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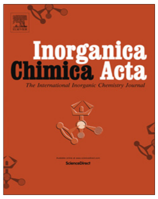

Synthesis of magnesium–aluminum layered double hydroxide intercalated with ethylene glycol by the aid of alkoxides

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ABSTRACT

Ethylene glycol (EG) intercalated magnesium–aluminum layered double hydroxide (LDH) was synthesized via ion exchange method under mild conditions by the aid of alkoxides. Nitrate LDH and EG were used as precursor and solvent, respectively, and alkoxides including sodium methoxide, sodium ethoxide and potassium tert-butoxide were used to facilitate the deprotonation of EG. It is found that potassium tert-butoxide shows superior promotion effect due to its strong ability to capture proton. The effects of synthesis temperature and time on EG intercalated LDH were investigated. EG intercalated LDH can be synthesized at 80 °C for 12 h or at 120 °C for 6 h. The characterization results of XRD, TG–DSC, FT-IR, elemental analysis, ^{13}C NMR and Hammett indicator and benzene carboxylic acid titration confirm the successful intercalation of EG in LDH.

1. Introduction

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, are anionic layered clays that consist of positively charged brucite-like layers and interlayer compensating anions. LDHs can be represented by the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot yH_2O$, where M^{II} and M^{III} are divalent and trivalent metal cations, respectively, and A^{n-} is a counter anion [1–4]. Due to their interesting properties such as anion mobility, anion exchange, surface basicity and reconstruction behavior, LDHs have attracted widespread attentions and been successfully applied as adsorbents, catalysts, ion exchange hosts, fire retardant additives, nano-composites, drug delivery hosts, and cement additives [5]. Intercalation of functionalized anions into LDHs through various methods, such as coprecipitation, thermal or melt reaction, ion exchange, acid-base and donor–acceptor reactions [6,7], can further modify the properties of LDHs and expand their applications [8,9].

Recently, some researchers reported the synthesis of ethylene glycol (EG) intercalated materials, such as kaolinite, gibbsite, FeOCl and LDHs [1,4,10–18]. Table 1 summaries the synthesis methods and conditions of EG intercalated materials in the literature. It can be seen that rigorous conditions like high reaction temperature, long reaction time, protection of inert gas or vapor synthesis are required to synthesize EG intercalated materials. In the case of EG intercalated LDH, Guimarães et al. [1] synthesized EG intercalated Zn–Al LDH using carbonate Zn–Al LDH as precursor and EG as media at 80 °C for 5 days. Stanimirova et al. [17] synthesized EG intercalated Mg–Al LDH with carbonate Mg–Al LDH and its low temperature intermediate phases as precursors and the intercalation process was performed over EG vapor at 80 °C for 30 h or in liquid EG at 80 °C for 5 days. They found that the LDHs with Mg:Al ratios of 3:1 and 4:1 could be intercalated by EG but that with 2:1 ratio failed. As a very weak acid, EG molecule is difficult to lose its proton to convert into anion, which is considered as a key factor inhibiting EG from entering the interlayer through ion exchange. Xi et al. [4] used sodium methoxide/methanol solution to intercalate EG into yttrium hydroxide layered materials. They suggested that the formation of EG anions was accomplished by a proton transfer between methoxide anion and EG, which induces EG entering the interlayer of yttrium hydroxide. However, the intercalation process was carried out at 140 °C for 20 h. It is expected that alkoxides may help the deprotonation of EG and promote EG anions intercalating into LDH under mild conditions, such as lower temperature, shorter time or without inert gas protection. To our knowledge, the synthesis of EG intercalated LDH with the aid of alkoxides has been seldom reported.

In this work, EG intercalated Mg–Al LDH (MA-EG) was synthesized via ion exchange under mild conditions by using nitrate Mg–Al LDH (MA-NO_3) as precursor and EG as media and with the aid of alkoxides. The effects of alkoxides, synthesis temperature and time on the structure of MA-EG were investigated, and the property of the resulting LDH was characterized.

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Table 1
The synthesis methods and conditions of EG intercalated materials reported in the literature.

Precursor	Temperature (°C)	Time (h)	Media	Method	References
FeOCl(4-aminopyridin)$_{1/4}$	110	168	4-aminopyridin	mixed in glass vessel	[10]
Gibbsite	250	2	EG	mixed in Pyrex glass and placed in autoclave under N_2 protection	[11]
Kaolinite	140–190	72	dimethylsulfoxide	mixed in glass vessel	[13]
Kaolinite–dimethylsulfoxide		16	EG-water	mixed under N_2 protection	[12]
Gibbsite	250–300	2	EG	mixed in Pyrex glass and placed in autoclave	[14]
Zn–Al CO_3 LDHs	80	120	EG	mixed in glass vessel	[1]
$Mg(OH)_2$	150	24	EG	mixed in glass vessel	[15]
Layered basic zinc acetate film	room temperature	48	EG	mixed in glass vessel	[16]
Mg–Al CO_3 LDHs	80	30 (vapor) 120 (liquid)	EG (vapor or liquid)	mixed in glass vessel	[17]
Kaolinite–potassium acetate	65	>504	EG	mixed without air	[18]
Yttrium hydroxide	140	20	sodium methoxide/methanol	mixed in autoclave	[4]

2. Experimental

2.1. Synthesis of MA-EG

MA-NO_3 (Mg/Al = 2) was synthesized as the following steps. Firstly, magnesium nitrate hexahydrate (17.15 g) and aluminum nitrate nonahydrate (12.37 g) were dissolved in water. Secondly, a base solution was obtained by dissolving sodium hydroxide (8.00 g) in water. Thirdly, the above two solutions were mixed dropwise in a beaker under vigorous stirring at 40 °C and the pH of the mixture was adjusted to 8 by controlling the adding rate of solutions. Finally, the resulting slurry was transferred into a Teflon-skinned autoclave and aged at 100 °C for 12 h, then filtered, washed with water and dried at 80 °C for 6 h in vacuum.

MA-EG was prepared from MA-NO_3 via ion exchange. Firstly, MA-NO_3 (1.21 g) was added to a solution of alkoxides (0.1 mol/L) prepared by dissolving sodium methoxide, sodium ethoxide or potassium tert-butoxide (Acros, 98 wt%) in 100 mL EG. Secondly, the mixture was placed in a three-necked flask equipped with a thermometer, stirrer and condenser tube, and then magnetically stirred at the given temperature for the given time in an oil bath. Finally, the product was collected by filtrating, washing with acetone and drying at 80 °C for 6 h in vacuum. It is worth mentioning that the synthesis process was performed under air atmosphere.

2.2. Characterization

X-ray diffraction (XRD) was carried out on a X'Pert Pro diffractometer (Panalytical, Netherlands) equipped with a X'Celerator detector, using Cu Kα radiation and operating at 40 kV and 40 mA. The data were recorded in the scan range of 2θ from 5° to 70° with a 0.02° per step and 12 s at each step. The unit cell parameters a and c represent the average distance between metal ions located in the same brucite-like layer and the thickness of unit cell, respectively [19]. Values of a and c were calculated by the formulae: $a = 2d_{110}$ and $c = 3d_{003}$ [20], where d_{110} and d_{003} are the basal spacing values of (1 1 0) and (0 0 3) planes, respectively.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were carried out on a STA-449F3 (Netzsch, Germany) instrument. About 10 mg sample was loaded in an alumina crucible and heated at a rate of 10 °C/min from 40 to 650 °C in an air flow of 60 mL/min.

Fourier transform infrared spectra (FT-IR) were recorded with a WQ520 spectrophotometer (Beifen, China) using the KBr pellet technique at room temperature. A total of 32 scans were taken for each sample with a resolution of 2 cm^{-1}.

CHON element contents analysis was performed on a Vario EL III (Elementar, Germany) elemental analyzer. Mg and Al contents in hydrotalcites were measured by EDTA titration method.

^{13}C NMR spectra were recorded by a Bruker AV III-400 NMR spectrometer (Bruker, Switzerland). $CDCl_3$ was used as solvent for liquid samples. ^{13}C solid state magic-angle spinning nuclear magnetic resonance (MAS NMR) spectrum was carried on the above spectrometer operating at a frequency of 125.773 MHz for ^{13}C and at a spinning rate of 5000 Hz with a 5 s pulse delay.

The strength and amount of basic sites were determined by non-aqueous Hammett indicator and benzene carboxylic acid titration technique [21,22]. Bromthymol blue ($pK_a = 7.2$), phenolphthalein ($pK_a = 9.3$), 2.4-dinitroaniline ($pK_a = 15.0$) and 4-nitroaniline ($pK_a = 18.4$) were used as indicator, respectively, and H_- was referred as base strength. All the samples were heated at 80 °C for 2 h in vacuum before measurement.

3. Results and discussion

3.1. Effect of alkoxides

To study the effect of alkoxides on synthesis of MA-EG, the reaction was performed at 120 °C for 12 h, using sodium methoxide, sodium ethoxide or potassium tert-butoxide, respectively; the corresponding products were named as MA-EG-SM, MA-EG-SE and MA-EG-PT. Their XRD patterns are shown in Fig. 1, and the values of basal spacing and lattice parameters are given in Table 2.

It is known that EG has lower pK_a (14.77) than methanol (15.54), ethanol (16.00) and tert-butanol (17.00) [23,24]. Therefore, the alcohol exchange reactions probably occur between the alkoxides and EG [25]. Due to the great excess of EG, it is deduced that only one proton is removed from each EG molecule [26]. Furthermore, the reaction temperature (120 °C) is much higher than the boiling points of three alcohol products (methanol 66.0 °C, ethanol 78.4 °C, tert-butanol 82.0 °C), which is beneficial to

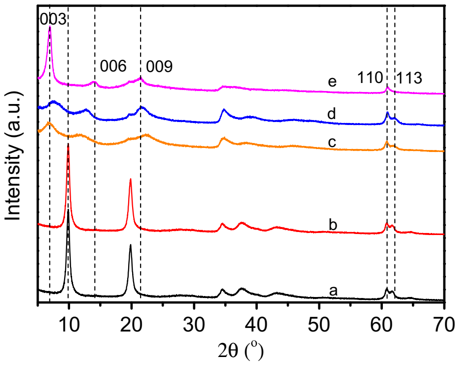

Fig. 1. XRD patterns of the samples synthesized with different alkoxides, (a) MA-NO_3, (b) MA-NO_3 + EG, (c) MA-EG-SM, (d) MA-EG-SE and (e) MA-EG-PT.