# A new approach in the synthesis of LDH-type materials used in the condensation reaction

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**Silvana-Denisa Mihăilă[1], Bogdan Cojocaru[1], Gheorghiţa Mitran[1], Mihai Cosmin Corobea[2], Octavian Dumitru Pavel[1*], Rodica Zăvoianu[1*]**

*[1]University of Bucharest, Faculty of Chemistry, Department of Organic Chemistry, Biochemistry and Catalysis, 4-12 Regina Elisabeta Av., S3, 030018, Romania*
*[2]INCDCP-ICECHIM, Splaiul Independenței 202, Bucharest, 060021, Romania*

## Introduction

- ✓ The utilization of Layered Double Hydroxides (LDH) and LDH-derived mixed oxides is an area of growing interest due to some advantages: easy separation of catalysts from the reaction mixture, reusable catalysts, easy modification of the basic strength sites and their pore structure.
- ✓ Herein we report the results related to $Mg_{0.75}Al_{0.125}Y_{0.125}$ LDH-type materials preparation using two methods, *e.g.* co-precipitation and mechano-chemical route, as well as the structural properties of these solids in correlation to their activity and selectivity in the aldol condensation reaction between benzaldehyde and cyclohexanone. Also, mixed oxides obtained by calcination of LDH and reconstructed LDH by memory effect are considered in this reaction.

## Experimental

The LDH synthesis was carried out under low super-saturation conditions using a solution, ***A***, containing 1.5 M of $Mg^{2+}$, $Al^{3+}$ and $Y^{3+}$ nitrates (0.2 mol $Mg^{2+}$, 0.0333 mol $Al^{3+}$ and 0.0333 mol $Y^{3+}$) in distilled water, and a volume of TMAH (Tetra Methyl Ammonium Hydroxide) solution, ***B***, such that the pH during precipitation is 10. Both solutions, ***A*** and ***B***, were simultaneously added in a batch reactor at a feed flow of 60 $mL \cdot h^{-1}$ at room temperature under vigorous stirring of 600 $rot \cdot min^{-1}$. The obtained gel was then aged 18h at 75°C, cooled to room temperature, filtered and washed with distilled water until the neutral pH of the washing water was reached. The drying of the LDH gel was performed at 90°C for 24h in air atmosphere (**LDH-MgAlY-TMAH-CP**). For the mechano-chemical route the required amounts of nitrates and TMAH were directly milled in a mortar for 1 h, at 25°C, without any addition of water. The resulted white paste was then washed with freshly distilled water until pH of 7, and dried at 90°C for 24 h in air flow (**LDH-MgAlY-TMAH-MC**). The mixed oxide was obtained via the calcination of LDH at 460°C for 18h in an air atmosphere (**c-LDHY-MgAlY-TMAH-CP**; **c-LDHY-MgAlY-TMAH-MC**). The reconstruction of the layered structure by a "memory effect" was performed by impregnation of the mixed oxides with a double volume of distilled water compared with the volume of the solid for 24h. The reconstructed solids were then separated by filtration and dried at 90°C for 24 h in the air atmosphere (**hy-LDHY-MgAlY-TMAH-CP**; **hy-LDHY-MgAlY-TMAH-MC**). Aldol-condensation between benzaldehyde and cyclohexanone, was carried out for 2h at 120°C by placing a mixture of benzaldehyde (10mmol) and cyclohexanone (5mmol) under batch and solvent-free conditions with a specified amount of catalyst (0.1061g of catalyst, wt. benzaldehyde/catalyst ratio of 10/1).

## Characterization

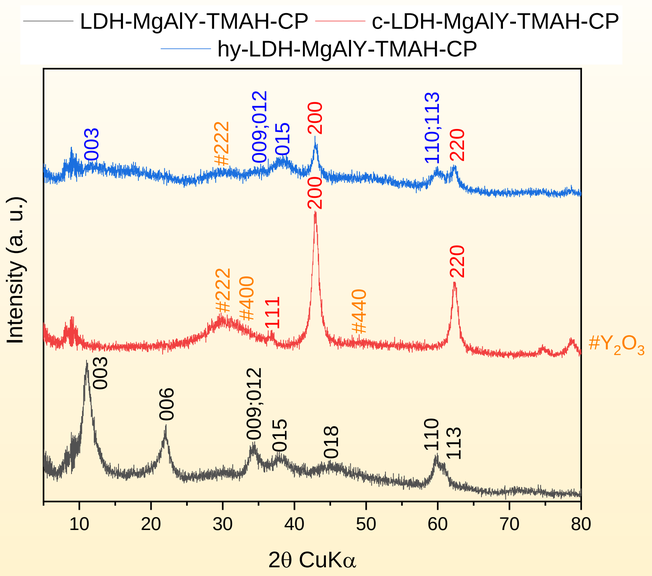



*Fig. 1. XRD patterns of samples obtained by co-precipitation method*

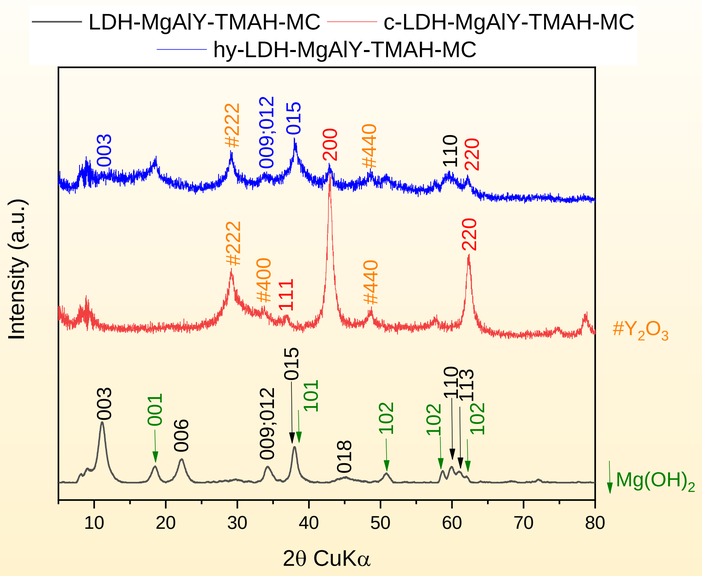



*Fig. 2. XRD patterns of samples obtained by mechano-chemical method*

| Entry | Samples | a (Å) | c (Å) | IFS* (Å) | Crystallite size (003) (Å)**/ (200) (Å)*** |
|---|---|---|---|---|---|
| 1 | LDH-MgAlY-TMAH-CP | 3.0933 | 23.9544 | 3.18 | 54 |
| 2 | c-LDH-MgAlY-TMAH-CP | 4.2080 | - | - | 80 |
| 3 | hy-LDH-MgAlY-TMAH-CP | 3.0480 | 26.6380 | 4.08 | 65 |
| 4 | LDH-MgAlY-TMAH-MC | 3.0799 | 23.8294 | 3.14 | 65 |
| 5 | c-LDH-MgAlY-TMAH-MC | 4.2098 | - | - | 98 |
| 6 | hy-LDH-MgAlY-TMAH-MC | 3.0663 | 23.6355 | 3.08 | 92 |

**IFS = c/3–4.8 Å, where 4.8 Å is the thickness of the brucite-like layer (represents the interlayer free distance).*
***Corresponds to LDH-phases*
****Corresponds to the mixed oxides phases.*

*Table 1. Structural data of the investigated samples*

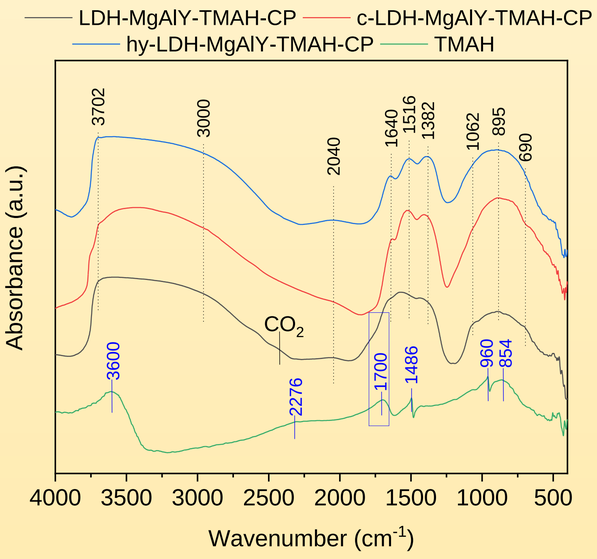



*Fig. 3. DRIFT spectra of samples obtained by co-precipitation method*

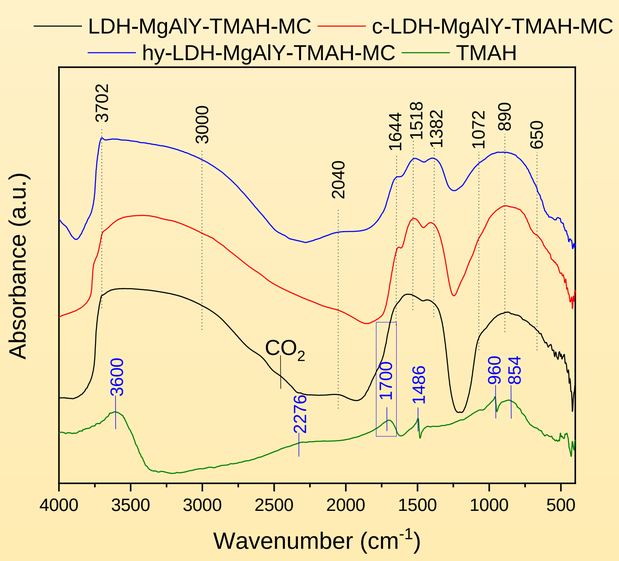


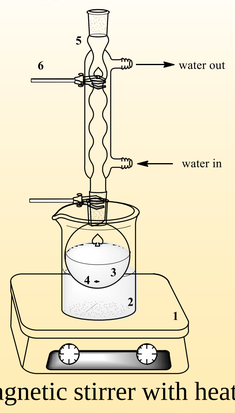

*Fig. 4. DRIFT spectra of samples obtained by mechano-chemical method*

| No. | Samples | Surface area ($m^2 \cdot g^{-1}$) | Pore volume ($cm^3 \cdot g^{-1}$) | Total number of base sites* (mmol AA $\cdot g^{-1}$) | Distribution of base sites | |
|---|---|---|---|---|---|---|
| | | | | | Strong base sites** (mmol PhOH $\cdot g^{-1}$) | Weak and medium strength base sites# (mmol $\cdot g^{-1}$) |
| 1 | LDHY-MgAlY-TMAH-CP | 79 | 0.10 | 8.23 | 0.45 | 7.78 |
| 2 | c-LDHY-MgAlY-TMAH-CP | 181 | 0.36 | 8.46 | 0.52 | 7.94 |
| 3 | hy-LDHY-MgAlY-TMAH-CP | 15 | 0.05 | 8.33 | 0.48 | 7.85 |
| 4 | LDHY-MgAlY-TMAH-MC | 61 | 0.08 | 8.25 | 0.66 | 7.59 |
| 5 | c-LDHY-MgAlY-TMAH-MC | 160 | 0.26 | 8.48 | 0.69 | 7.79 |
| 6 | hy-LDHY-MgAlY-TMAH-MC | 10 | 0.05 | 8.36 | 0.69 | 7.67 |

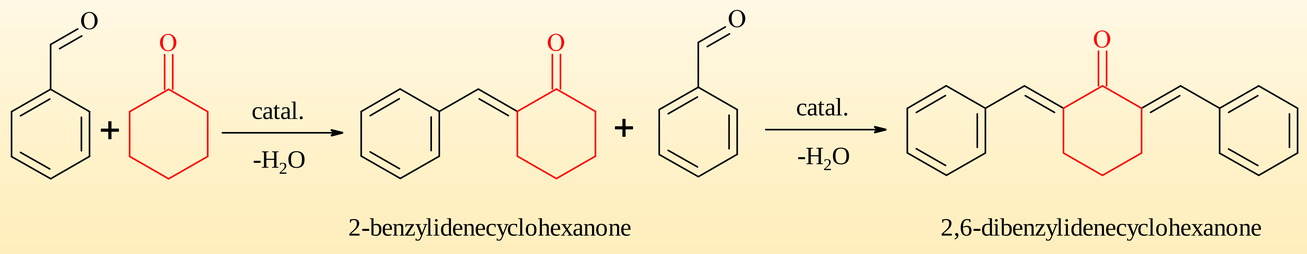
**AA=acrylic acid; **PhOH=phenol;*
*#equal to the difference: Total number of base sites - Strong base sites*

*Table 2. The textural properties of the considered samples*

## Results

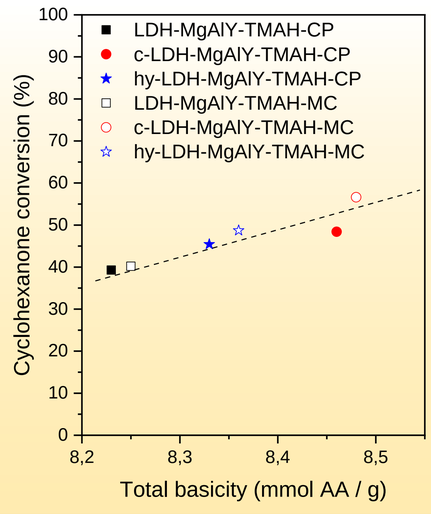


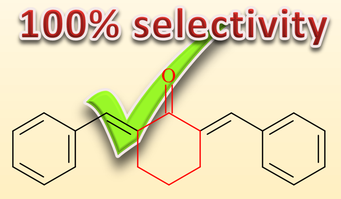

1. Magnetic stirrer with heating 2. Silicon oil bath
3. Reaction mixture 4. Magnetic stirrer
5. Condenser 6. Clamp




2-benzylidenecyclohexanone

2,6-dibenzylidenecyclohexanone




2,6-dibenzylidenecyclohexanone

## Conclusions

- ✓ LDH $Mg_{0.75}Al_{0.125}Y_{0.125}$ can be prepared by both co-precipitation and mechano-chemical methods.
- ✓ The XRD patterns prove the hydrotalcites structure of dried samples contaminated with Y or Mg impurities phases.
- ✓ Basicity keep the trend: mixed oxides > reconstructed > dried samples.
- ✓ The catalytic activity for aldol condensation shows a linearity between conversion of cyclohexanone and total basicity with selectivity toward di-condensated compound of 100%.

## Acknowledgements

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