



# Phosphoric acid intercalated Mg–Al hydrotalcite-like compounds for catalytic carboxylation reaction of methanol in a continuous system

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## ABSTRACT

Mg–Al-hydrotalcite-like catalysts (HTLcs) with different amount of P/Mg molar ratio were prepared via co-precipitation method and calcined at 450 °C. The synthesized catalysts were tested in the direct-carboxylation reaction of methanol in gas phase in a continuous system such as chemical route for CO<sub>2</sub> valorization. Activities around 2% with total selectivity towards the dimethyl carbonate (DMC) was obtained at moderate temperatures (150 °C) with both Mg/Al mixed oxides (HTO) and phosphated Mg/Al mixed oxides (HTc-9c). Even though the conversion increased until 16% at higher temperatures (200 °C), the selectivity with both catalysts (HTO and HTc-9c) decreased due to the decomposition of DMC to dimethyl ether (DME). Nevertheless, the catalyst with P showed less DMC decomposition and a higher selectivity towards the desired product. This is explained by the presence of orthophosphate species bonded to the Al<sup>3+</sup> metals of the HTs (O–P(OAl)<sub>3</sub>) which give to the catalyst a higher structural stability and specific acid properties.

In addition, the solids were characterized in-depth by XRD, ICP, NH<sub>3</sub>-TPD, FTIR, Raman, <sup>27</sup>Al and <sup>31</sup>P MAS NMR spectroscopy and SEM.

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## 1. Introduction

Hydrotalcite-like compounds (HTLcs) are layered double hydroxides (LDHs) also known as anionic clays and have the general formula  $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}[A^{n-}]_{x/n} \cdot y\text{H}_2\text{O}$ , where M<sup>2+</sup> and M<sup>3+</sup> are di- and tri-valent metal cations, respectively, A<sup>n-</sup> is a charge-balancing anion, and x is the molar ratio M<sup>3+</sup>/(M<sup>3+</sup> + M<sup>2+</sup>) ranging from 0.1 to 0.5. Although, the x ratio of a pure hydrotalcite phase ranges from 0.17 to 0.33 [1]. The structure consists of brucite-like layers [Mg(OH)<sub>2</sub>] with an edge-sharing hydroxyl octahedral occupied by metal M<sup>2+</sup>. Some di-valent cations in hydrotalcites are isomorphically substituted by tri-valent ones. The positive charge generated on the layers is balanced by anions located in

the interlayer alongside water molecules. Hydrotalcites are usually prepared by co-precipitation from metal salts in alkaline media at constant pH followed by a hydrothermal treatment of the precipitate. The usual activation protocol for these materials is a controlled thermal decomposition that leads to the formation of mixed oxides with a good dispersion of metals, a large specific surface area and Lewis basic properties. The rehydration of calcined hydrotalcite under a CO<sub>2</sub> free atmosphere allows the recovery of a layered structure that interlayer anions made of OH<sup>-</sup> and therefore very good Brønsted basic properties [2].

The literature shows the capacity of hydrotalcite-like compounds to adsorb or intercalate phosphates and phosphoric acid derivatives. For example, Hayashi et al. were able to synthesize Al–Mg hydrotalcites with intercalated phosphate ions from Cl-intercalated Al–Mg hydrotalcites due to the large ion-exchange capacity of hydrotalcites [3,4]. Parida et al. studied the ability of Cl-intercalated Mg–Al hydrotalcites to adsorb phosphates. They concluded that these hydrotalcites can be used as an effective adsorbent for removing phosphates from aqueous solutions with a maximum loading capacity of 44 mg of phosphate/g HTLcs and that the competing anions in solution had a strong effect on phosphate

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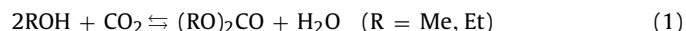
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adsorption [5]. Calcinating the hydrotalcite-like compound also increased its phosphate adsorption capacity. This is attributed to the following physicochemical properties of the calcined hydrotalcite: (i) the memory effect of the hydrotalcite layers, which allow phosphates to be incorporated as an interlayer anion, (ii) the greater surface area, which allows higher surface adsorption of the phosphates, and (iii) the elimination of the interlayer carbonate, which is the major obstacle to the incorporation of the phosphates as an interlayer anion [6]. Recently, Parida et al. have prepared new materials based on molybdophosphoric and tungstophosphoric acid intercalated in Zr/Al-hydrotalcite-like compounds by co-precipitation using an indirect method based on the terephthalic acid intercalated Zr/Al hydrotalcite as precursor [7].

The synthesis of dimethyl carbonate (DMC) by carboxylation reaction is a very interesting catalytic process since DMC is a safe, non-corrosive, and environmentally acceptable alternative to methylating and carbonylating agents [8]. Nowadays, industrial scale DMC synthesis is based on the oxidative carbonylation of MeOH by means of phosgene-free technologies. However, the reactant mixture used in this process is highly flammable and toxic; consequently, DMC synthesis using CO<sub>2</sub> represents an eco-friendly and economic alternative. Moreover, DMC has been proposed for use as an octane booster in gasoline and as an additive to diesel fuel to decrease particulate matter emissions [9].

The advantages of heterogeneous catalysts over their homogeneous counterparts mean they are preferred by the chemical industry [9]. Recently, it has been reported that DMC can be synthesized selectively and directly from CH<sub>3</sub>OH and CO<sub>2</sub> in the presence of CeO<sub>2</sub> [10] and ZrO<sub>2</sub> [11] as heterogeneous catalysts in a batch reactor with a conversion of around 1%. The results of the catalyst characterization suggest that the acid–base bifunction is an important factor for a selective DMC synthesis. In this context, the LDH materials, especially Mg(Al)O mixed oxides, are potential candidates for use as successful heterogeneous catalysts in this reaction.

Developing a more active direct heterogeneous reaction between CO<sub>2</sub> and the alcohols MeOH and EtOH in order to synthesize the carbonic acid diesters dimethyl carbonate or diethyl carbonate (DEC) (Eq. (1)) is a very attractive prospect in terms of CO<sub>2</sub> chemical fixation and green chemistry, and may also help to further the substitution of phosgene for CO<sub>2</sub> [12]. Therefore, it is worthwhile exploring new ways to valorize CO<sub>2</sub> by generating fine chemicals such as carbonates.



The keys for achieving this aim are the design and development of an efficient process with a success catalyst. For the catalyst, the challenge remains to develop easy, environmentally friendly and versatile methods for the synthesis of layered double hydrotalcites with tuneable morphology, textures, chemical compositions and desirable acid and basic properties. Furthermore, obtaining an in-depth characterization and understanding of the properties of phosphate intercalated HTLcs is critical for their practical use as catalysts and it will help to avoid the trial-and-error practice. On the other hand, the process design should facilitate displacing equilibrium to DMC.

In this context, the current study describes the synthesis by co-precipitation of hierarchical Mg–Al HTLcs containing phosphates. The solids were characterized by NH<sub>3</sub> TPD, elemental analysis and Raman, IR and NMR spectroscopies. Furthermore, to the best of our knowledge, the present work also describes for the first time the use of hydrotalcite-like materials as heterogeneous catalyst in the carboxylation reaction of methanol using a continuous reactor. The preliminary results obtained in this work have slightly improved with respect to the described in the literature. In addition, they are in the direction of designing more-efficient heterogeneous catalysts and reaction systems for CO<sub>2</sub> valorization as a potential

source of economic and environmental benefits for the industry and the society.

## 2. Experimental

### 2.1. Catalyst preparation

All chemicals used for synthesis were purchased from Fluka or Merck.

The hydrotalcite-like materials were obtained by the co-precipitation method, which involved either the simultaneous addition of de-carbonated MgCl<sub>2</sub>·6H<sub>2</sub>O and AlCl<sub>3</sub>·9H<sub>2</sub>O solutions (Table 1, entries 1–6); or Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Table 1, entries 7–9) in a molar ratio of Al/(Al + Mg) = 0.25. The pH was controlled by the simultaneous addition of 2 M NaOH solution. Both solutions were mixed under vigorous stirring. A 0.1 M Na<sub>2</sub>HPO<sub>4</sub> solution was added during the synthesis to incorporate the phosphates species in the interlayer space of the HTLc materials. The reactants were added under inert atmosphere to prevent carbonate species from entering the interlayer space of the HTLcs. After the precipitation, the resulting gel was maintained under a vigorous agitation at 80 °C for 18 h. The precipitated solid was filtered and washed several times with decarbonated water to remove the excess ions and dried at 100 °C to yield the different materials. The experimental conditions for the synthesis of the different samples are presented in Table 1.

### 2.2. Catalyst characterization

The crystallographic characterization of the different samples was performed by X-ray powder diffraction (XRD). Diffraction patterns of intensity versus two theta (2θ) were recorded with a Phillips XRD 1050/70 X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å). Mg, Al, Cl and P analyses were performed by inductive coupled plasma (ICP) using a Perkin Elmer 3300 instrument. The carbon analysis was performed using a Bernard Calcimeter. The presence of nitrate ions was determined by ionic chromatography of the NE-ENIS 10304-1-1995 type.

FTIR spectra of the samples were recorded in a Perkin Elmer spectrum BX, averaging 100 scans with a nominal resolution of 4 cm<sup>-1</sup>. The Raman spectra were measured using a Renishaw Raman imaging microscope system 2000, with laser excitation at 785 nm in the range between 100 and 4000 cm<sup>-1</sup> (resolution 2 cm<sup>-1</sup>). <sup>27</sup>Al NMR and <sup>31</sup>P NMR spectra were recorded at ambient temperature on Varian Mercury V-400 spectrometer using 7 mm CPMAS probes. The resonance frequencies were 162 and 149 MHz for <sup>31</sup>P and <sup>27</sup>Al, respectively.

Specific surface areas of the samples were determined by nitrogen adsorption at –196 °C using a Micromeritics ASAP 2000 equipment. Samples were previously degassed in situ at 120 °C under vacuum for 4 h. The surface area of the catalysts was calculated using the Brunauer–Emmet–Teller (BET) method over a *p/p*<sub>0</sub> range where linear relationship was maintained.

Morphological features of the HTLcs samples were studied using a scanning electron microscope (SEM, model: JEOL model JSM-6400). For the preparation of the samples for SEM, the powdered materials were first spread on sample buttons using conducting cement and then sputtered with gold. The acidity measurements were determined by the temperature programmed desorption (TPD) of NH<sub>3</sub>, on a Thermo Finnigan TPDR0 1100 equipped with a TCD detector. Typically, ca. 0.200 g of sample were pretreated with Ar at 80 °C during 1 h and then cooled to room temperature and treated NH<sub>3</sub> flow (5% NH<sub>3</sub> in He). The desorption of NH<sub>3</sub> were measured heating the sample from room temperature to 700 °C and at heating rate of 10 °C/min in He flow (20 ml/min). The water

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