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Mechano-chemical versus co-precipitation for the preparation of Y-modified LDHs for cyclohexene oxidation and Claisen-Schmidt condensations



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ABSTRACT

Y-modified LDHs with atomic $Mg^{2+}/(Al^{3+} + Y^{3+})$ of 3 and Al^{3+}/Y^{3+} ratios of 0.5, 1 and 1.5 were prepared following two preparation methods, *i.e.* the co-precipitation and mechano-chemical one. The substitution of Al by Y in the brucite-type layer was less effective for the samples prepared by co-precipitation compared to those prepared *via* mechano-chemical route. In spite the fact yttrium has a larger ionic radius (0.9Å) the structural characterizations of these solids confirmed that the layered structure incorporates part of it in the octahedral positions. Further, the reconstruction of the layered structure after an exposure to water for 1 h was more effective for the solid prepared by co-precipitation. The yttrium modified LDHs showed better catalytic activities for cyclohexene oxidation to the corresponding epoxide than the un-modified LDH sample. Then, mixed oxides derived from yttrium-LDH showed very high conversions and selectivities for the synthesis of chalcone.

1. Introduction

Besides the interest for the synthesis of base-type materials and controlled mixed oxides, Layered Double Hydroxides (LDH) have attracted an increased attention due to the facile preparation mechanism, *i.e.* shorter reaction times and low amounts of wastes [1–4]. To this respect, most of the reported investigations focused on the control of the factors affecting the kinetics of the process, the purity of the crystallographic phases, the homogeneous distribution of the cations in the structure and the diminution of the operation steps. The general formula of the LDH corresponds to $[M_{1-x}^{2}M_x^{3+}(OH)_2]^{x+}[A_{x-n}^{n}]$ ·mH₂O, where M^{2+} and M^{3+} are divalent and trivalent cations in the brucite-type layers, and A is the interlayer anion which balances the exceeding charge resulting after the isomorphic substitution of M^{2+} by M^{3+} ; x is usually 0.20-0.33 and m accounts for the water of crystallization [4].

Co-precipitation is the traditional preparation method of these materials. It consists in the mixing of aqueous salts solutions containing the targeted cations with an alkaline solution [5–11] at appropriate pH values. Although it is a reliable procedure, it has some disadvantages such as multitude steps, different specific equipments and high energy consumption. As a more simplistic alternative, the mechano-chemical method requires only a ball-milling of the reactants followed by

washing and drying. In this method, water is provided by the hydration molecules coming from the employed inorganic salts.

Taking into account these advantages, a consistent number of reports already utilized this method for the LDH preparation. They demonstrate the role of the anion (carbonate [12], nitrate [13], sulfate [14]), the effect of the peptization [15], pre-milling [16,17] and reaction time [18] in these syntheses. The substitution of the cations like Al^{3+} by Fe^{3+} [19–21] or Mg^{2+} by Ca^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , Cd^{2+} or Co^{2+} was successfully achieved [21–23]. Mechano-chemistry was also reported for the synthesis of LDH containing monovalent species like Li⁺ [24–27], including Li-Al-B₄O₇-LDH [28], tetravalent like Sn⁴⁺ [29] but also for LDHs containing intercalated organic moieties such as aminoacids [30,31] or dodecyl sulfate [32]. The same method allowed the production of LDH nanoparticles [33-37]. However, to date, the successful substitution of large cations, like lanthanides, was scarcely reported. Most of the above structures demonstrated catalytic activities. especially after a thermal treatment when the LDH structure has been destroyed.

The base properties of the LDH and derived oxides also recommended these as catalysts for organic reactions. In this respect, Claisen-Schmidt condensations represent an important base catalyzed carbon-carbon bond formation reaction [38]. Using this route

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compounds such as chalcone (or chalconoids) and flavone can be prepared. They are subsets of compounds known as flavonoids exhibiting anti-oxidant, anti-inflammatory and anti-cancer activity properties with great potential applications in medicine [39]. Flavones have proven to be effective for several diseases associated to an oxidative stress, such as arteriosclerosis, diabetes, cancer, Alzheimer or Parkinson [40,41]. Benzylidene acetophenone (1,3-diphenyl-2-propen-1-one), the parent member of the chalcone series, can be prepared *via* a Claisen-Schmidt condensation between benzaldehyde and acetophenone in one-pot synthesis. Flavone can be obtained in the same manner as the chalcone, by substituting acetophenone with its derivative 2'-hydroxyacetophenone. Accordingly, various basic solid catalysts have already been investigated in these reactions. However, to-date they were less effective than the layered double hydroxides [42,43].

The partial substitution of Al^{3+} by Y^{3+} may provide the basicity required by these reactions as a result of the lower electronegativity of Y^{3+} (1.22) compared to Al^{3+} (1.61) [5,44–46]. This advantage has already been confirmed for both the cyanoethylation of ethanol [5,46,47] and epoxidation of styrene [45]. However, there are no reports concerning the utilization of these base-solids as catalysts for Payne-oxidation of cyclohexene or Claisen-Schmidt condensation.

This work aimed: *i*) a selection of the beneficial Al^{3+}/Y^{3+} ratio for the partial substitution of aluminum (ionic radius 0.535 Å) by yttrium (ionic radius 0.9 Å) in the octahedral positions of the LDH lattice through samples prepared by co-precipation with $Mg^{2+}/(Al^{3+} + Y^{3+}) = 3$ and $Al^{3+}/Y^{3+} = 0.5$, 1 and 1.5 molar ratios; *ii*) the comparative study of yttrium modified LDH catalysts $Mg^{2+}/(Al^{3+} + Y^{3+}) = 3$ and $Al^{3+}/Y^{3+} = 1$ molar ratios prepared via co-precipation and mechanical routes, thermal treatment and reconstruction; and *iii*) the behavior of these catalysts for cyclohexene oxidation with H_2O_2 and Claisen-Schmidt condensation.

2. Experimental

2.1. Preparation of the catalysts

Yttrium-modified LDH (LDHY-cp) was prepared via: i) the co-precipitation, and *ii*) mechano-chemical route. In the route *i*) the synthesis was carried out at a pH of 10 under low supersaturation conditions using a solution <u>**A**</u> containing 1.5 M of nitrates of Mg²⁺, Al³⁺ and Y³⁺ (0.2 mol Mg²⁺, 0.0333 mol Al³⁺ and 0.0333 mol Y³⁺ for Al³⁺/Y³⁺ = 1) in bi-distilled water, and an equal volume of solution <u>**B**</u> containing 0.18 mol of Na₂CO₃ and 0.44 mol of NaOH in bi-distilled water. Both solutions, \underline{A} and \underline{B} , were simultaneously added in a batch reactor at a feed flow of 60 mL h⁻¹ with a Gilson peristaltic pump and mixed at room temperature under vigorous stirring of 600 rot \cdot min⁻¹. The obtained gel was then aged 18 h at 75 °C, cooled to room temperature, filtered and washed with bi-distilled water until the neutral pH of the washing water was reached. The drying of the LDH gel was performed at 90 °C for 24 h in an air flow. The corresponding mixed oxide (cLDHY-cp) was obtained via the calcination of LDHY-cp at 460 °C for 18 h in an air flow. The reconstruction of the layered structure (partial recovering the original LDH structure) by a "memory effect" was performed by impregnation of the mixed oxides (samples calcined at 460 °C) with a volume of bi-distilled water exceeding with 10 vol% the volume of pores. After impregnation the samples were kept for 24 h at 25 °C under a pure nitrogen flow in order to avoid any contamination with carbonate anions. The reconstructed solids were then separated by filtration and dried at 90 °C for 24 h in the same N2 flow (hyLDHY-cp).

In the route *ii*) the required amounts of nitrates, Na_2CO_3 and NaOH were mixed directly in a Mortar Grinder RM 200 for 1 h without the addition of water or another compound. The obtained white paste was then washed with bi-distillated water until the neutral pH value. The drying of the obtained gel was performed at 90 °C for 24 h in air flow, yielding the solid **LDHY-m**. The calcination of the dried sample at

460 °C for 18 h in air flow led to the mixed oxide (cLDHY-m). The corresponding reconstructed sample was named hyLDHY-m.

2.2. Characterization of the catalysts

The chemical analysis was performed by Atomic Absorption Spectrometry on Pye-Unicam AAS Spectrometer to determine the metal content, while N, H and C were determined by elemental analysis on a Carlo Erba automatic analyzer. Powder X-ray diffraction patterns were recorded with a Shimadzu XRD 7000 diffractometer using the Cu K_a radiation $(\lambda = 1.5418 \text{ Å}, 40 \text{ kV}, 40 \text{ mA})$ at a scanning speed of $0.10^{\circ} \text{ min}^{-1}$ in the $5-80^{\circ}$ 20 range. DRIFTS spectra obtained from accumulation of 400 scans in the domain $400-4000 \text{ cm}^{-1}$ were recorded with a NICOLET 4700 spectrometer. N2 adsorption - desorption isotherms were determined using a Micromeritics ASAP 2010 instrument. Prior to the nitrogen adsorption, samples were out gassed under vacuum for 24 h. The base properties of the catalysts were determined by in situ UV-vis titration with organic molecules with different pK_a values, e.g. acrylic acid, $pK_a = 4.2$, and phenol, $pK_a = 9.9$ [48-51] (the detailed working procedure is described in a previous publication [50]). The number of weak and medium base sites was calculated as the difference between the chemisorbed acrylic acid and phenol. XPS measurements were performed at normal angle emission with a Specs spectrometer, using the Al K α monochromatic radiation (h ν = 1486.7 eV) of an X-ray gun, operating with 300 W (12 kV / 25 mA) power. A flood gun with an electron acceleration at 1 eV and electron current of 100 µA was used in order to avoid charging effects. The energy of the photo ejected electrons was measured using a Phoibos 150 analyzer, operating with a pass energy of 30 eV. The XP spectra were fitted using Voigt profiles combined with their primitive functions for inelastic backgrounds.

2.3. Catalytic tests

The catalytic performances of the synthesized LDHs were evaluated in *i*) the oxidation of cyclohexene with hydrogen peroxide in acetonitrile (Scheme 1), and ii) synthesis of chalcone and flavones (Schemes 2 and 3). The oxidation was performed in the presence of 3% (w/w) catalyst reported to the weight of the reaction admixture consisting of 4 mmoles cyclohexene and 32 mmoles acetonitrile. This mixture was dissolved in 20 mL of solvent made of equal volumes of acetone and water. The reactions were carried out at 60 °C, for 5 h reaction time in a stirred flask. An amount of hydrogen peroxide (30 wt. % H₂O₂) respecting the overall molar ratio H₂O₂/cyclohexene of 32/1 was step wisely added in the reaction mixture in the first 4 h. The reaction was monitored hourly by the analysis of the organic phase extracted in diethyl ether using a GC K072320 Thermo Quest Chromatograph equipped with a FID detector and a capillary column of 30 m length with DB5 stationary phase. The reaction products were identified by mass spectrometer coupled chromatography, using a GC/MS/MS Varian Saturn 2100 T equipped with a CP-SIL 8 CB Low Bleed/MS column of 30 m length and 0.25 mm diameter. The H₂O₂ consumption was determined by iodometric titration at the end of the reaction.

The condensation reactions were performed in a 50 mL stirred flask, under reflux conditions, for 4 h reaction time using a catalyst concentration of 5% (w/w) reported to the weight of the reaction admixture. Benzaldehyde, acetophenone and 2'-hydroxyacetophenone were purchased from Merck. The catalytic tests were performed at three different benzaldehyde/methylenic compound molar ratios, *i.e.* 1/1, 5/1, 10/1. The analysis of the organic reaction products extracted in ethanol was performed using the above mentioned equipments.

3. Results and discussion

3.1. Catalysts characterization

The chemical analysis of the synthesized LDH, Table 1, showed the absence of nitrogen confirming that nitrate ions were completely



possible by-products

Scheme 1. Mechanism of cyclohexene oxidation.

removed during the washing step. The content of carbon was lower for mechano-chemical prepared samples compared to the co-precipitated ones suggesting that the first method allows the incorporation of more OH^- than CO_3^{2-} . Then, the comparison of the initial materials with the reconstructed ones revealed a decrease of the content of C. During the calcinations, a part of carbonate was lost (the entire amount being removed at temperatures higher than 650-700 °C). Also, due to the lack of carbonate in the bi-distilled water, the content of OH embedded in the rebuilt material was higher as a result of the increase of the H content.

The XRD patterns of Y-modified solids at high yttrium contents $(Al^{3+}/Y^{3+} = 0.5; 1 \text{ and } 1.5) \text{ and } Mg^{2+}/(Al^{3+} + Y^{3+}) = 3 \text{ are displayed}$ in Fig. 1. Their structural data were gathered in Table 2. The unit cell parameter a is related to the distance between two metallic cations present in the brucite-like layer and is regard as an index of the chemical composition of LDH phase [4,52]. Considering the octahedral arrangement of the cations, $a = \sqrt{2} \cdot d(M-O)$, where d(M-O) is the mean metal-oxygen distance and depends on the proportion of the metal components and their ionic radii. Although there is an important difference in their Shannon ionic radii $(Y^{3+}/Al^{3+} = 0.9/0.535)$, for very low Y concentration (Al^{3+}/Y^{3+}) molar ratio of 11.5), it is most likely not to observe an effect on the *a*-lattice parameter as we had found and reported [53]. Starting from $Al^{3+}/Y^{3+} = 4$ and at a higher amount of $Al^{3+}/Y^{3+} = 1$, which is ten times higher, the slight increase of the *a*lattice parameter due to the partial substitution of Al³⁺ with Y³⁺ was confirmed [45].

For the solids obtained by co-precipitation, *i.e.* for Al^{3+}/Y^{3+} ratios of 0.5 and 1.5, the *a*-parameter does not change significantly compared to that of the unmodified reference Y-free hydrotalcite $Mg^{2+}/Al^{3+} = 3$ LDH (e.g. 3.06 [52], Table 3), consequently for these samples,



Scheme 3. Synthesis of flavone.

apparently there are insignificant or no substitution of Al^{3+} by Y^{3+} in the brucite-like layer. For the solid prepared with an Al^{3+}/Y^{3+} molar ratio of 1 an increase of the *a*-lattice parameter is observed, indicating a partial substitution of Al^{3+} by Y^{3+} . Additionally, the above samples obtained by co-precipitation in the presence of large amount of yttrium, exhibit significant larger and less intense lines compared to the reference Y-free HT-cp solid (Fig. 2) revealing a decline of their overall crystallinity with the increase of yttrium content. The same effect attributed to the distortions induced in the layers by the large difference between the ionic radii of Y^{3+} and Al^{3+} was observed also by Fernandez et al [44]. The influence of the increasing Y amount on the crystallinity could be surveyed by the reduction of their crystallites sizes. The D₀₀₃ crystallites size were extracted via the Scherrer formula from the broadness (full width at half maximum, FWHM) of the (003) reflection. The values for Y-modified LDHs are proportional with the vttrium content and significant smaller (Table 2) compared to the Yfree reference sample of 84 Å (Table 3). The D₀₀₃ crystallite size is related to the brucite-like layers stacking distance, therefore one could assume that larger yttrium amount impeded the long distance packing of the layers along the c-axis. For small Y loading, we observed and described the slight increase of the *c*-lattice parameter [45,53], as



Scheme 2. Claisen-Schmidt condensation for the synthesis of benzylidene acetophenone.



(methylene component)



5	-						
Sample	Imple Chemical composition, wt% (moles %)					$Mg^{2+}/(A^{13+}+V^{3+})$ ratio ^(a)	Al^{3+}/Y^{3+} ;
	С	Н	Mg ²⁺	Al ³⁺	Y^{3+}		
HT-cp [52]	2.1(1.9)	4.2(44.3)	24.1(10.4)	8.9(3.5)	-(-)	3.008	-; [0.531]
HT-m [52]	1.9(1.7)	4.3(44.9)	24.2(10.4)	8.8(3.4)	-(-)	3.055	-; [0.486]
LDHY-cp	1.8(1.8)	3.6(42.9)	22.5(11.0)	4(1.8)	13.4(1.8)	3.097	0.983; [0.502]
hyLDHY-cp	0.5(0.5)	4.5(48.9)	22.3(10.0)	4.2(1.7)	13.5(1.6)	2.985	1.024; [0.136]
LDHY-m	1.7(1.7)	3.8(44.4)	22.4(10.8)	4.1(1.8)	13.8(1.8)	3.001	0.978; [0.461]
hyLDHY-m	0.4(0.4)	4.2(47.1)	22.1(10.2)	3.9(1.6)	13.9(1.8)	3.023	0.924; [0.111]

^a As determined from the results of AAS analysis.



Fig. 1. The XRD patterns of the LDHs with at $Mg^{2+}/(Al^{3+} + Y^{3+})$ and $Al^{3+}/Y^{3+} = 0.5$; 1 and 1.5 respectively, prepared by co-precipitation. On top the XRD pattern of the reference Y-free LDH (Mg^{2+}/Al^{3+}) (denoted HT-cp in [52]) is included.

Table 2

The structural data of the LDH samples $Mg^{2+}/(Al^{3+} + Y^{3+}) = 3$ produced by co-precipitation method.

Al ³⁺ /Y ³⁺ molar ratio	Lattice parameters		IFS (Å) ^a	D ₀₀₃ (Å)
	a (Å)	c (Å)		
1.5	3.058	22.244	2.61	22
1	3.076	22.213	2.60	17
0.5	3.058	21.894	2.50	12

^a IFS = c/3-4.8 Å, where 4.8 Å is the thickness of the brucite-like layer [54].

Table 3

Structural data of the investigated samples.

Samples	a (Å)	c (Å)	IFS* (Å)	FWHM (003) ¹ / (200) ²	20 (003)	Crystallite size (003) (Å) ¹ / (200) (Å) ²
HT-cp [52] HT-m [52] LDHY-cp cLDHY-cp hyLDHY-cp LDHY-m cLDHY-m hyLDHY-m	3.060 3.053 3.076 4.210 3.051 3.098 4.230 3.101	23.357 23.022 22.213 - 22.415 21.894 - 21.136	2.99 2.87 2.60 - 2.67 2.50 - 2.25	$\begin{array}{c} 0.9917^{(1)}\\ 0.9134^{(1)}\\ 3.68^{(1)}\\ 2.5933^{(2)}\\ 1.8667^{(1)}\\ 0.355^{(1)}\\ 2.2100^{(2)}\\ 1.5200^{(1)} \end{array}$	11.3549 11.5963 12.1536 - 11.8017 12.6092 - 13.1896	$84^{(1)} \\91^{(1)} \\22^{(1)} \\28^{(2)} \\43^{(1)} \\41^{(1)} \\28^{(2)} \\53^{(1)}$

* IFS represents the interlayer free distance.

¹ Corresponds to LDH-phases.

² Corresponds to the mixed oxides phases.

expected, due to the larger size and lower polarizing ability of Y^{3+} compared to Al^{3+} , causing the decrease of the Coulombic attraction force between the brucite-like layers [55,56]. Similar results were reported also by Rives and coworkers [44,57]. Swirk et al. reported either



Fig. 2. The XRD patterns of LDH with $Mg^{2+}/(Al^{3+}+Y^{3+}) = 3$ and $Al^{3+}/Y^{3+} = 1$ produced *via* co-precipitation (cp) and mechano-chemical (m) routes.

a slight increase of *c*-parameter [58,59] or no modification of both lattice parameters [60] for relatively low amounts of yttrium. In the case of these as-prepared samples Y-modified LDHs, with high amounts of yttrium, we observed a decrease of *c*-parameter, in particular for the $Al^{3+}/Y^{3+} = 0.5$ sample. This result could be associated with the significant distortion effect produced by the high amount of Y generating an important degree of stacking disordering along the c-axis, with a modification of anions composition and orientation, e.g. high amount of OH^- and lower amount CO_3^{2-} groups along with the formation of amorphous material containing yttrium, more likely basic yttrium carbonate Y(OH)CO₃ or Y(OH)₃ [61]. The sample obtained by co-precipitation at $Al^{3+}/Y^{3+} = 1$ for which the increase of the *a*-parameter endorsed an Al^{3+} partial substitution by Y^{3+} and the *c*-parameter a reduced CO32- amount is labeled catalyst LDHY-cp. Indeed, the elemental analysis for this sample, presented in Table 1, revealed a smaller $CO_3^2/(Al^{3+} + Y^{3+})$ ratio of 0.502 for this sample compared to the ratio CO_3^{2-}/Al^{3+} of 0.531 for Y-free HT-cp. The $Al^{3+}/Y^{3+} = 1$ molar ratio with prospects to secure a partial substitution of Al^{3+} by Y^{3+} in the "brucite-like" layer was selected for the preparation of the Y-modified LDH catalysts tested for their catalytic performance in the oxidation of cyclohexene with H₂O₂ and Claisen-Schimdt condensation.

The XRD patterns of the Y-modified LDHs as-prepared either by coprecipitation or mechanical routes, thermally treated and reconstructed *via* memory effect are presented in Fig. 2. The structural data of the LDHY catalysts are included in Table 3 alongside with the corresponding data for Y-free reference LDHs (Mg/Al = 3 molar ratio) that were already reported [52].

The survey of the structural data included in Table 3 exposed some aspects associated with yttrium incorporation. It is to be observed that the mechanical route leads to a higher *a*-parameter thus, to a higher partial substitution of Al^{3+} by Y^{3+} compared to the co-precipitation route. Its *c*-lattice parameter is considerable smaller than for LDHY-cp, indicative of a change of the interlayer anionic composition namely, a

reduction of the number of the larger CO_3^{2-} anions. It is worth to notice that the *c*-parameter of the reference HT-m sample is smaller than that of the HT-cp sample. The observations are consistent with the analytical measured $\text{CO}_3^{2-}/(\text{Al}^{3+} + \text{Y}^{3+})$ and $\text{CO}_3^{2-}/\text{Al}^{3+}$ ratios respectively, which indicate a decrease of these ratios for the mechanical route as compared with the co-precipitation route *e.g.* from 0.502 to 0.461 for the LDHY catalysts and from 0.531 to 0.486 for the reference HT samples, respectively (Table 1).

Large ion Y^{3+} induces a similar distortion effect in the sample obtained *via* the mechanical route as observed by the its XRD curve profile but, apparently the order along the *c*-axis is less affected in comparison with its corresponding LDHY obtained by co-precipitation: the D_{003} crystallite size is 41 nm for LDHY-m and only 22 nm for LDHY-cp. The products obtained by their calcination are mixed oxides Mg(Al/Y)O of periclase-type structure (ICDD card no.045-0946) and are Miller indexed consequently in Fig. 2. In the cLDHY-m pattern a very small line, assignable to the most intense line of cubic Y2O3 (ICDD card no.041-1105) is detectable. The cubic lattice parameters a of the references cHT-cp and cHT-m had smaller values than the standard value of 4.2112 Å of MgO-pure (ICDD card no. 045-0946) as expected due to the difference between Shannon ionic radii of Al3+ and Mg2+ (0.535Å/ 0.72Å). The lattice *a*-parameter of the cLDHY solids are larger, in particular for the cLDHY-m sample, preserving the difference between the brucite-like layer related *a*-parameter of their parent LDHYs. The crystallites sizes for cLDHY-m and cLDHY-cp are equal and smaller than their reference Y-free samples due to the distortion effect of Y insertion. The reconstruction occurred for both hyLDHY-cp and hyLDHY-m samples with the same characteristics as for Y-free LDH [51], namely: a decrease of the *c*-parameter marking the predominance of OH⁻ anions replacing the CO₃²⁻ anions and, an improved layers stacking along the *c*axis revealed by larger crystallites sizes. The differences observed between the two routes are preserved in their "reconstructed" formed: slight larger *a*-lattice parameter, smaller *c*-parameter, thus lower amount of CO322 and larger crystallite size. The analytically measured $CO_3^{2-}/(Al^{3+} + Y^{3+})$ ratios of the hyLDHY catalysts corroborate the XRD results: 0.136 for hyLDHY-cp and 0.111 for hyLDHY-m (Table 1). The (222) line of the Y₂O₃ are less detectable in the XRD pattern of hyLDHYm compared to cLDHY-m. Therefore, it may be inferred that the samples prepared via the mechanical route are structurally promising in view of their ability to accommodate Y^{3+} in the brucite-like layer and a slightly better crystalline order.

The DRIFTS spectra of the yttrium modified LDHs are shown in Fig. 3. The band at $3700-3400 \text{ cm}^{-1}$ corresponds to the OH group vibration, ν (O–H), in the LDH structure while that at 3070 cm^{-1} relates to the hydrogen bonds between water and carbonate in the interlayer of the hydrotalcite. The band at $1640-1650 \text{ cm}^{-1}$ is due to the H₂O bending vibration of interlayer water in the hydrotalcite structure.

The bands at 1400 cm⁻¹ and 680 cm⁻¹ were assigned to the CO₃²⁻ group vibration while those at 600 – 500 cm⁻¹ and below 500 cm⁻¹ correspond to Mg–O and Al–O bonds. The intensity of these bands is well correlated with the results of XRD and chemical analyses. By calcination, part of OH and $CO_3^{2^2}$ groups are removed from the structure as CO₂ and H₂O leading to a decrease of the intensity of the bands located at 3070 and 1640–1650 cm⁻¹, respectively. However, a complete removal of CO₂ has been achieved only after calcination at temperatures higher than 650 °C. The hydration of the mixed oxides restored the bands at 3070 and 1640–1650 cm⁻¹. Unfortunately, such a treatment led to an additional segregation yttrium in the LDH as Y₂O₃ (new characteristic bands at 440–442 cm⁻¹).

Table 4 presents the surface areas of the investigated samples. The presence of the interlayer yttrium determined a quite drastic decrease of the surface area [4]. Also, the reconstructed samples (hyLDHY-cp and hyLDHY-m) had smaller surface areas confirming the fact that the restoration of the LDH structure is only partial.

Mechano-chemical route led as well to smaller surface areas compared to LDH produced by co-precipitation proving the presence of a



Fig. 3. The DRIFT of the synthesized catalysts.

 Table 4

 Textural characteristics and basicity of the investigated samples.

No.	Samples	Surface area (m ² ·g ⁻¹)	Pore volume (cm ³ .g ⁻¹)	Total	Distribution of base sites	
				number of base sites* (mmol $AA \cdot g^{-1}$)	Strong base sites* (mmol PhOH·g ⁻¹)	Weak and medium strength base sites [#] (mmol·g ⁻¹)
1	LDHY-cp	84	0.12	8.00	0.39	7.61
2	cLDHY-cp	190	0.26	8.25	0.42	7.83
3	hyLDHY-cp	44	0.06	8.06	0.36	7.70
4	LDHY-m	70	0.10	8.12	0.61	7.51
5	cLDHY-m	163	0.22	8.34	0.63	7.71
6	hyLDHY-m	38	0.05	8.17	0.59	7.58

* AA = acrylic acid; PhOH = phenol.

[#] Equal to the difference: Total number of base sites-Strong base sites.

lower density of anions (such as OH^- groups) in the catalyst structure. This result may be also attributed to a partial release of the CO_2 during the milling of the reagents, as an effect of heating.

The basicity measurements results were compiled in the same Table 4. Mixed oxides possessed a stronger basicity than the LDH precursor or reconstructed layered double hydroxides regardless the preparation route. The stronger basicity is associated to surface O^{2-} species [62], the weak base sites to surface OH⁻ species and the medium strength basic ones to the oxygen bridging Mg²⁺, Al³⁺ and Y³⁺ cations. These results indicated that the materials obtained *via* the mechanochemical route present an enhanced basicity compared to the co-precipitated ones that is accordance to the higher concentration of the OH groups. Very important, the addition of yttrium induced a slightly more increased basicity compared to the reference LDH material [52].

Y has the lowest electronegativity in the series Y (1.22) < Mg (1.31) < Al (1.61) that corresponds to an increased basic character [63]. This fact has also been confirmed by our basicity measurements (Table 4) and agrees with the literature reports [64–67].

The XPS spectrum of dried LDHY-cp and LDHY-m samples in the region of Y3d level (Fig. 4 a,b) has been deconvoluted into two doublets assigned to the binding energy of this element in hydroxide and carbonate, respectively (Table 5) [68,69]. Taking as reference the $3d_{5/2}$



Fig. 4. XPS core level spectra: Y3d of LDHY-cp (a) and LDHY-m (b); C1s of LDHY-cp (c) and LDHY-m (d); O1s of LDHY-cp (e) and LDHY-m (f); Mg2p of LDHY-cp (g) and LDHY-m (h); Al2p of LDHY-cp (i) and LDHY-m (j).

Table 5The XPS binding energies for the analyzed levels.

XPS level/ LDH		Binding energi	es/bond	
Y3d LDHY-cp LDHY-m C1s LDHY-cp	Y-OH⁻ 3d_{5/2} 157.9 eV 157.9 eV C-O-H 286.5 eV	Y-OH⁻ 3d_{3/2} 160.2 eV 159.8 eV C-O 287.7 eV	Y-CO₃²⁻ $3d_{5/2}$ 159.6 eV 158.7 eV O-C = O 289.6 eV	Y- CO₃²⁻ 3d_{3/2} 162.0 eV 160.7 eV 291.5 eV 291.5 eV
LDHY-m O1s LDHY-cp	– Y-OH 531.6 eV	$\underline{O} = C - O$ 532.2 eV	- O-C-O 533.5 eV	$- \mathbf{O} = \mathbf{C} \cdot \mathbf{O}$ 534.6 eV
LDHY-m Mg2p LDHY-cp LDHY-m	530.9 eV Mg(OH)₂ 49.6 eV –	532.5 eV MgCO₃ 51.8 eV –	533.6 eV Hydroxycarbon - 50.2 eV	- ate
Al2p LDHY-cp LDHY-m	Al₂O₃ 74.2 eV 74.1 eV		AlOOH (boehm 75.1 eV 76 eV	ite)

component, the ratio between the Y–OH and Y– CO_3^{2-} was of 1.45 for LDHY-m and 0.89 for LDHY-cp. This result fits the conclusions resulted from the X-ray analysis of these samples. The deconvolution of the C1s and O1s spectra also provided arguments for its association to hydroxyl and carbonate groups (Fig. 4c–f). For C1s this is reflected by the bands at 286.5 eV (C–O–H), 287.7 eV (C–O), and 289.6 eV (O–C=O) while for O1s 532.2-532.5 eV (\underline{O} =C–O) [70], 533.5 eV (O–C–O) and 534.6 eV (O=C– \underline{O}). In a good connection to the XPS spectrum of the Y3d level, for LDHY-m the intensity of the bands assigned to the O=C–O bonds was also very small.

The bands at 531.6 and 530.9 eV accounts for the O1s level attributable to an oxygen directly connected to Y [71]. The XPS spectrum of the Mg2p level (Fig. 4g,h) indicated a broad band in the range 44-54 eV for LDHY-cp that could be deconvoluted in a component at 49.6 eV attributable to Mg in Mg(OH)₂ and a second one at 51.8 eV

attributable to MgCO₃ [72]. For LDHY-m the XPS spectrum had only one component at 50.2 eV corresponding to Mg in magnesium hydroxycarbonate [73].

The XPS spectrum corresponding to the Al2p level (Fig. 4i,j) showed a broad band that has been deconvoluted in two components at 74.2 eV corresponding to Al_2O_3 and second one at 75.1 attributed to AlOOH (boehmite) [74].

3.2. Catalytic tests

In the absence of the catalyst, after 5 h, the decomposition of H_2O_2 (determined by the iodometric titration) was in the range of 5–7 % (w/w) from the total introduced amount.

The oxidation of cyclohexene may lead to several products, Scheme 1. Without any catalyst only cyclohexanol and cyclohexenone were produced with very small conversions. Without the solvent the oxidation occurred with high conversions of cyclohexene but with yields in cyclohexene epoxide below 10 %. Only the presence of the catalyst conducted the oxidation of cyclohexene towards cyclohexene oxide. Also, the presence of water enables the extraction of the acetamide by-product in the aqueous phase thus affording an easier separation of the epoxide from the reaction mixture. The water–acetone as solvent is appropriate for this oxidation reaction due to its requiring of a smaller amount of organic solvent, being more eco-friendly [50].

Fig. 5 presents the variation of the conversion vs. time. The catalytic activity was influenced by the basic active sites strength, resulting the following variation trendlines: calcined sample $(O^{2^-}) >$ hydrated sample (OH⁻ majority) > dried sample (mixture of OH⁻/CO₃^{2^-}).

It is worth to note that the initial activity of the mechano-chemical catalysts was superior to that of the co-precipitated ones (after 1 h reaction time, the conversions were almost double). This result is in line with the information provided by both XPS (showing an increased population of Y–OH compared to $Y-CO_3^{2-}$) and titration with organic molecules with different pK_a values. It is also consistent to the XPS



Fig. 5. The catalytic activity of the LDHY catalysts for the oxidation of cyclohexene (blue points [52]) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



Fig. 6. The variation of the yield to cyclohexene oxide *vs.* the sum of weak and medium strength basic sites.



Fig. 7. The cyclohexene oxide yield of LDHY-cp and LDHY-m after fourth reaction cycles.



Fig. 8. Comparison between the XRD patterns of the reconstructed samples in water after 24 h by memory effect synthesis (hyLDHY-cp and hyLDHY-m) and layered samples reconstructed during 1 h reaction time (hyLDHY-cp-1 h and hyLDHY-m-1 h).

patterns showing a better insertion of Y in the LDH lattice for LDHY-m. Longer reaction times had as an effect the diminution of these differences. The variation of the yield to cyclohexene oxide *vs.* the sum of



Fig. 9. Catalytic performances for the synthesis of chalcone and flavone using cLDHY-cp and cLDHY-m as catalysts and different benzaldehyde/methylenic compound ratios: 1/1 (A), 5/1 (B) and 10/1 (C).

the weak and medium strength base sites is presented in Fig. 6. This dependence was linear irrespective of the preparation route.

Indeed, the interaction of H_2O_2 with base surface sites led to active peroxo species, Scheme 1 [52]. However, the stronger base sites of

mixed oxides, for a higher conversion level, change the selectivity in the favor of large by-products.

Recycling experiments demonstrated the stability of the parent LDHY-m and LDHY-cp catalysts. After the fourth reaction cycles there were no sensible changes in the initial yield of cyclohexene-epoxide (Fig. 7).

The stability presented by the parent materials over several cycles is not valid in the case of mixed oxides. The XRD patterns of calcined catalysts, cHTY-cp and cHTY-m, recovered by filtration from the reaction mixture after 1 h were quasi identical to those obtained by synthesis involving the memory effect, hyHTY-cp and hyHTY-m, Fig. 8.

The reconstruction of the parent layered structure during the chemical reaction was also reported in the literature for the mixed oxides derived from the calcinations of LDH at a temperature not exceeding 460 $^{\circ}$ C [52].

Moving to a more challenging reaction, *i.e.* Claisen-Schmidt condensation to chalcone and flavone, the catalytric tests confirmed both co-precipitation and mechano-chemical prepared LDH as very selective catalysts (Fig. 9).

Under the investigated conditions, the selectivity to chalcone was higher than 90 %, while that to flavone varied in the range of 57.4-65 %. The conversion of the methylenic compound increased significantly for reaction mixtures containing an excess of benzaldehyde. Besides acting as a reactant, benzaldehyde can also play a role in the solubilisation of the condensation products thus facilitating their removal from the surface of the solid catalyst. However, a further increase of the benzaldehyde/methylenic compound molar ratio beyond 5/1 does not bring a significant improvement of the performances. Except for an equimolar benzaldehyde/2'-hydroxyacetophenone ratio, for both the chalcone and flavone synthesis, the catalyst prepared from the co-precipitated precursor was barely more active than the one obtained via the mechano-chemical route, due to the presence of diffusion hindrances as a result of the lower specific porosity and specific surface areas in the case of materials prepared by the mechano-chemical method and the larger dimension of the condensation reaction products.

4. Conclusions

The layered double hydroxides with a $M^{2+}/M^{3+} = 3$ molar ratio modified with yttrium (Al/Y = 1 molar ratio) were prepared by both mechano-chemical and co-precipitation routes. The mechano-chemical route provides a faster activation of the reagents [75]. In this route the generation of the heat necessary to induce the chemical reaction takes place in a confined space affording a better interaction of the structural entities compared to co-precipitation. Carbon dioxide is removed from the immediate reaction environment leading to a more pronounced incorporation of OH⁻ groups than CO₃²⁻; this energy seems also to be adequate for the Y insertion in the LDH network [76]. Such effects were demonstrated in this study by the Y insertion in a LDH octahedral position as certified by XRD and XPS data.

The prepared LDHY-cp and LDHY-m presented a superior activity for cyclohexene oxidation with H_2O_2 (30 wt%) compared to the LDH reference. Mixed oxides produced *via* calcination of above LDHs at 460 °C were investigated in the same reaction when the presence of water induced the reconstruction of the LDH structure. This effect was more pronounced for the mixed oxides produced from LDHY-cp. In accordance to the evaluation of the base properties it resulted that the oxidation of cyclohexene to cyclohexene oxide is indeed favored by weak and medium strength base sites.

Further investigation of the LDHY-cp and LDHY-m for the synthesis of chalcone and flavone showed poor performances. However, the mixed oxides obtained *via* calcination of the LDHY (*i.e.* cLDHY-cp and cLDHY-m) led to close conversions and good selectivities to both molecules.

CRediT authorship contribution statement

Octavian Dumitru Pavel: Conceptualization, Methodology, Supervision, Funding acquisition. Alexandra-Elisabeta Stamate: Investigation, Writing - review & editing. Rodica Zăvoianu: Conceptualization, Investigation, Supervision. Ioana Cristina Bucur: Investigation. Ruxandra Bîrjega: Investigation, Writing - review & editing, Visualization. Emilian Angelescu: Conceptualization, Methodology, Supervision. Vasile I. Pârvulescu: Conceptualization, Methodology, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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