



Research paper

Innovative method for hydrocalumite-like compounds' preparation and their evaluation in the transesterification reaction



Manuel Sánchez-Cantú ^{*,1}, Sebastian Camargo-Martínez ¹, Lydia M. Pérez-Díaz ¹, María E. Hernández-Torres ¹, Efraín Rubio-Rosas ¹, Jaime S. Valente ²

Benemérita Universidad Autónoma de Puebla, Facultad de Ingeniería Química, Avenida San Claudio y 18 Sur, C.P. 72570 Puebla, Puebla, Mexico

ARTICLE INFO

Article history:

Received 25 April 2015

Received in revised form 1 July 2015

Accepted 2 July 2015

Available online 10 July 2015

Keywords:

Hydrocalumite

Mayenite

Layered double hydroxide

Transesterification

Biodiesel

ABSTRACT

Hydrocalumite-like compounds (HLCs) were synthesized by a simple, economical and environmentally friendly method. The solids were characterized by X-ray powder diffraction (XRD), thermogravimetric analysis (TGA), nitrogen adsorption–desorption at $-196\text{ }^{\circ}\text{C}$, scanning electron microscopy (SEM) and CO_2 temperature-programmed desorption (CO_2 -TPD). Transesterification of castor oil with methanol was selected as a probe reaction to stress the effect of HLC purity and the presence of distinct anions in the interlayer region.

By X-ray powder diffraction it was demonstrated that by only mixing hydrated lime and boehmite either in deionized or in deionized–decarbonated water, HLCs were obtained as the main crystalline phase, together with hydrogarnet, calcite and calcium hydroxide as secondary crystalline phases, respectively. The effect of the system's pH and of the purity of the calcium source was confirmed by adjusting the pH and using calcium hydroxide; in this way, pure nitrate-intercalated hydrocalumite was obtained after aging for 3 h at $80\text{ }^{\circ}\text{C}$. Although, pure HLCs were effectively synthesized, after their thermal activation all samples (including those where other crystalline phases were detected) presented the same crystalline phases. When the calcined solids were tested as heterogeneous catalysts in the transesterification reaction, the highest conversions were attained with solids with a combination of both weak and strong basic sites, revealing that initial crystalline phase purity is not a requirement to prepare an active catalyst for this reaction.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Layered double hydroxides (LDHs) represent a huge family of materials that exhibit the general formula $[\text{M}^{2+}_{(1-x)}\text{M}^{3+}_x(\text{OH})_2](\text{A}^{n-})_{(x/n)}\cdot m\text{H}_2\text{O}$ where M^{2+} is a divalent cation such as Mg, Cu, and Zn, M^{3+} is a trivalent cation such as Al^{3+} , and Fe^{3+} , A^{n-} represents an anion which resides in the interlayer region and m correspond to the water amount. Their structure resembles that of brucite, where $\text{M}^{2+}(\text{OH})_6$ octahedra share edges to build infinite $\text{M}(\text{OH})_2$ sheets. Thus, an LDH is created by the partial isomorphic substitution of divalent cations for trivalent ones, in which the layered array is positively charged. This charge is electrically balanced by anionic species located in the interlayer region, along with hydration water molecules.

Hydrocalumite (HC) and hydrocalumite-like compounds (HLCs) belong to a branch of the LDH family which has been scarcely reported in the bibliography in comparison with other members of the LDH family such as hydrotalcite. Their general formula is

$[\text{Ca}_2\text{M}^{3+}(\text{OH})_6](\text{A}^{n-})_{(1/n)}\cdot m\text{H}_2\text{O}$, where M^{3+} is generally an Al^{3+} cation. The layered structure is built by the periodical stacking of positively charged $[(\text{Ca}^{2+}, \text{M}^{3+})(\text{OH})_6]$ octahedral layers related to brucite and negatively charged interlayers consisting of anions and water molecules. For hydrocalumite, Ca^{2+} and M^{3+} , fixed in a molar ratio of 2, are seven- and sixfold coordinated, respectively; being the seventh ligand of the Ca-polyhedron, a water molecule from the interlayer.

In recent years, these compounds have been applied successfully as hardening accelerator in concrete (Xu et al., 2009) and other distinct applications which include: aldol condensation (Cota et al., 2010), transesterification (Campos-Molina et al., 2010; Kuwahara et al., 2012; Sankaranarayanan et al., 2012), cycloaddition (Kuwahara and Yamashita, 2013), isomerization (López-Salinas et al., 1996), Meerwein–Ponndorf–Verley reaction (Aramendía et al., 2001; Mora et al., 2010), in situ polymerization of interleaved monomers (Vieille et al., 2004) and intercalation (Plank et al., 2008) reactions. Additionally, HC and HLC materials have been employed in environmental remediation for chloride, nitrate and carbonate (Phillips and Vandeperre, 2011), borate, sulfate, and arsenate (Reardon and Valle, 1997), chromate and phosphate (Qian et al., 2012), Cd^{2+} (Zhang et al., 2013), B, Cr, Mo, and Se (Hang and Reardon, 2003), Zn^{2+} (Liu et al., 2011), perchlorate (Kim et al., 2011), dye (Pereira de Sá et al., 2013); (Zhang et al., 2012a) and organic pollutant (Zhang et al., 2012b) removal.

* Corresponding author.

E-mail address: manuel.sanchez@correo.buap.mx (M. Sánchez-Cantú).

¹ Facultad de Ingeniería Química, Benemérita Universidad Autónoma de Puebla, Mexico.

² Instituto Mexicano del Petróleo, Eje Central #152, C.P. 07730 México, D. F., Mexico.

Due to their growing importance, distinct synthesis methods have been applied in order to prepare HC and HLC, which include: hydrothermal (François et al., 1998; Renaudin and François, 1999; Renaudin et al., 1999), ultrasound (Li et al., 2012; Li et al., 2013), microwave (Pérez-Barrado et al., 2013), sol–gel and homogeneous precipitation with urea (Mora et al., 2010). However, the coprecipitation method is preferred among the others (Rousselot et al., 2002; Vieille et al., 2003; Radha et al., 2005; Segni et al., 2006; Domínguez et al., 2011; Xu et al., 2011). Nevertheless, it is important to recognize that this method requires thermal treatments and prolonged aging times to crystallize HC and HLC, together with intensive washing to eliminate undesirable ions. In this sense, all these issues generate environmental, process and economic drawbacks restricting their large-scale production (Valente et al., 2008, 2009). An alternative is given by the use of raw materials which do not introduce undesirable anions into the process, adjusting the process variables such as pH, aging temperature and time. From this point of view, some researchers have employed synthesis methods and raw materials that do not introduce undesirable anions and, by consequence, do not require purifying steps (François et al., 1998; Renaudin et al., 1999). Another alternative is the use of industrial solid wastes for obtaining HC and HLC (Reardon and Valle, 1997). However, although relatively pure crystalline phases have been obtained, these synthesis procedures were time- and energy-consuming, restricting their large scale production.

In this work, hydrocalumite-like compounds were prepared by a simple, economical and environmentally-friendly method. The methodology employed in this study was very similar to that reported for hydrotalcite-like compound preparation reported by Valente et al. (2008, 2009) where the raw materials are insoluble oxides, and the method is based on dissociation, hydrolysis, and peptization reactions. Materials are obtained under mild conditions and short synthesis times, using a minimal amount of water providing a sustainable method for obtaining LDH. The effect of the water kind, synthesis pH and the calcium source purity was evidenced. The transesterification reaction between castor oil and methanol was used as a probe reaction to elucidate the effect of the material's purity.

2. Experimental section

2.1. Materials

Technical-grade hydrated lime ($\text{Ca}(\text{OH})_2$) and HiQ-10 boehmite (AlOOH) were purchased from Cales Santa Emilia (Mexico) and BASF, respectively. HNO_3 (66.1%), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.4%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.9%) and KOH (85%) were acquired from J. T. Baker, Golden Bell, Fermont and Meyer, correspondingly.

2.2. Synthesis procedures

Pure $\text{Ca}(\text{OH})_2$ was synthesized as follows. First, as received hydrated lime was calcined at for 775 °C for 2 h (the annealing temperature was determined from the TGA results). Then, the sample was rehydrated for 1 h at 60 °C under nitrogen flow and vigorous stirring using decarbonated water. Finally, the sample was filtered and dried at 150 °C for 1 h.

HLCs obtained by coprecipitation were synthesized by the method described elsewhere (Sánchez-Cantú et al., 2013). 75.884 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 60.333 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 417 mL of deionized and decarbonated water (solution A). Separately, a solution containing 58.1 g of KOH in 202 mL of deionized and decarbonated water (solution B) was prepared. A nominal $\text{Ca}^{2+}/\text{Al}^{3+}$ molar ratio of 2 was established. Afterwards, solution A was placed in a glass reactor and solution B was added drop wise into the slurry until a pH of 12 was achieved. The slurry was aged for 6 h at room temperature under vigorous stirring. A helium flow was used to avoid atmospheric CO_2 contamination. The precipitate was washed with hot

deionized and decarbonated water and dried at 60 °C for 3 h. The sample was labeled as CP.

Hydrocalumite-like compounds prepared by the method developed in this work were synthesized as follows: Technical grade hydrated lime, $\text{Ca}(\text{OH})_2$ synthesized as previously described and boehmite were used as calcium and aluminum sources, respectively. The amount of calcium and aluminum sources was fixed in order to achieve a nominal Ca/Al molar ratio of 2. 11.87 g of hydrated lime were dispersed at 5000 rpm for 30 min in 250 mL of water (deionized and/or decarbonated) (A). Separately, 5.44 g of boehmite was dispersed in 300 mL of water at 5000 rpm for 30 min (B). Thereafter, the product resulting from the addition of (A) to (B) was dispersed at 8000 rpm for 30 min (C). Then, the slurry was aged at 80 °C for 3 h with a stirring speed of 300 rpm. After the aging step the solid was filtered and dried at 60 °C overnight. It is worth mentioning that the samples were not washed at any moment. The sample where only deionized water was used was labeled as DI while the compound prepared with deionized and decarbonated water under nitrogen flow was identified as DC.

For the pH-adjusted samples, deionized water and 7 mL of HNO_3 were employed. Before mixing one-half (3.5 mL of HNO_3) was added to (A) and the other one to (B), respectively. Then, the same reaction conditions were followed. The samples were identified as THL and HD where technical-grade hydrated lime or $\text{Ca}(\text{OH})_2$ were used as starting materials, respectively. Table 1 presents sample labels, calcium sources, water kinds and the final pH determined after aging.

2.3. Characterization techniques

The X-ray powder patterns of the fresh and calcined samples at 700 °C were acquired in a Bruker D8 Discover Series 2 diffractometer with $\text{Cu K}\alpha$ radiation. Data were collected in the 2θ range from 5 to 70° with 0.04° step size and a counting time of 0.6 s per point. The crystalline phases were identified by means of the JCPDS (Joint Committee of Powder Diffraction Standards) database. Average crystal sizes were calculated by the Scherrer equation $L = K\lambda / (B(\theta)\cos\theta)$ where L is the average crystal size, K is the shape factor (a value of 0.9 was used), λ is the wavelength of $\text{Cu K}\alpha$ radiation, $B(\theta)$ is the Full Width at Half Maximum (FWHM) and θ is the diffraction angle (Azároff and Buerger, 1958). Cell parameter a was obtained from the reflection located at ~ 31.1 while cell parameter c was acquired from reflections found at 10.2 (CP, HD, THL) and 11.7 (DC and DI) of 2θ , respectively.

Scanning Electron Microscopy (SEM) analysis was carried out in a JEOL JSM-6610 LV with an acceleration voltage of 20 keV. Prior to analysis, the sample was covered with gold and mounted over a carbon film. The images were acquired from secondary electron signals.

Thermogravimetric analyses were carried out using a TGAi 1000 series system which was operated under nitrogen flow at a heating rate of 20 °C min^{-1} from room temperature to 800 °C. In the determination, ~ 20 mg of finely powdered dried sample were used.

Specific surface areas were obtained from N_2 adsorption at -196 °C in a ChemiSorb 2750 (Micromeritics, GA, USA) using the one-point BET method. Prior to the analysis, the calcined samples at 700 °C were degassed for 1 h at 300 °C.

Table 1
Sample labels, calcium sources, water kind and final pH.

Sample label	Calcium precursor	Water kind	Final pH
CP	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	Deionized and decarbonated	11.9
HD	$\text{Ca}(\text{OH})_2$	Deionized	11.3
THL	Technical-grade hydrated lime	Deionized	10.7
DC	Technical-grade hydrated lime	Deionized and decarbonated	12.4
DI	Technical-grade hydrated lime	Deionized	12.2

Download English Version:

<https://daneshyari.com/en/article/1694403>

Download Persian Version:

<https://daneshyari.com/article/1694403>

[Daneshyari.com](https://daneshyari.com)