

Using Kaolinitic Clay for Preparation of a Hydrotalcite-Like Compound

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ABSTRACT

In this study, Mg-Al-CO₃ hydrotalcite was synthesized from a kaolinite as natural source aluminium using two simple methods. The first method uses the kaolinite in natural solid state, the second method use the filtrate of the kaolinite after dissolution by acidic solutions. The structure of the materials was characterized by X-ray diffraction, Fourier transform infrared spectroscopy, differential scanning calorimetry (DSC) and Brunauer, Emmett, and Teller (BET) measurements.

Keywords: Hydrotalcite, Kaolinite, Layered Compound, XRD, Memory Effect

1. Introduction

A wide range of compositions are possible for synthetic hydrotalcites based on the general formula

$[M_{1-y}^{II}L_y^{III}(OH)_2]^{y+}[X^{n-}]_{y/n}[H_2O]_z$, where M^{II} and M^{III} are the divalent and trivalent cations in the octahedral positions within the hydroxide layers. The value y can have a range between 0.17 and 0.33, while Xⁿ⁻ is an interlayer anion with a negative charge n⁻ [1,2], and z is the number of water molecules. Many anions or anionic complexes, both organic and inorganic, can be incorporated into the hydrotalcite structure. The hydrotalcite can be abbreviated as [M^{II} - M^{III} - X], where, M^{II} = Mg²⁺, Zn²⁺, Cu²⁺, Ca²⁺, Mn²⁺; M^{III} = Al³⁺, Cr³⁺, Fe³⁺, ...; and Xⁿ⁻ = Cl⁻, NO³⁻, CO³⁻, PO₄³⁻, etc.

Hydrotalcite-like compounds, also called layered double hydroxides (LDHs), have received considerable attention in recent years owing to their layered structure and high anion-exchange capacity [3], which makes them potential materials for technical applications in various domains [4]. These materials have been investigated as solid ionic conductors [5] and sensors [6]. Layered double-metal hydroxides are, or may be used as, catalysts [4,7], photo-catalysts, catalyst supports [8], adsorbents [9,10], anion exchangers [11], medicines [12,13] and bonding materials. The reason for the potential application of hydrotalcites as catalysts rests with their ability to make mixed metal oxides at the atomic level, rather than the particle level. Such mixed metal oxides are formed through the thermal decomposition of the hydrotalcite

[14]. Also, LDH materials have been extensively studied in terms of their thermal evolution [15,16], textural properties [16], and the formation of nanosized metal particles [17] as well as for environmental purposes [18].

The present study reports simplified method to synthesize the carbonate forms of layered double hydroxides from a natural source of trivalent cations. Mg-Al-CO₃ hydrotalcite-like layered compounds have been synthesized with Mg/Al ratios of 3 by a mechanochemical method using kaolinite in solid state and by coprecipitation using the under product of the acidic dissolution of the kaolinite.

2. Experimental

2.1. Material Preparation

The Mg-Al-CO₃ hydrotalcite-like layered compounds has been synthesized by two simple methods using kaolinite as a natural source of trivalent cations and an aqueous solution of Na₂CO₃ as the precipitant.

Method 1

The sample was synthesized by crushing kaolinite with the magnesium nitrate hexahydrate (their amounts were so as to have the desired Mg²⁺/Al³⁺ molar ratio), followed by heating at 500°C for 4 hours. The product obtained was dispersed under constant stirring in an aqueous solution containing Na₂CO₃ (100 mL). The pH of the dispersion was maintained constant at 10 ± 0.1 by adding NaOH or HNO₃ when necessary. The slurry was subse-

quently agitated at room temperature for 24 h, and then aged at 150°C for 24 h. The resulting products were collected by centrifugal separation and washed thoroughly with deionised water to eliminate excess Na⁺ followed by drying overnight at room temperature.

The samples were identified as [*K_{sd}3P10-T150*], where *K_{sd}* represents the trivalent cation source (kaolinite) used to prepare the materials and “*sd*” represents the solid state. For example, *K_{sd}3P10-T150* stands for the product prepared with kaolinite in solid state, a Mg/Al ratio of 3, an aging temperature of 150°C, and a pH of synthesis of 10.

Method 2

The sample was synthesized using as aqueous solution of Na₂CO₃ as precipitant. The solutions containing Mg(NO₃)₂·6H₂O and Al³⁺, cation resulting from dissolution of the purified kaolinite by acidic attack, (their concentration varied so as to have the Mg/Al molar ratio of 3) were added dropwise to the aqueous solutions of Na₂CO₃ with vigorous stirring. The pH of the dispersion was maintained constant at 10 ± 0.1 by adding NaOH (10%). The slurry was subsequently agitated at room temperature for three days. The resulting products were collected by centrifugal separation and washed thoroughly with deionised water to eliminate excess Na⁺ followed by drying overnight at room temperature.

The samples were identified as [*K_{liq}3P10*], where *K_{liq}* represents the trivalent cation source (kaolinite) used to prepare the materials and “*liq*” represents its liquid state. For example, *K_{liq}3P10* stands for the product prepared with kaolinite in liquid state, an Mg/Al ratio of 3 and a pH of synthesis of 10.

2.2. Characterization of Materials

The dried precipitates were characterized by X-ray diffraction (XRD) in order to determine the species present and their degree of crystallinity. Diffractograms were obtained by using a ‘PANalytical X’Pert HighScore Plus’ diffractometer using monochromated CuKα radiation. Nitrogen adsorption measurements were performed at -196°C with an Autosorb-1 unit (Quantachrome, USA) for the determination of sample textural properties using the multipoint Brunauer-Emmet-Teller (BET) method. The samples were out gassed at 120°C under a vacuum at 10⁻³ mmHg for 3.5 h. Fourier-transformed infrared (FT-IR) spectra were recorded as KBr pellets using a Perkin-Elmer FT-IR (model 783) instrument. KBr pellets were prepared by mixing 5 wt% anionic clay with 95 wt% KBr and pressing. Differential scanning calorimeter (DSC) experiments were performed with Mettler Toledo DSC-823 type thermal analyzer at heating rates of 20.0°C·min⁻¹.

3. Results and Discussion

3.1. Characterization of the Clay

The sample selected for this study is Tabarka clay (Tunisian clay).

3.1.1. X-Ray Diffraction

The nature of the impurities was determined by examining the crude samples. Quartz (reflection at 3.35 Å) is the major impurity. The diffractogram of purified sample (**Figure 1(a)**) show the reflections at *d* = 7.21 Å and 10.05 Å characteristic of the kaolinite and illite respectively [19].

In **Figure 1(b)** is shown the powder XRD pattern of the mixture of kaolinitic clay and the magnesium nitrate after heating at 500°C. Owing to the fact of the absence of the peak corresponding of the *d*-spacing of 7.21 Å and attributed of the kaolin in the XRD pattern of the product shows that the structure of the original clay is completely destroyed and indicates metal oxide peaks, suggesting an almost total decomposition of the original clay. This observation is consistent with the result given by the study of the thermal stability for the clay sample. Indeed, heating the sample clay in air above 500°C (**Figure 2(b)**), the peak at 7.21 Å disappears while the peak characteristic of illite (*d* = 10.05 Å) persists. The treatment with ethylene glycol does not have any effect (**Figure 2(c)**).

3.1.2. Infrared Spectra

Figure 3(a) shows the Infrared spectra of purified clay over the frequency range of 4000 - 400 cm⁻¹. The figure shows that purified sample contain quartz (800 cm⁻¹). The spectrum exhibited the characteristic band at 3697 cm⁻¹ confirming the dominant presence of kaolinite. The band, at 1637 cm⁻¹ and 3450 cm⁻¹ corresponds to the bonding modes of absorbed and zeolitic water.

3.1.3. Chemical Composition

The purified clay sample was attacked by a mixture of three acids (HCl, H₂SO₄, and HNO₃). All elements were dissolved into solution expect for the Si which was determined by gravimetric method analysis. The Al and Fe were assayed by atomic absorption spectrophotometer (AAS Vario 6). The chemical composition data (**Table 1**) indicates that the percentage of Al₂O₃ is 30 % confirming that sample is kaolinitic clay

3.2. Characterization of the *K_{liq}3P10-LDH* and *K_{sd}3P10-LDH*

3.2.1. Powder X-Ray Diffraction

Figure 1 shows the XRD patterns for the precipitates obtained by method 1 and method 2. It is shown that the *K_{sd}3P10-LDH* and *K_{liq}3P10-LDH* samples patterns (**Figures 1(c)** and **1(d)**) were comparable to that pattern of

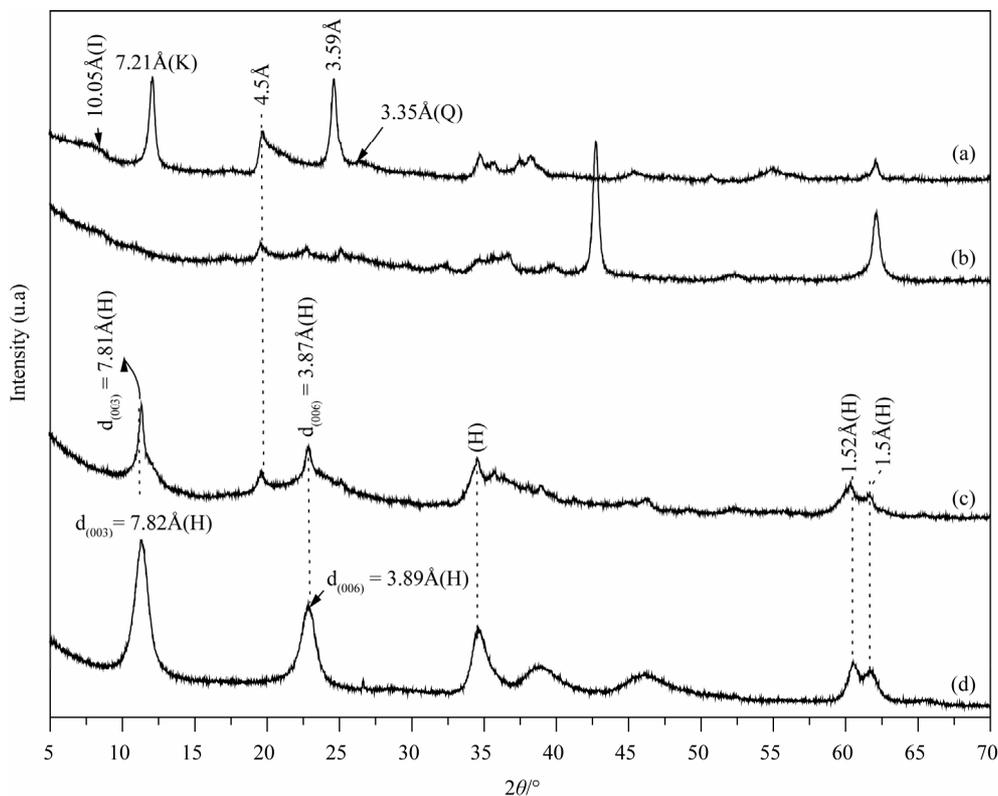


Figure 1. X-ray patterns of clay sample: (a) purified clay; (b) Clay + $\text{Mg}(\text{NO}_3)\cdot 6\text{H}_2\text{O}$ and heated at 500°C ; (c) $\text{K}_{\text{sd}}3\text{P10-T150}$; (d) $\text{K}_{\text{liq}}3\text{P10}$. [(K) Kaolinite, (I) Illite, (Q) Quartz, (H) hydrotalcite.

Table 1. The chemical composition of the purified clay.

%	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	MgO	K_2O	Ignition loss
Clay	48.75	30	3.39	0.33	1.45	0.07	1.95	13.93

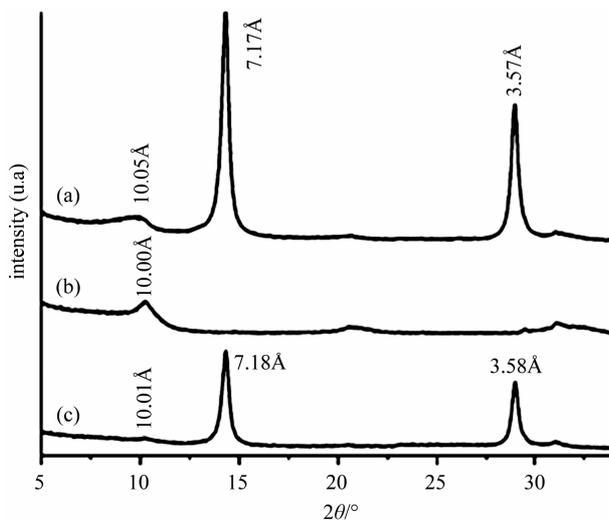


Figure 2. X-ray patterns of: (a) oriented crude simple; (b), oriented heated sample; (c) oriented sample treated with glycol.

the sample prepared by the conventional method. The $\text{K}_{\text{liq}}3\text{P10-LDH}$ sample showed a layered structure as observed from the peaks at 7.82, 3.89 and 2.61 Å, corresponding to planes (003), (006) and (009) for a layered hydrotalcite-like material, respectively [20]. The $\text{K}_{\text{sd}}3\text{P10-LDH}$ sample display very weak and broad peaks at a 2θ value of 11° compared to the sample prepared by coprecipitation at the same conditions ($\text{pH} = 10$ and $\text{Mg}^{2+}/\text{Al}^{3+} = 3$). $\text{K}_{\text{sd}}3\text{P10-LDH}$ shows a structure different from the previous samples; it was an ill-defined hydrotalcite contaminated with argillaceous phase ($d = 4.5\text{Å}$).

3.2.2. IR Spectroscopy

The FT-IR spectra of the $\text{K}_{\text{sd}}3\text{P10-LDH}$ and $\text{K}_{\text{liq}}3\text{P10-LDH}$ hydrotalcite are presented in **Figures 3(b)** and **3(c)**. It shows a broad band around 3470 cm^{-1} due to the stretching mode of the structural $-\text{OH}$ groups in the metal hydroxide. However, a small shoulder at $2900 - 3000\text{ cm}^{-1}$ suggests the presence of a second type of $-\text{OH}$ stretching vibration (possibly due to hydrogen bonding

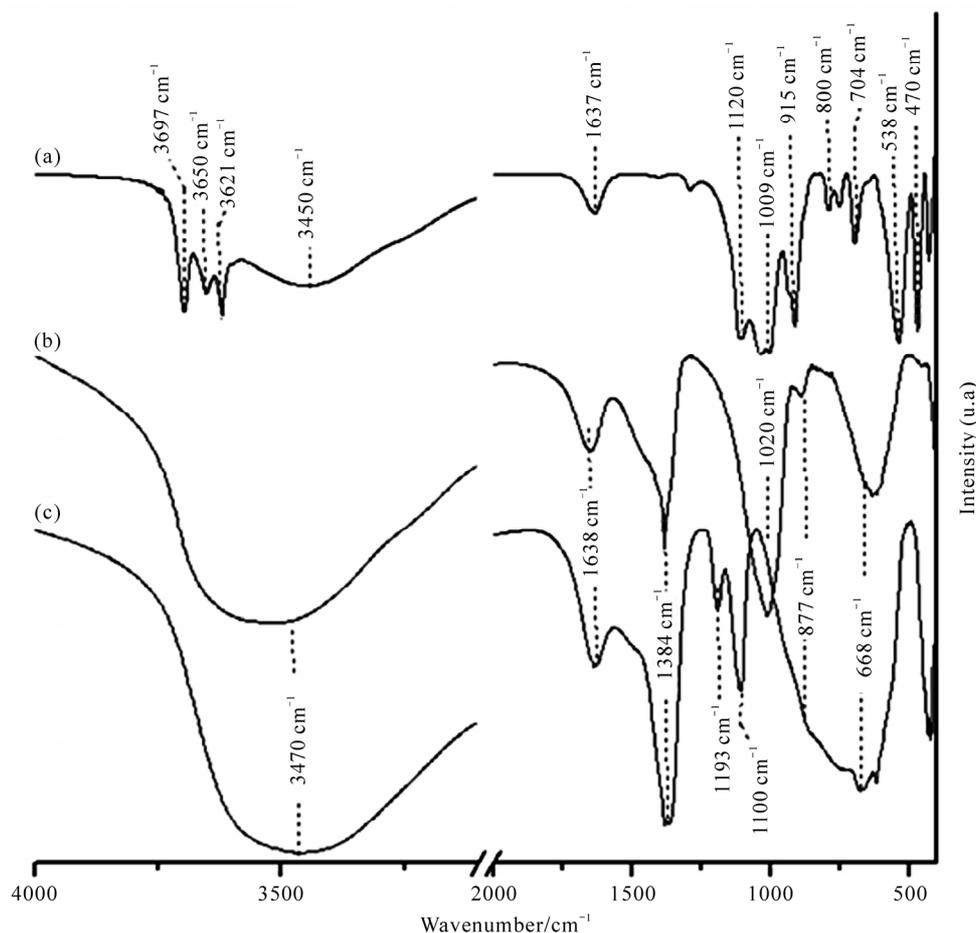


Figure 3. Infrared spectra of: (a) purified clay; (b) $K_{sd}3P10-T150$; (c) $K_{liq}3P10$.

with carbonate in the interlayer spacing [21].

The two spectra show:

1) A shoulder at 1638 cm^{-1} is ascribed to the bending mode of the interlayer water molecules [22].

2) The three characteristic bands of carbonate in hydrotalcite at around 1384 cm^{-1} (ν_3), 877 cm^{-1} (ν_2) and $\sim 1020\text{ cm}^{-1}$ (ν_1) [23,24].

3) The bands around 420 and 668 cm^{-1} , which are ascribed to the bending mode Al-O and Mg-O.

The infrared spectrum of the $K_{liq}3P10-LDH$ shows additional bands appearing at 1193 and 1100 cm^{-1} which could not be identified.

3.2.3. Surface Area and N_2 Adsorption-Desorption Studies

The N_2 adsorption-desorption isotherm is of type II for all samples, which is typical of mesoporous materials (Figure 4) [25]. All of the materials possessed zero micropore volume. Adsorption isotherms of this type are represented by mesoporous materials with no micropores and strong interactions between adsorbent and adsorbate molecules. This type of hysteresis loop is formed when

the adsorption and desorption curves do not coincide and is caused physically by the phenomenon of capillary condensation in the mesopores.

From Figure 4, it was determined that all samples shows a horizontal course of the hysteresis branch over an appreciable range of gas uptake ($p/p_0 \geq 0.6$), while it is vertical above this ratio. This type of hysteresis loop is often observed with aggregates of plate-like particles that give rise to slit-shaped pores.

The textural properties for samples prepared by different method are gathered in Table 2. Starting from these results we can conclude that $K_{sd}3P10-LDH$ presents significant textural properties. Indeed, the value of specific surface area ($80\text{ mg}\cdot\text{g}^{-1}$) is near that obtained for the sample prepared by conventional method. While, $K_{liq}3P10-LDH$ prepared by method 2 has a very weak value of specific surface area.

3.2.4. DSC Study

The DSC curves of the $K_{liq}3P10$ and $K_{sd}3P10$ hydrotalcite prepared by mechanochemical synthesis method and co-precipitation method using kaolinite clay as aluminum

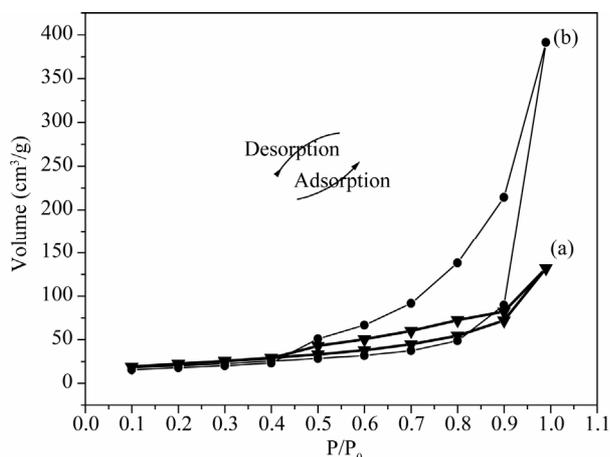


Figure 4. N₂ adsorption-desorption isotherms: (a) *K_{sd}3P10-LDH*; (b) *K_{liq}3P10-LDH*.

Table 2. Textural properties for various sorbent samples.

	<i>K_{sd}3P10</i>		<i>K_{liq}3P10</i>	
	<i>S</i> _{BET} (m ² /g)	<i>V</i> _{macropore} (cm ³ /g)	<i>S</i> _{BET} (m ² /g)	<i>V</i> _{macropore} (cm ³ /g)
Before calcination	80	0.2044	78	0.6052
After calcination	178	-----	165	-----

source are shown in **Figure 5**. Both the DSC profiles exhibited two apparent endothermic events during the thermal decomposition. The first event is at 200°C for *K_{sd}3P10* and at 198°C for *K_{liq}3P10*, the second thermal event is at 410°C for *K_{sd}3P10* and at 361°C for *K_{liq}3P10*. In the first decomposition stage, the crystal water released. And in the second decomposition stage, the hydroxyl (OH⁻) octahedral structure is destroyed; the hydroxyl (OH⁻) and gas of H₂O and CO₃²⁻ anion release, and CO₂, MgO and Al₂O₃ are formed. The second thermal event for *K_{sd}3P10* (410°C) which more larger than for *K_{liq}3P10* (361°C) indicated that the sample prepared by kaolinite clay in natural solid state possessed high thermal stability, this observation can be explained by the presence of SO₂ in the sample.

3.2.5. Memory Effect of Calcined *K_{liq}3P10* and *K_{sd}3P10* Hydrotalcite

The most important characteristic of layered double hydroxides is their ability to reconstruct themselves to their original structure. It has already been reported that Mg-Al hydrotalcites can be reconstructed when the samples are calcined below the temperature at which spinel formation does not take place. **Figures 6** and **7** show the XRD pattern of samples calcined at 500°C. From the pattern it was observed that the layered structure was

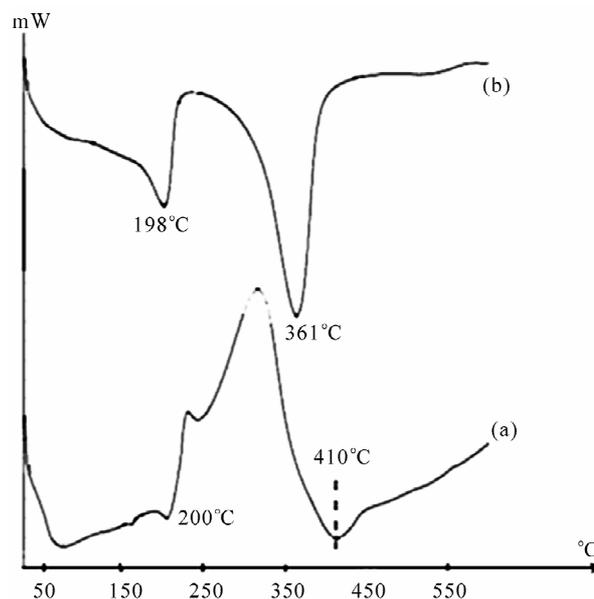


Figure 5. DSC curves of: (a) *K_{sd}3P10-LDH*; (b) *K_{liq}3P10-LDH*.

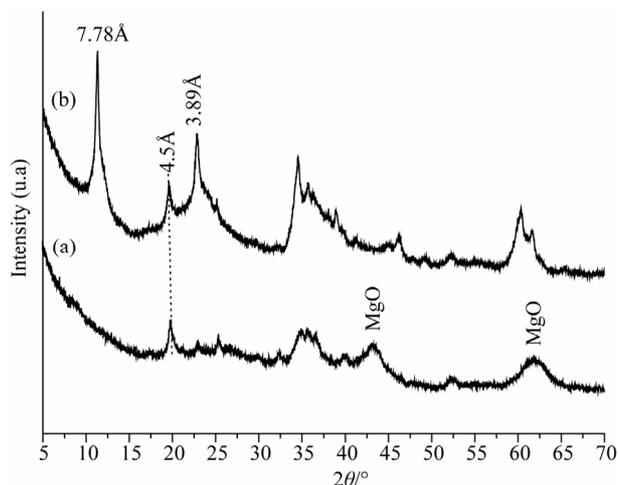


Figure 6. Powder XRD patterns of *K_{sd}3P10-LDH* (a) calcined in air at 500°C; (b) calcined at 500°C and treated in water for 2 days for reconstruction.

completely destroyed, which is clearly indicated by the disappearance of the (003) and (006) peaks at lower 2θ values in the original material (**Figures 1(c)** and **1(d)**).

For *K_{sd}3P10-LDH*, the **Figure 6(a)** shows the presence of a peak at 4.5Å due argillaceous phase, which is present as an impure phase, along with peaks due to MgO. To find out whether the hydrotalcite synthesized from the natural clay could be reconstructed to its original structure, the *K_{sd}3P10-LDH* and *K_{liq}3P10-LDH* samples, which were previously calcined at 500°C, was put in water for 2 days. As shown in **Figure 6(b)** and **Figure 7(b)**, the materials were completely reconstructed to its

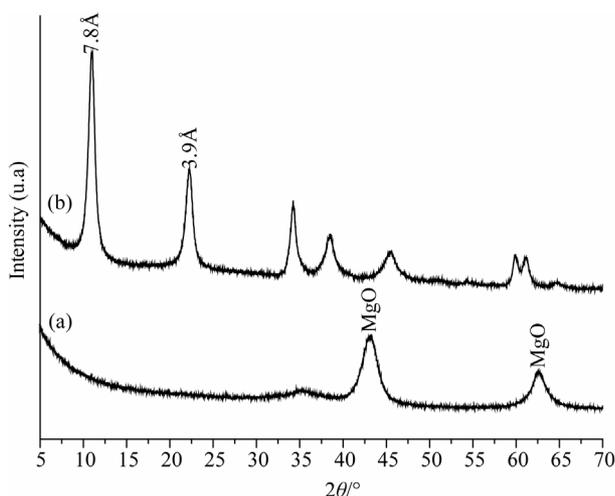


Figure 7. Powder XRD patterns of $K_{lig}3P10-LDH$ (a) calcined in air at $500^{\circ}C$; (b) calcined at $500^{\circ}C$ and treated in water for 2 days for reconstruction.

original layered structure, as indicated by the appearance of the (003) and (006) peaks.

3.3. The Optimisation of the Operating Conditions of Synthesis

3.3.1. The Effect of Mg^{2+}/Al^{3+} Molar Ratio

The XRD patterns of samples prepared by method 1 at different Mg^{2+}/Al^{3+} molar ratio show that no hydrotalcite structure was formed when $R < 3$. From **Figure 8**, well-crystalline LDH was obtained for $Mg^{2+}/Al^{3+} = 3.0$.

From **Figure 9**, it was determined that as the Mg^{2+}/Al^{3+} molar ratio increases, from 0.5 to 4, the intensity of 003 and 006 reflections increases, are corresponding to an increase of the formation of the LDH structure. Well-crystalline LDH was obtained for $Mg^{2+}/Al^{3+} = 1.0$ (**Figure 9**) belong $R = 1$, the intensity of 003 and 006 reflections decreases corresponding to the decreasing in crystallinity.

3.3.2. The Effect of pH of Synthesis

The pH of preparation is important in the formation of all hydrotalcite-type materials and the optimum pH depends on the cations used. From **Figure 10**, it was determined that samples prepared by method 1 and at $pH = 8$ displayed very weak, broad reflections at 2θ value of 11° compared to $K_{sd}3P10-LDH$ and $K_{sd}3P12-LDH$ prepared at $pH = 10$ and 12 respectively (**Figure 10**). The XRD patterns of $K_{sd}3P8$ ($pH = 8$) show that no hydrotalcite structure was formed under these synthesis conditions. The broadness of the reflections indicates that the sample was poorly crystalline; brucite was formed instead of hydrotalcite. Samples prepared within the pH range of 10 - 12 show patterns similar to that of hydrotalcite. The difference between these samples is in the intensity of the

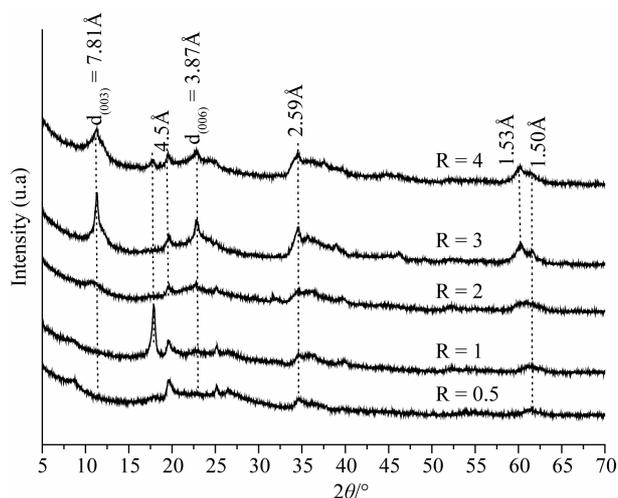


Figure 8. X-ray patterns of clay sample synthesized by method 1 at different Mg^{2+}/Al^{3+} molar ratio.

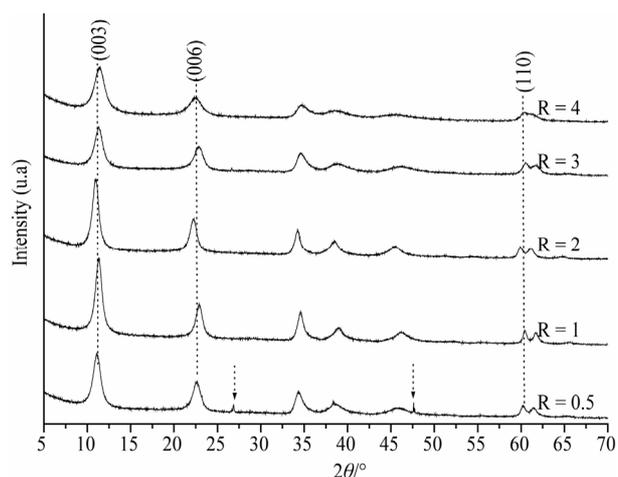


Figure 9. X-ray patterns of clay sample synthesized by method 2 at different R ($R = Mg^{2+}/Al^{3+}$ molar ratio).

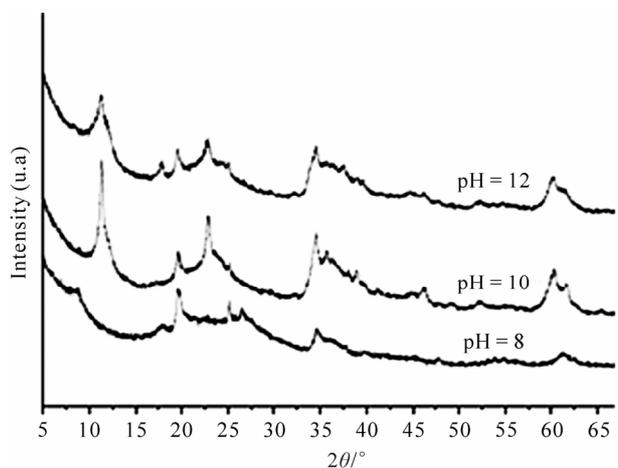


Figure 10. X-ray patterns of clay sample synthesized by method 1 at different pH.

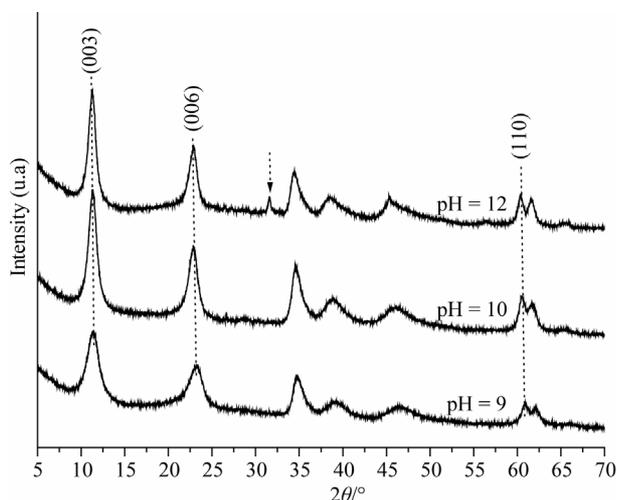


Figure 11. X-ray patterns of clay sample synthesized by method 2 at different pH.

(001) reflections. $K_{sd}3P10$ have the most intense and sharpest reflections, and thus are the most crystalline samples.

Samples prepared by method 2 and at pH = 9 displayed very weak, broad reflections at 2θ value of 11° . The broadness of the reflections indicates that the sample was poorly crystalline. Samples prepared within the pH range of 10 - 12 show patterns similar to that of hydrotalcite. The difference between these samples is in the intensity of the (00 l) reflections. The $K_{liq}3P10$ has the most intense and sharpest reflections. $K_{liq}3P12$ (pH = 12) shows a structure different from the previous samples; it was contaminated with $Al(OH)_2$.

4. Conclusions

Pure and well-crystalline phases of Mg-Al- CO_3 LDH can be prepared by coprecipitation and by mechano-chemical synthesis method from the cationic clay (the kaolinite) using an aqueous solution of Na_2CO_3 as a precipitant.

The pH of preparation was an important factor. At pH = 10 well-crystalline LDH was formed. Below this value, the crystallinity of the LDH decreased. Strong alkaline conditions seem no favourable for the synthesis. The optimum values of Mg^{2+}/Al^{3+} molar ratio depend of the method of synthesise. It was about 3 for synthesise by the method 1 and about 1 for the method 2. Below these ratios poorly crystalline products were obtained.

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