)Ox oxides was also investigated by TEM. In this case, the aggregates are consisted of several platelets but the micrographs (Fig. 3A) only show filamentous formations. These filaments are known as the characteristic of hydrotalcite-like compounds [13]. The filaments are constructed

by a large number of very tiny particles [14]. The length of the filaments was up to 200 - 400 nm (Figure 3C) while, in the case of Mg(Al)Ox oxides, a significant diminution of the fibrous formation is observable (Fig. 3D). FI-IR results also indicate a significant change in structure between the hydrotalcite parent and the calcined oxides [1].

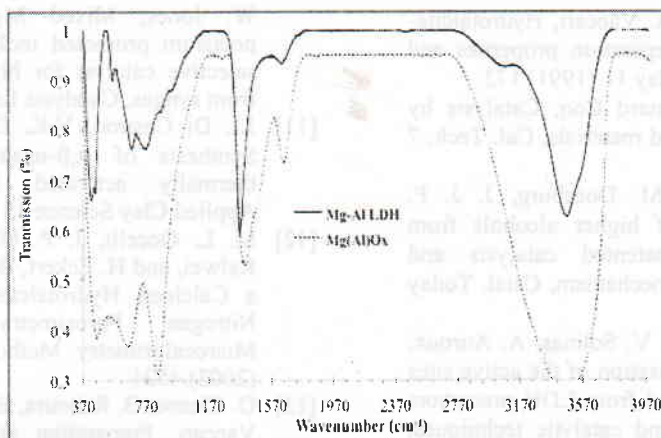


Figure 4. FTIR spectra of Mg-Al layered double hydroxide and calcined Mg(Al)Ox.

Figure 4 displays the IR spectra of Mg-Al layered double hydroxide and calcined Mg(Al)Ox oxides. The absorption at 3500-3600 cm^{-1} , presented in both specimens, is attributed to the H-bonding stretching vibration of the OH in water physically absorbed. A shoulder may be present around 3095 cm^{-1} , for the case of MgAl-LDH pattern, is attributed to the hydrogen bonding between H_2O and the anion in the interlayer [1]. The main absorption bands of the anions are observed between 1000 and 1800 cm^{-1} . The carbonate anions in a symmetric environment are characterized by three bands at 1369, 869, 686 cm^{-1} . The bands at 715, 1007 and 1161 cm^{-1} are all associated with Al-OH vibration frequencies, whereas signals at 660 and 852 are characteristics for the two absorption bands of the interlayer carbonate, respectively [15].

4. Conclusions

A target composition of $\text{Mg}_{0.7}\text{Al}_{0.3}(\text{OH})_2(\text{CO}_3)_{0.15} \cdot x\text{H}_2\text{O}$ layered double hydroxide sample was successfully prepared through the conventional recipe and characterized by several techniques. The uncalcined hydrotalcite solids present the filaments composed of numerous tiny particles. Both BET and TEM indicate the appearance of both micropores and mesopores and the lamellar structure of Mg-Al-LDH. After calcining Mg-Al-LDH, ion carbonates located in the interlayers are escaped, facilitating the porosity of the calcined oxides. The layered double hydroxide was globally destructed at 450°C, yielding an intimate contact between two or more oxide components. Thus, the calcined pattern exhibits better porosity and higher surface area (154 m^2/g) compared with the parent hydrotalcite (83 m^2/g).

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Tổng hợp và đặc trưng vật liệu Mg-Al-O kiểu hydrotalcite

Nguyễn Tiên Thảo

*Khoa Hóa học, Trường Đại học Khoa học Tự nhiên, ĐHQGHN
19 Lê Thánh Tông, Hoàn Kiếm, Hà Nội, Việt Nam*

Mẫu xúc tác hydroxit lớp đôi (LDH) điều chế theo phương pháp đồng kết tủa. Mẫu hydrotalcite và mẫu nung của nó đều được đặc trưng bằng các phương pháp vật lý hiện đại như XRD, BET, SEM, TEM, FT-IR. Mẫu Mg-Al-LDH có cấu trúc phiến có chứa các sợi nhỏ và các ion cacbonat nằm xen giữa các lớp. Sau khi nung, các sợi hydrotalcite biến mất, tạo thành một hỗn hợp oxit MgO và AlO_x pha trộn lẫn nhau có diện tích bề mặt riêng, kích thước hạt và mật độ mao quản lớn hơn mẫu hydrotalcite ban đầu.