



# Comparative study of physico-chemical properties of laboratory and industrially prepared layered double hydroxides and their behavior in aldol condensation of furfural and acetone



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## ABSTRACT

In this article, properties of laboratory and industrially prepared Mg–Al layered double hydroxides (LDH) with Mg:Al molar ratios varied in the range from 2 to 4 were compared. Physico-chemical properties of the studied materials were investigated with XRD, SEM, N<sub>2</sub> physisorption, TGA and CO<sub>2</sub>-TPD methods. Catalytic behavior of the LDH samples was examined in the liquid phase aldol condensation of furfural and acetone at 20 and 60 °C. It was found that LDH from the small-scale preparation have different physico-chemical characteristics than the LDH materials originating from the large-scale (industrial) preparation which is also reflected in their catalytic behavior. As-synthesized laboratory LDH catalysts are phase-pure crystalline samples with hydrotalcite structure while the industrial materials also possess MgO as admixture. The laboratory samples possess larger BET surface area and mesopore volume in comparison with the industrially prepared ones. Despite the similarity in basic properties of the studied materials, the samples with molar ratio Mg:Al = 3 in both groups of LDH using different method of preparation possess the best activity in aldol condensation. Generally, the calcined laboratory samples are more active than the industrial materials in the reaction. This is explained by the better textural properties of the former ones and their susceptibility to in-situ reconstruction in the presence of water formed during the reaction.

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## 1. Introduction

Layered double hydroxides (LDH) are formed by substitution of atoms of the matrix crystalline framework on atoms of elements with different valence. Among them, hydrotalcites (HTC) are mostly known, which possess a brucite-like [Mg(OH)<sub>2</sub>] network wherein isomorphous substitution of Mg<sup>2+</sup> ion by a trivalent cation M<sup>3+</sup> occurs and the excess positive charge is compensated by anions which are located in the interlayer along with water molecules. Consequently, they exhibit basic properties and could be used in a number of reactions of organic synthesis, including C–C bond formation, isomerization, cyclization, etc. [1–4].

Synthesis of fine chemicals from biomass by heterogeneously catalyzed reactions is a recent topic of great importance particularly in the view of the finite reserves of fossil resources and

the connected adverse environmental impacts of the use of these non-renewable resources [5,6]. Among them, aldol condensation is an important reaction as it allows obtaining compounds with larger number of C atoms starting from simple organic molecules [1,7,8] that are typical intermediates in biomass processing. Moreover, it makes possible the evaluation of the catalysts from the viewpoint of the peculiarities of their physicochemical characteristics. As a result, the attention is focused on the search of efficient catalysts for aldol condensation due to the prospect of creating new technologies for the synthesis of fine chemicals, pharmaceuticals, plasticizers and fragrances from renewable chemicals [3,9,10]. Until now the industrial aldol condensation technologies rely on the use of NaOH as a catalyst, which results in high operation costs and serious environmental problems [11,12]. Hence, the development of basic heterogeneous catalysts, for example HTC, for this field is essential. A lot of publications accessible in open literature deal with different methods of preparation of HTC materials on laboratory scale [13–16], as well as with study of their physico-chemical and catalytic properties [17,18]. Nevertheless,

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an objective assessment of the prospects of a new technology is hardly possible without estimation of the possibility to move from the laboratory synthesis of catalysts to the large-scale industrial preparation. However, publications on comparing the properties of laboratory and industrially prepared HTC samples in aldol condensation are missing. Therefore, the main objective of the present study is to provide information about differences between laboratory and industrially prepared hydrotalcites with respect to their physico-chemical and catalytic properties. Both groups of the materials were characterized by a number of methods (XRD, N<sub>2</sub> physisorption, ICP, TGA, CO<sub>2</sub>-TPD and SEM). Their catalytic properties were compared in aldol condensation of furfural and acetone which was chosen as a commonly used test reaction for evaluating basic properties of solids.

## 2. Experimental

### 2.1. Preparation of the samples

#### 2.1.1. Preparation of catalysts precursor

Industrially prepared Mg–Al hydrotalcites with Mg/Al molar ratio ranging from 2:1 to 4:1 were provided by Eurosupport Manufacturing Czechia (ESMC) as dried samples at temperature 150 °C. They were denoted HTC Mg/Al molar ratio-I; e.g. HTC 3:1-I denotes industrially prepared hydrotalcite sample having Mg/Al molar ratio equal approximately to 3:1.

Laboratory prepared Mg–Al hydrotalcites with Mg/Al the same molar ratio ranging from 2:1 to 4:1 were synthesized by coprecipitation at constant pH value. They were denoted HTC Mg/Al molar ratio-L; e.g. HTC 3:1-L denotes laboratory prepared hydrotalcite sample having Mg/Al molar ratio equal approximately to 3:1. The preparation procedure involves mixing of an aqueous solution of magnesium nitrate Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, p.a. (Lach-Ner) and aluminum nitrate Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, p.a. (Lach-Ner), solution A, and a basic solution of potassium carbonate K<sub>2</sub>CO<sub>3</sub>, p.a. (Lachema) and potassium hydroxide KOH, p.a. (Lach-Ner), solution B. Solution A contained always the same concentration of Mg(NO<sub>3</sub>)<sub>2</sub> 8.2 wt% and the appropriate amount of Al(NO<sub>3</sub>)<sub>3</sub> in order to obtain hydrotalcite with the desired Mg/Al molar ratio. Solution B used as precipitation agent was prepared by dissolving relevant amount of K<sub>2</sub>CO<sub>3</sub> and KOH in order to obtain content 5.9 wt% of K<sub>2</sub>CO<sub>3</sub> and 14.4 wt% of KOH.

In the synthesis procedure, 500 ml of demineralized water was placed in a 4000 ml baker and heated to temperature 60 °C. This temperature was stayed constant for the duration of the precipitation procedure. Solution A was dropped via membrane pump (STEPDOS FEM 08) into the baker under vigorous stirring. Flow rate of solution A was 10 ml per minute. At the same time, solution B was added into the baker via membrane pump (KNF Liquidport NF 100 FT.18RC) connected with pH controller (OMEGA INF3PH PHCH-37) which set up flow rate of solution B for constant pH value 9.5 maintaining.

After that, the obtained suspension was stirred at 60 °C for 1 h. Then the solid LDH was separated by filtration, washed with demineralized water and dried at temperature 60 °C for 12 h.

#### 2.1.2. Catalyst activation

The following calcination procedure was applied to transform the as supplied LDH materials into catalysts. As-prepared LDH materials were calcined at 450 °C in air and mixed Mg–Al oxide catalysts were obtained. The temperature during calcination was raised at the rate of 5 °C/min to reach 450 °C and maintained for 16 h. The calcined mixed oxides were used as catalysts in aldol condensation reaction directly.

### 2.2. Physico-chemical methods

The crystallographic structures of dried LDH catalysts were determined by X-ray powder diffraction using a Philips MPD 1880, working with the Cu-K<sub>α</sub> line (λ = 0.154 nm) in the 2θ range of 5–70° at a scanning rate of 2θ of 2.4°/min. The size and shape of hydroxide crystals were determined by scanning electron microscopy (Jeol, JSM-5500LV). The elemental composition was determined by ICP-OES equipment (HPST, Agilent 725). The textural properties of the catalysts (specific surface area and pore volume) were measured by nitrogen physisorption at 77 K using a Micromeritics TRISTAR 3000 surface area and porosity analyzer. Thermogravimetric analysis (TGA) of dried LDH catalysts were obtained using a TA Instruments TGA Discovery series operating at heating ramp 10 °C/min from room temperature to 900 °C in flowing of nitrogen (20 ml/min, Linde 5.0). Approximately 15 mg of sample was heated in an open alumina crucible.

Temperature programmed desorption of carbon dioxide as probe molecule (TPD-CO<sub>2</sub>) was carried out on AutoChem equipped with a TPD detector and mass spectrometry using quadrupole spectrometer (MS OmniStar). Approximately 100 mg of catalyst (grain of 0.25–0.5 mm) was placed in quartz reactor. Before TPD experiments the catalysts were outgassed at 450 °C for 4 h in a flow of helium. Subsequently the catalysts were cooled down to 0 °C and treated with a CO<sub>2</sub> flow (99% purity) for 30 min. Weakly adsorbed CO<sub>2</sub> was removed by flushing with He at 0 °C for 30 min. The desorption of CO<sub>2</sub> was measured by heating the catalyst from 0 to 900 °C at a heating rate of 10 °C/min in He flow. The desorbed products were analyzed by mass spectrometry. The number of basic sites was calculated from the CO<sub>2</sub> peaks (the molecular ion, *m/z* = 44) with help of calibration using a known amount of CO<sub>2</sub> desorbed from CaCO<sub>3</sub> [19].

### 2.3. Reaction studies

The experiments were carried out in a 100 ml stirred batch reactor (a glass flask reactor) at temperatures 20 and 50 °C. Before the start of an experiment, 2 g of catalyst was mixed together with a stirred mixture of 39.5 g acetone and 6.5 g furfural (acetone/furfural molar ratio 10:1, dried with molecular sieve 3A, pre-heated to the desired reaction temperature) and kept at this temperature for 6 h under intensive stirring. Before performing the series of experiments, it has been established that under the chosen reaction conditions the reaction is limited neither by external nor internal mass transfer by changing the stirring rate and catalyst particle size. As synthesized and calcined catalyst agglomerates with particle size less than 350 μm were used in the experiments. Samples were withdrawn from the reactor during the experiment (one sample per 1 h), filtered, and analyzed by Agilent 7890A gas chromatograph equipped with a flame ionization detector (FID), using a HP 5 capillary column (30 m/0.32 mm ID/0.25 μm). Reaction pathway of aldol condensation of furfural with acetone is shown in Scheme 1.

Catalytic results of aldol condensation of furfural and acetone have been described by conversion and selectivity parameters that have been calculated as follows:

$$\text{reactant conversion } (t) \text{ (mol\%)} = 100 \times \frac{(\text{reactant}_{t=0} - \text{reactant}_t)}{\text{reactant}_{t=0}};$$

$$\text{selectivity to product } i = \frac{(\text{mole of reactant converted to product } i)}{(\text{total number of mole of reactant converted})}$$

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