

## The impact of Copper modification on the selectivity performances of Layered Double Hydroxide-type materials

Octavian-Dumitru Pavel<sup>1</sup>, Anca Cruceanu<sup>1</sup>, Ruxandra Bîrjega<sup>2</sup>, Monica Răciulete<sup>3</sup>, Gheorghita Mitran<sup>1</sup>, Rodica Zăvoianu<sup>1\*</sup>

<sup>1</sup>University of Bucharest, Faculty of Chemistry, Department of Inorganic & Organic Chemistry, Biochemistry and Catalysis, 4-12 Regina Elisabeta Av., S3, 030018, Romania

<sup>2</sup>National Institute for Lasers, Plasma and Radiation Physics, 409 Atomistilor Street, PO Box MG-16, 077125, Măgurele, Romania

<sup>3</sup>Ilie Murgulescu Institute of Physical Chemistry, 202 Splaiul Independentei, 060021 Bucharest, Romania

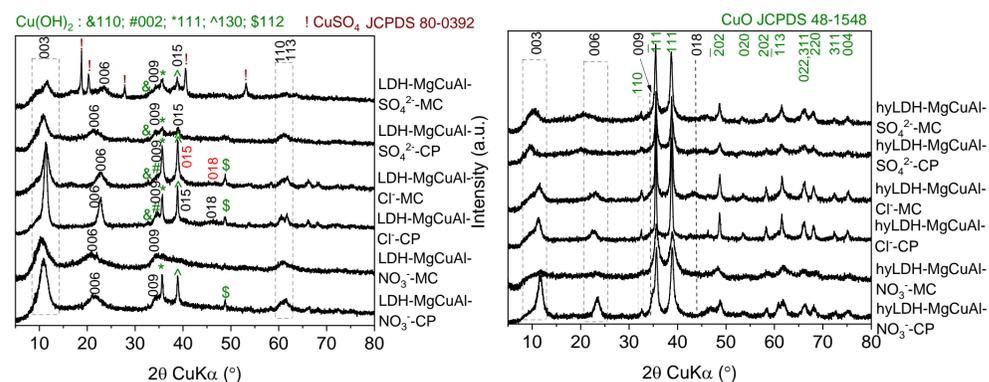
### INTRODUCTION & AIM

Usually, in the presence of base active sites, the Claisen–Schmidt condensation reaction between cyclohexanone and benzaldehyde leads to the formation of a *di*-condensed compound, e.g. 2,6-dibenzylidene cyclohexanone<sup>[1]</sup>. The optimization of layered double hydroxide-type catalysts by means of the partial substitution of Mg<sup>2+</sup> with Cu<sup>2+</sup> cations leads to a shift in the selectivity towards the *mono*-condensed product (e.g. 2-benzylidene cyclohexanone).

Traditionally, the Layered Double Hydroxides (LDH) are synthesized by the co-precipitation method which involves many steps and significant energy consumption. Mechano-chemical synthesis is a viable approach consisting of a simple mixing of precursors with hydrolysis agents without further addition of water.

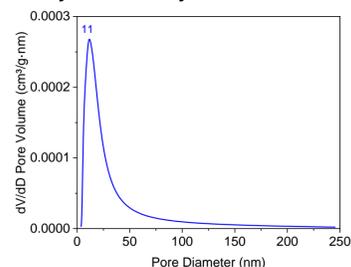
The aim of this study was to perform a comparative analysis of the physico-chemical properties and catalytic activity in Claisen–Schmidt condensation of Cu-LDH prepared by co-precipitation and mechano-chemical methods in presence of inorganic/organic alkalis from chlorides, nitrates and sulfate as metal precursors.

### RESULTS & DISCUSSION

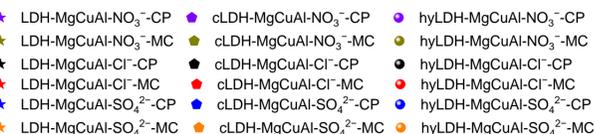
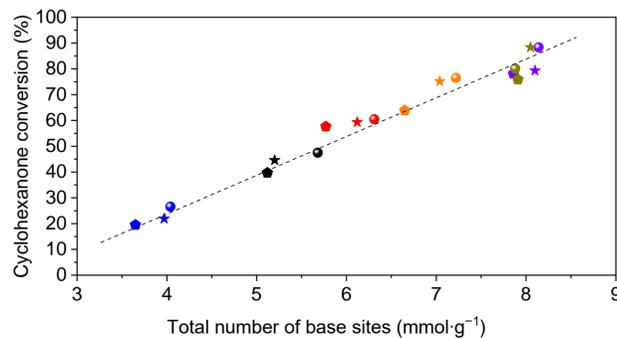


The XRD patterns of parent layered double hydroxides synthesized with TMAH

The XRD patterns of layered double hydroxides reconstructed by memory effect



The distribution of pore diameter for dried samples prepared from nitrate precursors LDH-MgCuAl-NO<sub>3</sub><sup>-</sup>-CP (blue), LDH-MgCuAl-NO<sub>3</sub><sup>-</sup>-MC (red) (TMAH as organic alkalis)



Linear trend variation of cyclohexanone conversion vs. total number of base sites for samples synthesized with TMAH

### METHOD

The Mg<sub>0.375</sub>Cu<sub>0.375</sub>Al<sub>0.125</sub> LDH materials were obtained at pH 10 by co-precipitation (CP) / mechano-chemical (MC) methods using metal chlorides, nitrates and sulfate as precursors and inorganic (NaOH/Na<sub>2</sub>CO<sub>3</sub>) / organic (Tetra Methyl Ammonium Hydroxide) as base solution under low supersaturation.

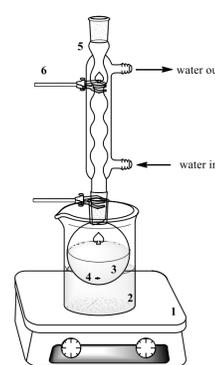
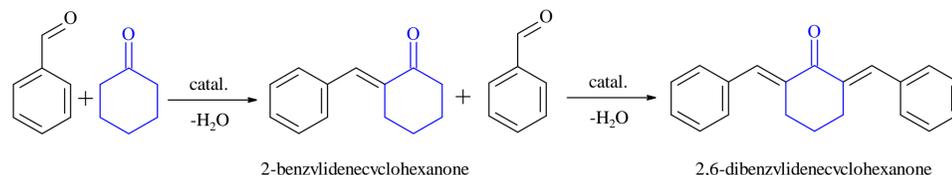
In the mechano-chemical method, all precursors were mechanically mixed in a Mortar Grinder RM 200 for 1h.

All dried samples were calcined in air atmosphere at 460 °C during 18h for mixed oxides synthesis.

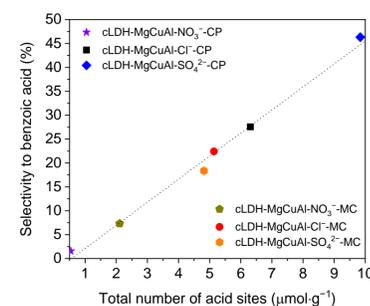
The resulted mixed oxides were hydrated with *bi*-distilled water in order to reconstruct the layered structure by *memory effect*.

The characterization of samples has been carried out by XRD, DRIFT, BET, irreversible adsorption of organic acids of different *pKa* values.

Claisen–Schmidt condensation was carried out for 2h at 120 °C by placing a mixture of cyclohexanone (5 mmol) and benzaldehyde (10 mmol) under batch and solvent-free conditions with a specified amount of catalyst (wt. benzaldehyde/catalyst ratio of 10/1).



1. Magnetic stirrer with heating
2. Silicon oil bath
3. Reaction mixture
4. Magnetic stirrer
5. Condenser
6. Clamp



The variation of selectivity to benzoic acid vs. total number of acid sites of samples synthesized with TMAH

### CONCLUSION

✓ Pure layered structure was contaminated with different amounts of copper hydroxide depending on the metal salt precursors.

✓ The *memory effect* did not lead to a total reintegration of the Cu<sup>2+</sup> in the octahedral positions of the layered structure, since part of it remained as stable CuO, obtained in the calcination step.

✓ The basicity and the catalytic activities for Claisen–Schmidt condensation showed similar variation trends, e.g., reconstructed LDH > parent LDH > mixed oxides.

✓ The copper's presence in the LDH structure decreased the basicity, leading to a higher selectivity to the *mono*-condensed product.

✓ The copper-containing catalysts also promoted the transformation of benzaldehyde into benzoic acid as a side reaction.

### REFERENCES

[1] B. Cojocar, B.C. Jurca, R. Zavoianu, R. Bîrjega, V.I. Parvulescu, O.D. Pavel, Catalysis Communications 170 (2022) 106485