



Research paper

Exploring an alternative route for meixnerite synthesis. The impact of the gaseous environment on the reconstruction of the lamellar structure and the catalytic performances



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ABSTRACT

This work investigates the possibility to obtain the meixnerite structure $Mg_6Al_2(OH)_{18} \cdot 4H_2O$ in carbonate-free environment by direct co-precipitation of Mg and Al nitrates using only NaOH solution as precipitation agent as well as the physico-chemical and catalytic performances of the mixed oxide (MO) obtained by thermal decomposition of this layered material at 460 °C under nitrogen flow. The influence played by different gaseous environments, air or nitrogen, during the hydration of the above mentioned mixed oxide on the structural characteristics and catalytic performances of the derived reconstructed layered double hydroxide (LDH) materials (RLDH-A and RLDH-N, respectively) is also scrutinized.

The characterization of the solids was performed by chemical and elemental analyses, XRD, DRIFTS, N_2 adsorption–desorption isotherms and adsorption of molecules with different pK_a in order to determine their basicity. The catalytic activity for cyanoethylation was discussed in relation with the structural properties of the catalytic materials.

The results showed that the co-precipitation method employed leads to the formation of an LDH containing also NO_3^- and CO_3^{2-} anions besides HO^- . Also, low amounts of C and N (< 1%) were still present in the derived mixed oxide as well as in the reconstructed layered materials. The use of different gaseous environments, air or nitrogen, during the reconstruction leads to different structural properties which affected the catalytic activity of the solids. It has been noticed that the presence of carbonate anion in the structure of parent LDH-materials as well as that of carbonate low amounts in the LDH-derived mixed oxide improved the ability of the latter to recreate the lamellar structure through memory effect. However this fact is not accompanied by an increase of catalytic activity since the presence of carbonate anions decreases the basicity of the solid. Among the layered materials, the sample reconstructed under nitrogen (RLDH-N) which has a low crystallinity, and hence a larger number of defects, has also the highest number of HO^- base sites and is the most active for catalytic cyanoethylation.

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1. Introduction

The preparation, characterization and utilization of layered double hydroxides (LDH) in different applications have been intensively investigated in the two last decades (Cavani et al., 1991; Rives and Ulibarri, 1999; Vaccari, 1999; Sels et al., 2001; Centi and Perathoner, 2008). LDH-compounds belong to the class of anionic clays (Vaccari, 1999) defined by the formula: $[M^{2+}_1 - xM^{3+x}(OH)_2]^{x+}[A^{n-x/n}]_m \cdot mH_2O$ where A^{n-} is the compensation anion placed in the interlayer space, m is the number of water molecules in the interlayer space

and x is a value in the range of 0.2–0.33 (Sels et al., 2001). The natural occurring forms of these materials include: hydrotalcite $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$; pyroaurite $Mg_6Fe_2(OH)_{16}CO_3 \cdot 4.5H_2O$; takovite $Ni_6Al_2(OH)_{16}CO_3 \cdot OH \cdot 4H_2O$; reevesite $Ni_6Fe_2(OH)_{16}CO_3 \cdot 4H_2O$; coalingite $Mg_{10}Fe_2CO_3(OH)_{24} \cdot 2H_2O$; woodwardite $Cu_4Al_2(OH)_{12}SO_4 \cdot 4H_2O$; iowaite $Mg_4Fe(OH)_{10}Cl \cdot 3H_2O$; or meixnerite $Mg_6Al_2(OH)_{18} \cdot 4H_2O$ (Cavani et al., 1991). Typical hydrotalcites with carbonate compensation anions can be prepared by methods such as: co-precipitation at variable or constant pH, under low or high supersaturation conditions, co-precipitation using urea, sol–gel technique or hydrothermal synthesis (Cavani et al., 1991).

The synthesis of the meixnerite is rather difficult since this type of compound has only HO^- as compensating anion. The first methods

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employed for the synthesis of meixnerite were based on the hydrothermal treatment of physical mixtures of magnesium and aluminum oxides and water (Mascolo and Marino, 1980; Pausch et al., 1986; Martin et al., 1996).

Another type of method for the synthesis of meixnerite is based on the hydration of MgAl(O) mixed oxides under CO₂-free conditions and was first investigated by Dimotakis and Pinnavaia (Dimotakis and Pinnavaia, 1990). The method is based on the so called “memory effect”, which is a peculiar property of the hydrotalcite-like materials allowing the reconstruction of the original structure upon the contact of their dehydrated form with water or aqueous solutions containing various anions (Cavani et al., 1991; Vaccari, 1999). Different authors explained this effect considering either a retro-topotactic process involving Al³⁺ and bivalent cations both located in the octahedral sites of the mixed oxides (Marchi and Apesteguia, 1998) or a dissolution–recrystallization (Takehira et al., 2005) process. This type of approach was further developed and made the subject of several patents after 1995 (Martin and Pearson, 1996; Easley, 1997; Easley and Horn, 1998).

Recently three other methods were reported for the synthesis of meixnerite, but none of those made the subject of an extended application. In 2007 Tongamp (Tongamp et al., 2007) developed a two step mechanochemical method which allows the obtaining of meixnerite at ambient conditions after the dry milling of a mixture of magnesium and aluminum hydroxides followed by the wet milling of the resulted mixture with water. In 2010 Yazici and Yilmaz (Yazici and Yilmaz, 2010) reported the synthesis of meixnerite by a sol gel method using aluminum-isopropoxide and magnesium-chloride-hexahydrate as starting materials, while Hidalgo and co-workers (Hidalgo et al., 2010) reported the preparation of meixnerite nanolayers via a combined delamination–ion exchange process using Mg/Al HTLCs containing dodecylbenzenesulfonate (DBS) anion in the interlayer region which was submitted to a procedure involving sonication and swelling of the interlayer region in the presence of 1-butanol as solvent.

However, despite all the precautions taken during the preparation, none of the above presented methods allowed the obtaining of a carbonate free meixnerite material. The synthesis of meixnerite presents a practical interest since this material is known to be a good catalyst for base catalyzed reaction such as aldol condensations (Tichit et al., 1999; Prinetto et al., 2000; Abelló et al., 2007, 2008) and cyanoethylation of alcohols (Valente et al., 2011) as well as a good adsorbent for CO₂ (Tongamp et al., 2007), NO_x, SO_x (Pinnavaia and Amarasekera, 1994), F anions from water (Guo and Reardon, 2012), etc. Also, the meixnerite obtained by the rehydration of calcined hydrotalcites, both in powder form (Navajas et al., 2010) and as a structured catalyst (Reyero et al., 2013), has been reported as active catalysts for biodiesel production by transesterification of triglycerides with methanol.

Taking into account the limitations of the data published so far concerning meixnerite synthesis, this work aims the investigation of the following aspects:

- i) the possibility to obtain meixnerite-type LDH by precipitation under low supersaturation conditions at pH 10 similarly to the preparation of the common Mg/Al hydrotalcite
- ii) the comparison between the meixnerite-type structure formed by precipitation and the one obtained by the hydration of mixed oxides derived from a common hydrotalcite precursor
- iii) the influence of the gaseous environment on the reconstruction of the layered structure during the hydration with decarbonated water of the mixed oxides derived from the precipitated meixnerite-type LDH.

The catalytic performances of the solids will be assessed by means of the base catalyzed cyanoethylation of ethanol by acrylonitrile since this is a simple application which yields only beta-ethoxypropionitrile as a reaction product (Bırjega et al., 2005; Pavel et al., 2008, 2010). This

valuable product can be converted to a carboxylic acid by hydrolysis and into the corresponding amine by reduction, giving compounds of industrial interest for drug intermediates (Kumbhar et al., 1998; Chaphekar and Samant, 2003).

2. Experimental

2.1. Catalyst preparation and thermal treatments

The LDH-meixnerite Mg₆Al₂(OH)₁₈·4H₂O was prepared under nitrogen inside of a glove box in order to protect the sample from contamination by CO₂ from air. The preparation involved the co-precipitation under low supersaturation conditions at pH 10, adapting a method published earlier (Bırjega et al., 2005; Pavel et al., 2008, 2010) for the synthesis of hydrotalcites with Mg/Al = 3 atomic ratio. For this purpose, two solutions were used: (A) a nitrate solution consisting of appropriate amounts of Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O (Merck reagents p.a.) dissolved in decarbonated water in order to reach a concentration of cations (Mg + Al) of 1.5 M with the Mg/Al = 3 atomic ratio and (B) a solution of NaOH with a concentration of 1 M in order to maintain the pH value at 10. During co-precipitation under vigorous stirring at room temperature, solution (A) was fed into the precipitation vessel with a constant flow rate of 60 mL·h⁻¹ concomitantly with solution (B) whose flow rate was adjusted in order to maintain the constant value of pH at 10. Inside the glove box, the resulting gel was aged in the mother liquor at 75 °C for 18 h, then cooled to room temperature, separated by filtration and finally washed several times with decarbonated water until the value pH = 7 was reached. The solid recovered by filtration was dried in nitrogen at 90 °C for 24 h and denoted LDH. Sample LDH was thermally decomposed in nitrogen flow at 460 °C for 18 h to obtain a sample denoted MO, containing the mixed oxides. Sample MO was then hydrated by immersion in decarbonated water for 24 h at room temperature followed by drying at 90 °C for 24 h either in atmospheric air or nitrogen (purity of 99.999%). Depending on the nature of the gaseous environment during the drying step, the two reconstructed layered materials obtained were named RLDH-A (reconstruction in atmospheric air.), and RLDH-N (reconstruction in nitrogen), respectively.

In order to compare the meixnerite-type structures obtained by the precipitation (LDH) and hydration of hydrotalcite-derived mixed oxides, a standard sample of meixnerite denoted MxHT-hy was prepared in carbonate-free conditions by the hydration of the mixed oxides derived from the thermal decomposition at 460 °C of the typical hydrotalcite Mg₃Al-CO₃.

In order to check the role played by carbonate anions in the reconstruction of the layered structure, 1 g of mixed oxides obtained by the thermal decomposition of the typical hydrotalcite Mg₃Al-CO₃ was left in contact with atmospheric air for 6 months yielding the sample HT-hy-6.

2.2. Catalyst characterization

The catalysts were characterized by chemical and elemental analyses. The determination of the metal content was performed by Atomic Absorption Spectrometry on Pye-Unicam AAS Spectrometer. N, H and C were determined by elemental analysis on Carlo Erba automatic analyzer.

Powder X-ray diffraction patterns were recorded with a Shimadzu XRD 7000 diffractometer using Cu Kα radiation (λ = 1.5418 Å, 40 kV, 40 mA) at a scanning speed of 0.10° min⁻¹ in the 7–70° 2θ range.

DRIFTS spectra obtained from the accumulation of 400 scans in the domain 400–4000 cm⁻¹ were recorded with NICOLET4700 spectrometer.

N₂ adsorption–desorption isotherms were determined using Micromeritics ASAP 2010 instrument. Prior to nitrogen adsorption, samples were out gassed under vacuum for 24 h.

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